



MTMS '21

9th International Symposium on
Molecular Thermodynamics and
Molecular Simulation

Program Book



September 7-9, 2021

Virtual



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写真：暁の伊達政宗公 写真提供：宮城県観光プロモーション推進室



Preface

The objective of “Molecular Thermodynamics and Molecular Simulation (MTMS)” is to provide a forum for scientists and engineers to discuss the recent advances in fluid properties and their theoretical description. MTMS was established in 1994 by the late Professor Koichiro Nakanishi. MTMS has been held and organized at three-year intervals since 1994:

Date Venue Chair/Organizer

1 st	1994	Kyoto	-Prof. Koichiro Nakanishi (Kyoto Univ.)
2 nd	1997	Tokyo	-Prof. Hideo Nishiumi (Hosei Univ.)
3 rd	2003	Sendai	-Prof. Hiroshi Inomata (Tohoku Univ.) Prof. Richard L. Smith (Tohoku Univ.)
4 th	2006	Makuhari	-Prof. Toshihiko Hiaki (Nihon Univ.)
5 th	2009	Kanazawa	-Prof. Kazuhiro Tamura (Kanazawa Univ.)
6 th	2012	Higashi-Hiroshima	-Prof. Shigeki Takishima (Hiroshima Univ.)
7 th	2015	Fukuoka	-Prof. Yoshio Iwai (Kyushu Univ.)
8 th	2018	Narashino	-Prof. Kiyofumi Kurihara (Nihon Univ.)

The 9th International Symposium on “Molecular Thermodynamics and Molecular Simulation (MTMS’21)” is held during September 7-9, 2021 on virtual. The symposium is organized by Division of Physical Properties, the Society of Chemical Engineers, Japan and Division of Supercritical Fluids, the Society of Chemical Engineers, Japan. We want to discuss not only the fluid properties but also the applications of fluid properties at the symposium. The symposium is structured with one plenary lecture, 7 keynote lectures by eminent scientists and engineers, 11 invited lectures on selected topics, 17 oral presentations, and 32 poster presentations with flash talk.

At this MTMS, as with the 3rd MTMS, we planned to gather at a hotel in Akiu hot springs, Sendai, to deepen discussions and friendships. The current situation in Japan is that the spread of COVID-19 has not stopped and a state of emergency has been issued in some areas. Although it was a very short preparation period, we can hold MTMS as an online conference with the cooperation of many people concerned.

On behalf of the organizing committee, we would like to thank all the authors for their contribution and also thank all the participants for their kind interest given to the symposium. we appreciate all the sponsors for their financial supports.

We hope all the participants will enjoy the symposium.

Yoshiyuki Sato
Mitsuhiko Kanakubo
Symposium Chair

MTMS ’21, September 7 – 9, 2021



Organizing Committees

Chair

Yoshiyuki Sato (Tohoku Inst. Tech., Japan)
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Ikuo Ushiki (Hiroshima Univ., Japan)
Hidetaka Yamada (Kanazawa Univ., Japan)

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Shiang-Tai Lin (National Taiwan University, Taiwan)
Bastian Schmid (DDBST, Germany)
Gang Xu (AVEVA, U.K.)



Timetable

September 7, 2021 (Tuesday)

8:40 – 8:50	Opening Remarks	
8:50 – 10:40	Session I	IL 01, OP 01, OP 02, OP 03, OP 04
10:40 – 11:00	Coffee Break	
11:00 – 11:50	Session II	IL 02, OP 05
11:50 – 13:20	Lunch	
13:20 – 15:10	Session III	IL 03, OP 06, OP 07, OP 08, OP 09
15:10 – 15:30	Coffee Break	
15:30 – 16:30	Session IV	OP 10, OP 11, OP 12
16:30 – 16:50	Coffee Break	
16:50 – 18:50	Session V	KL 01, KL 02, KL 03

September 8, 2021 (Wednesday)

8:20 – 9:30	Session VI	KL 04, IL 04
9:30 – 9:50	Coffee Break	
9:50 – 11:20	Session VII	IL 05, OP 13, KL 05
11:20 – 13:00	Lunch	
13:00 – 15:10	Session VIII	IL 06, IL 07, IL 08, KL 06
15:10 – 15:40	Coffee Break	
15:40 – 17:30	Session IX	IL 09, OP 14, OP 15, OP 16, OP 17
17:30 – 17:50	Coffee Break	
17:50 – 19:20	Session X	IL 10, PL 01

Poster sessions are available from 10:00 on September 6 to 17:00 on September 9 (JST).

Participants can view posters and ask questions via chat.

September 9, 2021 (Thursday)

8:20 – 9:30	Session XI	IL 11, KL 07	
9:30 – 9:40	Coffee Break		
9:40 – 12:20	Poster Session with Flash Talk		
	Room A	Room B	
9:40 – 10:40	PA 01 – PA 06	9:40 – 10:40	PB 01 – PB 06
10:40 – 11:05	PA 01 – PA 06 Questions	10:40 – 11:05	PB 01 – PB 06 Questions
11:05 – 11:10	Break	11:05 – 11:10	Break
11:10 – 12:00	PA 07 – PA 11	11:10 – 12:00	PB 07 – PB 11
12:00 – 12:20	PA 07 – PA 11 Questions	12:00 – 12:20	PB 07 – PB 11 Questions
12:20 – 13:30	Lunch		
13:30 – 14:40	Poster Session with Flash Talk		
	Room A	Room B	
13:30 – 14:20	PA 12 – PA 16	13:30 – 14:20	PB 12 – PB 16
14:20 – 14:40	PA 12 – PA 16 Questions	14:20 – 14:40	PB 12 – PB 16 Questions
14:40 – 14:50	Break		
14:50 – 15:10	Closing Remarks		
	Student Presentation Award		

Poster sessions are available from 10:00 on September 6 to 17:00 on September 9 (JST).

Participants can view posters and ask questions via chat.

September 7, Tuesday			September 8, Wednesday			September 9, Thursday		
Time	Number	Presenter	Chair	Time	Number	Presenter	Chair	Time
8:40	IL01	T. Hiaki	Opening Remarks	8:20	KL04	C. M ^c Cabe	H. Matsuda	8:20
8:50	OP01	H. Matsuda	K. Mishima I. Ushiki	9:00	IL04	G. Xu	H. Mori	8:50
9:20	OP02	T. Funazukuri		9:30		Coffee Break		9:30
9:40	OP03	S. Ohe		9:50	IL05	S.-T. Lin	G. Xu T. Tsuji	9:40
10:00	OP04	M. Osada		10:20	OP13	H. Mori		
10:20				10:40	KL05	P. Cummings		
10:40			Coffee Break	11:20		Lunch		12:20
11:00	IL02	H. Inomata	Y. Sato	13:00	IL06	T. Tsuji		13:30
11:30	OP05	I. Ushiki	M. Osada	13:30	IL07	E. May	S.-T. Lin	
11:50			Lunch	14:00	IL08	K. Shin	H. Yamada	14:40
- 13:20	IL03	R. Smith		14:30	KL06	V. K. Rattan		14:40
- 13:50	OP06	Y. C. Hung	T. Hoshina H. Machida	15:10		Coffee Break		14:50
14:10	OP07	A. Duereh		15:40	IL09	H. Yamada		
14:30	OP08	A. R. Agustin		16:10	OP14	H. Machida	D. Kodama T. Furuya	PL**
14:50	OP09	Y. Orita		16:30	OP15	T. Yamaguchi		KL**
15:10			Coffee Break	16:50	OP16	K. Tran		IL**
15:30	OP10	S. Tokunaga	A. Soto	17:10	OP17	H. Nishiumi		Invited Lecture
15:50	OP11	K. Mishima	A. Duereh	17:30				OP**
16:10	OP12	T. Sato				Coffee Break		Oral Presentation
16:30			Coffee Break	17:50	IL10	B. Schmid		PA**
16:50	KL01	I. G. Economou	Y. Iwai	18:20	PL01	G. M. Kontogeorgis	H. Inomata M. Sasaki	Poster Presentation with Flash Talk
17:30	KL02	A. Soto	R. Smith				Last Update	2021/8/26

PA or PB**** Chat discussions are available from 10:00 on September 6 to 17:00 on September 9 (JST).

September 9, Thursday						
Room A			Room B			
Time	Number	Presenter	Chair	Time	Number	Presenter
9:40	PA01	T. Yamada		9:40	PB01	Y. Aina
9:50	PA02	T. Tachibana		9:50	PB02	Y. Suzuki
10:00	PA03	J. Shimada	T. Makino	10:00	PB03	R. Kinoshita
10:10	PA04	K. Ikeda	M. Ota	10:10	PB04	T. Igosawa
10:20	PA05	S. Akiyama		10:20	PB05	A. Legaspi
10:30	PA06	Y. Tatsumi		10:30	PB06	N. Maeda
10:40	PA	Questions 25 min.		10:40	PB	Questions 25 min.
11:05		Break		11:05		Break
11:10	PA07	A. Tokoro		11:10	PB07	K. Matsubara
11:20	PA08	M. Yonori		11:20	PB08	R. Suzuki
11:30	PA09	T. Homma	M. Kanakubo	11:30	PB09	M. Kitahara
11:40	PA10	T. Wijakmatee	S. Muromachi	11:40	PB10	T. Kataoka
11:50	PA11	T. Maeda		11:50	PB11	Y. Hao
12:00	PA	Questions 20 min.		12:00	PB	Questions 20 min.
12:20		Lunch		12:20		Lunch
13:30	PA12	M. Ota		13:30	PB12	T. Makino
13:40	PA13	K. Tochigi		13:40	PB13	T. Sugahara
13:50	PA14	Y. Asakuma	Y. Shimoyama	13:50	PB14	C. Y. Kong
14:00	PA15	T. Hoshina	H. Miyamoto	14:00	PB15	T. Honma
14:10	PA16	K. Tochigi		14:10	PB16	J. L. Lee
14:20	PA	Questions 20 min.		14:20	PB	Questions 20 min.
					Last Update	2021/8/19



General Information

Web Conference System

MTMS '21 will be held using Zoom and web conference system shown in the image below. Participants can access Zoom link, abstract, proceedings, e-poster, chat, etc. using this web conference system. Further information will be uploaded in the MTMS '21 website <https://mtms21.jimdofree.com/>.

9th International Symposium on Molecular Thermodynamics and Molecular Simulation (MTMS'21)

Demo Program

[Program Book](#) → [Logout](#)

Poster Session with Flash Talk

Please note that for all participants, Room A is conference w/ Room B for the purpose of archiving the event for official purposes. Participants must not record lectures at the conference.

Poster sessions are available from 10:00 on September 6 to 17:00 on September 9 (JST).

Participants can view posters and ask questions via chat.

Oral	Poster A	Poster B
Time	September 7, Tuesday	Chair
08:40-08:50	Opening Remarks	
08:50-09:20	IL01 T. Hiaki	
09:20-09:40	OP01 H. Matsuda	
09:40-10:00	OP02 T. Funazukuri	K. Mishima I. Ushiki
Time	September 8, Wednesday	Chair
08:20-09:00	KL04 C. McCabe	H. Matsuda H. Mori
09:00-09:30	IL04 G. Xu	
09:30-09:50	Coffee Break	
09:50-10:20	IL05 S.-T. Lin	
Time	September 9, Thursday	Chair
08:20-08:50	IL11 C.-C. Chen	S. Oba
08:50-09:30	KL07 Y. Iwai	T. Furuya
09:30-09:40	Coffee Break	
09:40-11:05	Poster Session Room A: PA01 - PA11 Room B: PB01 - PB11	

9th International Symposium on Molecular Thermodynamics and Molecular Simulation (MTMS'21)

Demo

Plenary, Keynote, Invited Lectures

[Close](#)

Recording, taking screen shots, photos, or archiving materials is strictly prohibited.

Zoom Link → [Meeting](#)

September 7, Tuesday

Time	Session	Chair
08:40~08:50	Session 1 : Opening Remarks Prof. Yoshiyuki Sato (Tohoku Institute of Technology, Japan) Dr. Mitsuhiro Kanakubo (National Institute of Advanced Industrial Science and Technology, Japan)	
08:50~10:40	Session 2 : Session I Chair: Prof. Kenji Mishima (Fukuoka University, Japan) and Prof. Ikuo Ushiki (Hiroshima University, Japan)	
08:50~09:20	Measurement of vapor-liquid equilibria for azeotropic systems Toshihiko Hiaki* Nihon University, Japan	
09:20~09:40	Phase diagram of ternary mixtures water + n-alkane + non-ionic surfactant Hiroyuki Matsuda ^{1,2} , Yuki Nakazato ¹ , Rei Tsuchiya ¹ , Yoshihiro Inoue ¹ , Kiyofumi Kurihara ¹ , Tomoya Tsuji ² , Katsumi Tochigi ¹ , Kenji Ochi ¹ ¹ Nihon University, Japan ² Universiti Teknologi Malaysia, Malaysia	

Abstract **Proceeding**

Chat → [Abstract](#) [Proceeding](#)

[Abstract](#) [Proceeding](#)

9th International Symposium on Molecular Thermodynamics and Molecular Simulation (MTMS'21)

Demo

Poster Presentation with Flash Talk

Program Book

Program Book

Logout

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Oral Poster A Poster B

number	Title	e-Poster	Movie	Chat	Proceeding
PA01 09:40-09:50	Measurements and Modeling of Vapor-Liquid Equilibrium Properties for Low GWP refrigerants R1123/R1234yf/R32 Ternary Mixtures Tessei Yamada, Yuhei Nakamura, Kyouhei Minai, Hiroyuki Miyamoto Tohoku Prefectural University, Japan	Poster	Movie	Chat	Proceeding
PA02 09:50-10:00	Phase Behavior of CO₂/Toluene/PMMA ternary system Takumi Tachibana, Hiroaki Matsukawa, Yuya Murakami, Atsushi Shono, Katsuto Otake* Tokyo University of Science, Japan	Poster	Movie	Chat	Proceeding
PA03 10:00-10:10	Thermodynamic properties of tetra-n-butylphosphonium dicarboxylate semicellulose hydrates Jin Shimada ¹ , Moe Yamada ² , Takeshi Sugahara ^{*1} , Atsushi Tani ³ , Katsuhiko Tsunashima ² , Takayuki Hira ¹ ¹ Osaka University, Japan ² National Institute of Technology, Wakayama College, Japan ³ Kobe University, Japan	Poster	Movie	Chat	Proceeding

OP01

Phase diagram of ternary mixtures water + n-alkane + non-ionic surfactant

Hiroyuki Matsuda^{*,1}, Yuki Nakazato¹, Rei Tsuchiya¹, Yoshihiro Inoue¹, Kiyofumi Kurihara¹, Tomoya Tsuji², Katsumi Tochigi¹, Kenji Ochi¹

¹Nihon University, Japan ²Universiti Teknologi Malaysia, Malaysia

Enter question

Question from Participants

Send

Demo

Chat Discussion

Enter reply

Answer from authors

Reply

Attention

1. Presentation materials should be treated as public announcements that may affect future intellectual property rights such as patents. If you agree that the video files are to be downloaded by participants, then please upload your presentation materials at your discretion.
2. Downloaded files must only be used for personal reasons and must not be shared or stored on file servers. All files must be deleted from all digital devices including disk caches immediately after the end of the MTMS symposium.
3. Please note that for all participants and events, this conference will be recorded for the purpose of archiving the event for official purposes. Participants must not record lectures at the conference.

Instructions for Presenter

1. Oral Presentation (Plenary, Keynote, Invited, or Oral)

Authors should prepare oral presentations with a total duration of 60 minutes (plenary lecture), 40 minutes (keynote lecture), 30 minutes (invited lecture), or 20 minutes (oral presentation) including questions (approx. 4 or 5 minutes per talk).

2. Poster Presentation with Flash Talk

- (1) Chat discussions throughout a certain period in the symposium are available.
- (2) Flash talk is held on September 9. Please check Program.
- (3) Authors should prepare an oral presentation with 10 minutes.
- (4) Time of questions for 5 to 6 talks will be 20 to 25 minutes.
- (5) Poster and movie file
 - The poster presenter has to submit the poster file.
 - Submission of poster presentation movie file is optional.
 - The poster file is required to be submitted as PDF (Portable Document Format) file.
 - The movie file is required to be submitted as MP4 file.
 - The organizing committee recommend, for the ease of viewing on screen, that the poster PDF file is containing about 10 sheets of slideshow.
 - Please submit your poster and movie files via Online Submission Form by September 1, 2021.
 - Further information will be uploaded in the MTMS '21 website <https://mtms21.jimdofree.com/>.

Student Presentation Award

Undergraduate/graduate student presenters are considered for the student presentation award. Award ceremony will be held in the closing remarks on September 9.

Special Issue

We are pleased to announce a special issue of the 9th International Symposium on Molecular Thermodynamics and Molecular Simulation (MTMS '21) in the journal Fluid Phase Equilibria that will be edited by Prof. Yoshiyuki Sato and Dr. Mitsuhiro Kanakubo as guest-editors as guest-editors.

We invite all conference participants to submit a manuscript for publication in the special issue. Please note that all submissions must comply with the scope of Fluid Phase Equilibria and will be peer reviewed in the same manner as all other articles published in Fluid Phase Equilibria.

We are excited about this special issue and will do our utmost to ensure timely reviewing and publication.



Technical Program

September 7, 2021 (Tuesday)

8:40 – 8:50	Opening Remarks Prof. Yoshiyuki Sato (Tohoku Institute of Technology, Japan) Dr. Mitsuhiro Kanakubo (National Institute of Advanced Industrial Science and Technology, Japan)
8:50 – 10:40	Session I Chair: Prof. Kenji Mishima (Fukuoka University, Japan) and Prof. Ikuo Ushiki (Hiroshima University, Japan)
8:50 – 9:20	Invited Lecture IL 01 Measurement of vapor-liquid equilibria for azeotropic systems Toshihiko Hiaki* Nihon University, Japan
9:20 – 9:40	OP 01 Phase diagram of ternary mixtures water + <i>n</i>-alkane + non-ionic surfactant <u>Hiroyuki Matsuda</u> ^{*1} , Yuki Nakazato ¹ , Rei Tsuchiya ¹ , Yoshihiro Inoue ¹ , Kiyofumi Kurihara ¹ , Tomoya Tsuji ² , Katsumi Tochigi ¹ , Kenji Ochi ¹
¹ Nihon University, Japan	² Universiti Teknologi Malaysia, Malaysia
9:40 – 10:00	OP 02 Measurement and correlation of diffusion coefficients of Cr(acac)₃ in high temperature supercritical carbon dioxide Minoru Yamamoto ¹ , Junichi Sakabe ¹ , Chang Yi Kong ² , <u>Toshitaka Funazukuri</u> ^{*1}
¹ Chuo University, Japan	² Shizuoka University, Shizuoka
10:00 – 10:20	OP 03 Vapor pressure prediction method for pure substances Shuzo Ohe*
Tokyo University of Science, Japan	
10:20 – 10:40	OP 04 Prediction of solubility of organic compound for high-temperature water by machine learning <u>Mitsumasa Osada</u> [*] , Kotaro Tamura
Shinshu University, Japan	
10:40 – 11:00	Coffee Break
11:00 – 11:50	Session II Chair: Prof. Yoshiyuki Sato (Tohoku Institute of Technology, Japan) and Prof. Mitsumasa Osada (Shinshu University, Japan)
11:00 – 11:30	Invited Lecture IL 02 Methodology for applying equations of state to phase equilibrium calculation for mixture Hiroshi Inomata*
Tohoku University, Japan	

11:30 – 11:50 OP 05

Predicting the solubilities of acetylacetone-type metal precursors in supercritical CO₂:

Thermodynamic modeling using PC-SAFT

Ikuo Ushiki*, Ryo Fujimitsu, Azusa Miyajima, Shigeki Takishima

Hiroshima University, Japan

11:50 – 13:20 Lunch

13:20 – 15:10 Session III

Chair: Prof. Taka-aki Hoshina (Nihon University, Japan) and Prof. Hiroshi Machida (Nagoya University, Japan)

13:20 – 13:50 Invited Lecture IL 03

Application of analytical centrifugation to chemical systems for measurement of properties and phase equilibria

Kotaro Oshima, Kentaro Nakamura, Natsuki Sato, Haixin Guo and Richard Lee Smith Jr.*

Tohoku University, Japan

13:50 – 14:10 OP 06

Controlling the CO₂-lipid liquid phase separation via process tuning and lipid structural design

Ying-Chieh Hung¹, Yuna Tatsumi¹, Chieh-Ming Hsieh², Shiang-Tai Lin³, Yusuke Shimoyama^{*,1}

¹ Tokyo Institute of Technology, Japan ² National Central University, Taiwan

³ National Taiwan University, Taiwan

14:10 – 14:30 OP 07

Development of CO₂-assisted dispersibility of organic-inorganic hybrid nanoparticles with expanded liquid solvent mixtures

Alif Duereh^{*,1}, Masaki Ota¹ Yoshiyuki Sato², Hiroshi Inomata¹

¹ Tohoku University, Japan ² Tohoku Institute of Technology, Japan

14:30 – 14:50 OP 08

Surface modification of nano-TiO₂ with para-aminobenzoic acid in supercritical carbon dioxide for preventing aggregation of nanoparticles

Anggi Regiana Agustin, Kazuhiro Tamura^{*}

Kanazawa University, Japan

14:50 – 15:10 OP 09

Synthesis of decanoic acid-modified iron oxide nanocrystals using supercritical carbon dioxide as reaction medium

Yasuhiko Orita^{*}, Keito Kariya, Thossaporn Wijakmatee, Yusuke Shimoyama

Tokyo Institute of Technology, Japan

15:10 – 15:30 Coffee Break

15:30 – 16:30 Session IV

Chair: Prof. Ana Soto (Universidade de Santiago de Compostela, Spain) and Prof. Alif Duereh (Tohoku University, Japan)

15:30 – 15:50	OP 10
Production of spherical microparticles with Eudragit L100 by the PGSS process in supercritical CO₂-ethanol mixtures	
<u>Shinichi Tokunaga</u> , Miyuki Nakamura, Tanjina Sharmin, Taku M. Aida, Kenji Mishima*	
Fukuoka University, Japan	
15:50 – 16:10	OP 11
Application of direct sonication under high-pressure two-phase system	
<u>Kenji Mishima</u> *, Tanjina Sharmin, Taku Michael Aida, Kento Ono	
Fukuoka University, Japan	
16:10 – 16:30	OP 12
Analysis of the mechanism of hydrothermal carbon dioxide fixation into serpentine with estimation of equilibrium of chemical species	
<u>Takafumi Sato</u> *, Seitaro Yamamoto, Naotsugu Itoh	
Utsunomiya University, Japan	
16:30 – 16:50	Coffee Break
16:50 – 18:10	Session V
Chair: Prof. Yoshio Iwai (Kyushu University, Japan) and Prof. Richard L. Smith (Tohoku University, Japan)	
16:50 – 17:30	Keynote Lecture KL 01
Clean, high quality low emission fuels with Fischer-Tropsch synthesis: A multiscale study of transport properties in confined systems	
<u>Ioannis G. Economou</u> * ^{1,2} , Konstantinos D. Papavasileiou ¹ , Loukas D. Peristeras ¹ Andreas Bick ³	
¹ Institute of Nanoscience and Nanotechnology, Greece	
² Texas A&M University at Qatar, Qatar ³ Scienomics SAS, France	
17:30 – 18:10	Keynote Lecture KL 02
Phase equilibria and enhanced oil recovery	
Ana Soto*	
Universidade de Santiago de Compostela, Spain	
18:10 – 18:50	Keynote Lecture KL 03
Applications of deep eutectic solvents and gas hydrates in gas purifications	
<u>Samah E. E. Warrag</u> ^{1,2} , Muhammad Naveed Khan ^{3,4} , <u>Cor J. Peters</u> * ^{1,2,4}	
¹ Khalifa University of Science and Technology, United Arab Emirates	
² Eindhoven University of Technology, The Netherlands	
³ University of Hafr Al Batin, Kingdom of Saudi Arabia	
⁴ Colorado School of Mines, USA	

September 8, 2021 (Wednesday)

8:20 – 9:30	Session VI
Chair: Prof. Hiroyuki Matsuda (Nihon University, Japan) and Prof. Hirotoshi Mori (Chuo University, Japan)	
8:20 – 9:00	Keynote Lecture KL 04
Exploring the effect of cholesterol on stratum corneum lipid assemblies	
Parashara Shamaprasad, Chloe Frame, Timothy C. Moore, Chris Iacobella, <u>Clare McCabe*</u> Vanderbilt University, USA	
9:00 – 9:30	Invited Lecture IL 04
Performance improvement on dynamic simulation for high pressure polyethylene synthesis by PC-SAFT	
<u>Gang Xu*</u> , Nevin Gerek Ince AVEVA, USA	
9:30 – 9:50	Coffee Break
9:50 – 11:20	Session VII
Chair: Dr. Gang Xu (AVEVA, USA) and Prof. Tomoya Tsuji (Universiti Teknologi Malaysia, Malaysia)	
9:50 – 10:20	Invited Lecture IL 05
Improvements on the predictive COSMO-SAC model and its applications in process and produce design	
<u>Shiang-Tai Lin</u> ^{*,1} , Cheih-Ming Hsieh ² , Chang-Che Tsai ¹ , Chen-Hsuan Huang ¹ ¹ National Taiwan University ² National Central University, Taiwan	
10:20 – 10:40	OP 13
Ultimately large-scale <i>ab initio</i> molecular dynamics with effective fragment potential opens an era for predicting physicochemical properties of mixed liquids and supercritical fluids	
Nahoko Kuroki ^{1,2} , <u>Hirotoshi Mori</u> ^{*,1,3} ¹ Chuo University, Japan ² JST, ACT-X, Japan ³ Institute for Molecular Science, Japan	
10:40 – 11:20	Keynote Lecture KL 05
Molecular modeling of supercapacitor systems	
Peter T. Cummings* Vanderbilt University, USA	
11:20 – 13:00	Lunch
13:00 – 15:10	Session VIII
Chair: Prof. Shiang-Tai Lin (National Taiwan University, Taiwan) and Prof. Hidetaka Yamada (Kanazawa University, Japan)	
13:00 – 13:30	Invited Lecture IL 06
Mercury solubility measurements in glycols and amines for natural gas processing plant	

Tomoya Tsuji^{*,1}, Junya Yamada², Midori Kawasaki², Machie Otsuka², Atsushi Kobayashi²

¹ Universiti Teknologi Malaysia, Malaysia ² INPEX Corporation, Japan

13:30 – 14:00 Invited Lecture IL 07

Solids formation risk in natural gas, LNG and liquid hydrogen production

Eric F. May^{*,1,2}, Peter Metaxas¹, Paul Stanwix¹, Peter Falloon¹, Vincent Lim¹, Matthew Hopkins¹, Catherine Sampson¹, Arman Siahvashi¹, Zachary Aman¹

¹ The University of Western Australia, Australia

² Future Energy Exports Cooperative Research Centre, Australia

14:00 – 14:30 Invited Lecture IL 08

Molecular behavior of 1-pentanol guest in the NH₄F-doped clathrate hydrate

Byeonggwan Lee^{1,2}, Jeongtak Kim^{1,3}, Kyuchul Shin^{*,1}, Ki Hun Park⁴, Minjun Cha⁴, Saman Alavi^{*,5,6}, John A. Ripmeester⁶

¹ Kyungpook National University, Republic of Korea

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⁴ Kangwon National University, Republic of Korea

⁵ University of Ottawa, Canada ⁶ National Research Council of Canada, Canada

14:30 – 15:10 Keynote Lecture KL 06

Kinetic viscosities prediction using ASOG-VISCO group contribution method for binary liquid mixtures

V. K. Rattan^{*,1}, Hiroyuki Matsuda², Katsumi Tochigi², Kiyofumi Kurihara², Toshitaka Funazukuri³

¹ GNA University, India ² Nihon University, Japan ³ Chuo University, Japan

15:10 – 15:40 Coffee Break

15:40 – 17:30 Session IX

Chair: Prof. Daisuke Kodama (Nihon University, Japan) and Dr. Takeshi Furuya (National Institute of Advanced Industrial Science and Technology, Japan)

15:40 – 16:10 Invited Lecture IL 09

Physical chemistry of amine-based carbon dioxide separation

Hidetaka Yamada*

Kanazawa University, Japan

16:10 – 16:30 OP 14

High throughput CO₂ solubility measurement in amine solution using HS-GC

Hiroshi Machida^{*}, Keiichi Yanase, Tran Viet Bao Khuyen, Mikiro Hirayama, Koyo Norinaga

Nagoya University, Japan

16:30 – 16:50 OP 15

A new approach to the study of amine-CO₂ system based on the absolute reaction rate theory

Toru Yamaguchi^{*,1}, Hidetaka Yamada², Syohei Sanada¹, Kenji Hori^{1,3}

¹ Transition State Technology Co. Ltd., Japan

² Kanazawa University, Japan

³ Yamaguchi University, Japan

16:50 – 17:10 OP 16

Temperature dependent of absorption heat in phase-change solvent in carbon dioxide capture

Tran Viet Bao Khuyen, Yamaguchi Tsuyoshi, Machida Hiroshi*, Koyo Norinaga

Nagoya University, Japan

17:10 – 17:30 OP 17

Prediction of CO₂ solubility in ionic liquids and glymes with modified generalized BWR Eos

Hideo Nishiumi*,¹ Daisuke Kodama²

¹ Hosei University, Japan ² Nihon University, Japan

17:30 – 17:50 Coffee Break

17:50 – 19:20 Session X

Chair: Prof. Hiroshi Inomata (Tohoku University, Japan) and Dr. Masakazu Sasaki (Toyo Engineering Co, Japan)

17:50 – 18:20 Invited Lecture IL 10

DDBST and LTP – Your source for reliable thermophysical properties

Bastian Schmid*

DDBST GmbH, Germany

18:20 – 19:20 Plenary Lecture PL 01

How can molecular concepts help in the development of more predictive advanced equations of state?

Georgios M. Kontogeorgis*, Xiaodong Liang

Technical University of Denmark, Denmark

September 9, 2021 (Thursday)

8:20 – 9:30	Session XI
Chair: Dr. Shigeo Oba (Applied Thermodynamics and Physical Properties Co., Ltd., Japan) and Dr. Takeshi Furuya (National Institute of Advanced Industrial Science and Technology, Japan)	
8:20 – 8:50	Invited Lecture IL 11
	Association-based activity coefficient models for nonelectrolyte and electrolyte solutions
	Chau-Chyun Chen*
	Texas Tech University, USA
8:50 – 9:30	Keynote Lecture KL 07
	Prediction of vapor-liquid equilibria for multicomponent systems by a modified concentration dependent surface area parameter model
	Yoshio Iwai*
	Kyushu University, Japan
9:30 – 9:40	Coffee Break
9:40 – 11:05	Poster Session with Flash Talk Room A
Chair: Prof. Masaki Ota (Tohoku University, Japan) and Dr. Takashi Makino (National Institute of Advanced Industrial Science and Technology, Japan)	
9:40 – 9:50	PA 01
	Measurements and modeling of vapor-liquid equilibrium properties for low GWP refrigerants R1123/R1234yf/R32 ternary mixtures
	Tessei Yamada, Yuuhei Nakamura, Kyouhei Minai, Hiroyuki Miyamoto*
	Toyama Prefectural University, Japan
9:50 – 10:00	PA 02
	Phase behavior of CO₂/toluene/PMMA ternary system
	Takumi Tachibana, Hiroaki Matsukawa, Yuya Murakami, Atsushi Shono, Katsuto Otake*
	Tokyo University of Science, Japan
10:00 – 10:10	PA 03
	Thermodynamic properties of tetra-<i>n</i>-butylphosphonium dicarboxylate semiclathrate hydrates
	Jin Shimada ¹ , Moe Yamada ² , Takeshi Sugahara ^{*1} , Atsushi Tani ³ , Katsuhiko Tsunashima ² , Takayuki Hirai ¹
¹ Osaka University, Japan	² National Institute of Technology, Wakayama Collage, Japan
³ Kobe University, Japan	
10:10 – 10:20	PA 04
	Gas separation properties of semiclathrate hydrates for CH₄+CO₂ mixed gas
	Kosuke Ikeda ¹ , Takuya Yasoyama ¹ , Hiroyuki Miyamoto ^{*1} , Sanehiro Muromachi ²
¹ Toyama Prefectural University, Japan	
² National Institute of Advanced Industrial Science and Technology, Japan	
10:20 – 10:30	PA 05

Host-guest chemistry of antibacterial molecular crystal in supercritical CO₂ with solvent

Seika Akiyama*, Yingquan Hao, Yusuke Shimoyama

Tokyo Institute of Technology, Japan

10:30 – 10:40 PA 06

Itraconazole cocrystallization in fatty acid under high-pressure CO₂

Yuna Tatsumi, Hao Yingquen, Yasuhiko Orita, Yusuke Shimoyama*

Tokyo Institute of Technology, Japan

10:40 – 11:05 PA 01 – PA 06 Questions

9:40 – 11:05 Poster Session with Flash Talk Room B

Chair: Prof. Takafumi Sato (Utsunomiya University, Japan) and Prof. Tetsuo Honma (National Institute of Technology (KOSEN), Hachinohe College, Japan)

9:40 – 9:50 PB 01

CO₂ solubility of deep eutectic solvent consisting of choline chloride and ethylene glycol

Yuto Ainai, Ayaka Taniguchi, Daisuke Kodama*

Nihon University, Japan

9:50 – 10:00 PB 02

CO₂/hydrocarbon selectivity of phosphonium based ionic liquids

Yuki Suzuki¹, Daisuke Kodama*,¹, Hirotoshi Mori^{2,3}, Nahoko Kuroki^{2,4}, Hidetaka Yamada⁵

¹Nihon University, Japan ² Chuo University, Japan

³ Institute for Molecular Science, Japan

⁴ JST, ACT-X, Japan ⁵ Kanazawa University, Japan

10:00 – 10:10 PB 03

Thermodynamic study of extraction behavior for precious metals using phosphonium-based ionic liquids

Ryoma Kinoshita¹, Yusuke Tsuchida¹, Masahiko Matsumiya*,¹, Yuji Sasaki²

¹ Yokohama National University, Japan ² Japan Atomic Energy Agency, Japan

10:10 – 10:20 PB 04

Thermodynamic study of W(VI) extraction using amine-based extractant and phosphonium ionic liquids

Tatsuki Igosawa¹, Yusuke Tsuchida¹, Masahiko Matsumiya*,¹, and Yuji Sasaki²

¹ Yokohama National University, Japan ² Japan Atomic Energy Agency, Japan

10:20 – 10:30 PB 05

Effects of water in the decarboxylation of aromatic carboxylic acids in supercritical water

Anna Legaspi*, Makoto Akizuki, Yoshito Oshima

The University of Tokyo, Japan

10:30 – 10:40 PB 06

Calculation of solubility of organic compounds in supercritical carbon dioxide using machine learning with molecular descriptors

Naoya Maeda, Junichi Sakabe, Hirohisa Uchida*

Kanazawa University, Japan

10:40 – 11:05 PB 01 – PB 06 Questions

11:05 – 11:10	Break
11:10 – 12:20	Poster Session with Flash Talk Room A
	Chair: Dr. Mitsuhiro Kanakubo (National Institute of Advanced Industrial Science and Technology, Japan) and Dr. Sanehiro Muromachi (National Institute of Advanced Industrial Science and Technology, Japan)
11:10 – 11:20	PA 07
	Volumetric behavior of HFO-1234ze(E) + acetone liquid mixture at 303.2 K
	<u>Atuski Tokoro</u> ¹ , Masaki Okada ¹ , Taka-aki Hoshina ^{*,1} , Tomoya Tsuji ² , Takeshi Furuya ³
	¹ Nihon University, Japan
	² Universiti Teknologi Malaysia (UTM) Kuala Lumpur, Malaysia
	³ The National Institute of Advanced Industrial Science and Technology (AIST), Japan
11:20 – 11:30	PA 08
	Measurement of the density of carbon dioxide/methanol and dioxide/ethanol homogeneous mixtures and correlation with equations of state
	<u>Masamune Yomori</u> ¹ , Hiroaki Matsukawa ¹ , Yuya Murakami ² , Atsushi Shono ¹ , Tomoya Tsuji ² , Katsuto Otake ^{*,1}
	¹ Tokyo University of Science, Japan ² University Technology Malaysia, Malaysia
11:30 – 11:40	PA 09
	Measurement and correlation of PVT for organic-inorganic hybrid nanoparticles
	<u>Taiki Homma</u> ^{*,1} , Masaki Ota ¹ , Yoshiyuki Sato ^{1,2} , Hiroshi Inomata ¹
	¹ Tohoku University, Japan ² Tohoku Institute of Technology, Japan
11:40 – 11:50	PA 10
	Micro-flow process of emulsification and supercritical fluid extraction of emulsion for stearic acid lipid nanoparticle production
	<u>Thossaporn Wijakmatee</u> , Yasuhiko Orita, Yusuke Shimoyama [*]
	Tokyo Institute of Technology, Japan
11:50 – 12:00	PA 11
	Study for hydration structure through the refractive index during microwave irradiation
	<u>Tomoisa Maeda</u> ¹ , Yusuke Asakuma ^{*,1} , Shinya Ito, Shuji Taue ² , Anita Hyde ³ , Chi Phan ³
	¹ University of Hyogo, Japan ² Kouchi Institute of Technology
	³ Curtin University, Australia
12:00 – 12:20	PA 07 – PA 11 Questions
11:10 – 12:20	Poster Session with Flash Talk Room B
	Chair: Prof. Takeshi Sugahara (Osaka University, Japan) and Prof. Chang Yi Kong (Shizuoka University, Japan)
11:10 – 11:20	PB 07
	Simultaneous correlation of liquid-liquid equilibria for ternary systems and phase equilibria for constitutive binary systems by modified new activity coefficient model
	<u>Koji Matsubara</u> , Yoshio Iwai [*]
	Kyushu University, Japan
11:20 – 11:30	PB 08

Anionic states play more important role: electronic structure informatics of gas-phase acidity toward fast and precise acids design for engineering

Rima Suzuki¹, Nahoko Kuroki^{1,2}, Hirotoshi Mori^{*,1,3}

¹ Chuo University, Japan ² JST, ACT-X, Japan

³ Institute for Molecular Science, Japan

11:30 – 11:40 PB 09

Optimization of an artificial neural network for pure component parameters based on a group contribution method of PC-SAFT EoS

Masayuki Kitahara, Hiroaki Matsukawa, Yuya Murakami, Atsushi Shono, Katsuto Otake^{*,2}

Tokyo University of Science, Japan

11:40 – 11:50 PB 10

Screening of phase-separation CO₂ absorbent using machine learning combined with molecular information

Taishi Kataoka, Yingquan Hao, Ying-Chieh Hung, Yusuke Shimoyama*

Tokyo Institute of Technology, Japan

11:50 – 12:00 PB 11

Prediction of melting point and fusion enthalpy of cocrystal by machine learning combined with molecular informatics

Yingquan HAO, Yusuke Shimoyama*

Tokyo Institute of Technology, Japan

12:00 – 12:20 PB 07 – PB 11 Questions

12:20 – 13:30 Lunch

13:30 – 14:40 Poster Session with Flash Talk Room A

Chair: Prof. Yusuke Shimoyama (Tokyo Institute of Technology, Japan) and Prof. Hiroyuki Miyamoto (Toyama Prefectural University, Japan)

13:30 – 13:40 PA 12

Development of a predictive dimensionless distribution coefficient (pDD) model for fractionation of Hops extracts

Masaki Ota^{*,1}, Aruto Kuwahara¹, Yuki Hoshino¹, Yusuke Ueno¹, Shun Nomura¹, Yoshiyuki Sato^{1,2}, Richard Lee Smith Jr.¹, Hiroshi Inomata¹

¹ Tohoku University, Japan ² Tohoku Institute of Technology, Japan

13:40 – 13:50 PA 13

Evaluation of solid-liquid equilibria for drug + water + cyclodextrin derivatives systems using activity coefficient model

Hiroyuki Matsuda, Kiyofumi Kurihara, Katsumi Tochigi*

Nihon University, Japan

13:50 – 14:00 PA 14

Prediction for modification of liquid-liquid interface by energy concentration of microwave heating

Yusuke Watanabe¹, Yosuke Shibata¹, Satoshi Sonobe¹, Yusuke Asakuma^{*,1}, Anita Hyde², Chi Phan²

¹ University of Hyogo, Japan

² Curtin University, Australia

14:00 – 14:10 PA 15

Dielectric properties of liquefied dimethyl ether + ethanol + water mixtures at 303.2 K

Taka-aki Hoshina^{*1}, Shohei Koizumi¹, Masaki Okada¹, Tomoya Tsuji², Toshihiko Hiaki¹

¹ Nihon University, Japan

² Universiti Teknologi Malaysia (UTM) Kuala Lumpur, Malaysia

14:10 – 14:20 PA 16

Prediction of thermal conductivities for liquid mixture using ASOG-ThermConduct model

Katsumi Tochigi^{*1}, Hiroyuki Matsuda¹, Kiyofumi Kurihara¹, Tomoya Tsuji², Toshitaka Funazukuri³, V. K. Rattan⁴

¹ Nihon University, Japan

² Universiti Teknologi Malaysia, Malaysia

³ Chuo University, Japan

⁴ GNA University, India

14:20 – 14:40 PA 12 – PA 16 Questions

13:30 – 14:40 Poster Session with Flash Talk Room B

Chair: Hirohisa Uchida (Kanazawa University, Japan) and Prof. Makoto Akizuki (University of Tokyo, Japan)

13:30 – 13:40 PB 12

Cation effects on physical properties of acetate-based ionic liquids

Takashi Makino^{*1}, Tatsuya Umecky², Mitsuhiro Kanakubo¹

¹ National Institute of Advanced Industrial Science and Technology, Japan

² Saga University, Japan

13:40 – 13:50 PB 13

Thermodynamic stabilities of clathrate hydrates including tetrahydrofuran and quaternary onium salts

Takeshi Sugahara^{*1}, Hironobu Machida²

¹ Osaka University, Japan

² Panasonic Corporation, Japan

13:50 – 14:00 PB 14

Measurements of diffusion coefficient for triolein in various pressurized fluids with different viscosities

Guoxiao Cai¹, Wataru Katsumata¹, Idzumi Okajima¹, Takeshi Sako¹, Toshitaka Funazukuri², Chang Yi Kong^{*1}

¹ Shizuoka University, Japan

² Chuo University, Japan

14:00 – 14:10 PB 15

Molecular dynamics study on nucleation process for supersaturated ZnO solutions in hydrothermal conditions

Tetsuo Honma^{*1}, Kouichiro Kurosawa¹, Tasuku Murata^{1,2}, Takafumi Sato²

¹ National Institute of Technology (KOSEN), Hachinohe College, Japan

² Utsunomiya University, Japan

14:10 – 14:20 PB 16

Correlation of solubilities in mixed-solvents with local-composition-regular solution theory

Jia Lin Lee¹, Gun Hean Chong^{*,1}, Asami Kanno², Masaki Ota², Haixin Guo², Richard Lee Smith,
Jr.²

¹ Universiti Putra Malaysia, Malaysia ² Tohoku University, Japan

14:20 – 14:40 PB 12 – PB 16 Questions

14:50 – 15:10 Closing Remarks and Student Presentation Award

Prof. Yoshiyuki Sato (Tohoku Institute of Technology, Japan)

Dr. Mitsuhiro Kanakubo (National Institute of Advanced Industrial Science and Technology, Japan)



Invited Lectures

Plenary Lecture PL 01

How can molecular concepts help in the development of more predictive advanced equations of state?

Authors and affiliation

Georgios M. Kontogeorgis* and Xiaodong Liang

Center for Energy Resources Engineering

Department of Chemical and Biochemical Engineering

Technical University of Denmark

Key Word (3 words)

Association models (SAFT, CPA), molecular simulation, electrolytes

Abstract (less than 300 words)

Since about 1990's, advanced equations of state which incorporate the concept of association have brought a new dimension in engineering thermodynamics [1]. 30 years after these models are not just theoretical curiosity but are being implemented in simulators and also otherwise used in practice. These models perform in many cases superior over classical models and for a wider range of systems and conditions but they do require many parameters and extension to mixtures e.g. uncertainties of mixing and combining rules make their use cumbersome. On the other hand, the theoretical origin of these association theories is a strong positive feature and could imply that molecular concepts e.g. from statistical thermodynamics, quantum chemistry, spectroscopy and molecular simulation may provide valuable input in some cases. In this presentation, we will illustrate examples from recent research in our group [2-5] of how some of these molecular concepts can contribute to the development of predictive approaches, which can enhance the range of applicability of these modern approaches. But also cases where limitations exist and further studies are needed [6-11].

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MTMS '21

Keynote Lecture KL 01

Clean, High Quality Low Emission Fuels with Fischer-Tropsch Synthesis: A Multiscale Study of Transport Properties in Confined Systems

Authors and affiliation

Ioannis G. Economou^{1,2,*}, Konstantinos D. Papavasileiou¹, Loukas D. Peristeras¹ and Andreas Bick³

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Key Word (3 words)

Fischer-Tropsch, molecular simulation, confined systems

Abstract (less than 300 words)

The Fischer-Tropsch (FT) route is a polymerization reaction used extensively in the Gas-to-Liquids (GTL) process to transform synthesis gas into high quality low emission transportation fuels. The main FT reaction products, namely water, wax and small amounts of oxygenates (e.g. alcohols < 10 wt %), form a mixture through which the dissolved reactants diffuse, reach the catalytic nanoparticles and react. Key factors in ensuring FT reactor's activity and stability is the selection of the catalyst (e.g. Co) and the support material (e.g. TiO₂, Al₂O₃, graphene). Unfortunately, FTS catalysts deactivate over time and the role of oxygenates and excess water in the loss of catalyst activity remain as open questions.[1]

In order to gain a better understanding of the phase behavior of confined wax – water – alcohol mixtures in either hydrophilic or hydrophobic environment at reaction conditions, our efforts concentrated on the the *n*-C₂₈ – H₂O – 1-dodecanol mixture at 473.15 K inside pristine graphene (G) and graphene oxide (GO) pores by means of Coarse Grained Molecular Dynamics (CGMD) simulations. Our simulations show that CG approaches capture the mixture phase separation and individual component diffusivity. The Co NP does not affect the mixture phase separation but it is extensively covered by water. Our results showcase that CGMD can be employed to study FTS related processes at this scale [2,3] and are expected to open new pathways in the investigation of the effect of NPs on catalyst support interfaces in the presence of FTS relevant mixtures.

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MTMS '21

Keynote Lecture KL 02

Phase Equilibria and Enhanced Oil Recovery

Authors and affiliation

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Key Word (3 words)

Winsor; Interfacial Tension; Flooding.

Abstract (less than 300 words)

Currently imagining a world without oil is imagining a debacle. With each passing day, our comfort requires more energy and a greater number of materials to synthesise commodities. The eventual need to move towards total independence from crude oil is undeniable, but we need time whilst trying to achieve the required technological development. Approximately two thirds of the oil still remain inside an already exploited reservoir, so the full exploitation of existing wells could be a way to buy that time.

Surfactant enhanced oil recovery (EOR) methods are promising. A very low concentration of surfactant in brine is injected into the reservoir to reduce the water-oil interfacial tension, thus enhancing the mobility of oil retained in the pores of the rocks. The surfactant must meet many requirements: it must be miscible in water, stable in the presence of salts, and show a significant and equilibrated solubilization of oil and water. The search for this surfactant has been carried out many times in an arbitrary manner, frequently performing a large number of interfacial tension measurements until the goal is reached. However, the study of the phase equilibria involved (brine, oil and surfactant) is the shortest way to reach the goal. Winsor type III systems lead to ultra-low interfacial tensions and suitable surfactants for EOR.

Thanks to the possibility of designing a practically unlimited number of them, ionic liquids (ILs) have become a powerful tool in the improvement of many processes, among them EOR applications. In this work, some studies involving ILs for oil recovery are presented. Studies based on interfacial tension, rigorous liquid-liquid equilibrium determinations, or pipette tests looking for Winsor type III systems, have been different attempts to define a suitable formulation for EOR. Many unsuccessful attempts but also some successful results are presented.

Acknowledgements

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MTMS '21

Keynote Lecture KL 04

Exploring the effect of cholesterol on stratum corneum lipid assemblies

Authors and affiliation

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Key Word (3 words)

Coarse-graining, Skin, Molecular dynamics

Abstract (less than 300 words)

The stratum corneum (SC) is the outermost layer of the skin and functions as the primary barrier between the body and the environment. The SC, composed of dead corneocyte cells surrounded by a matrix of lipid lamellae that provides the only continuous path through which external chemical penetrants and water can cross the SC. The SC lipids are primarily composed of ceramides of 18 subclasses, cholesterol, and free fatty acids. In addition, it has been discovered that deficiencies in certain lipid components and an altered lamellar structure in the SC lipids are associated with skin diseases such as eczema and psoriasis. Thus, exploring the composition-function relationship of the SC lipids, using both real SC samples as well as synthesized membranes, has been the focus of countless publications. Experimental studies, such as neutron scattering and x-ray diffraction have found that two lamellar phases coexist in the SC lipids: the 6 nm short periodicity phase (SPP) and the 13 nm long periodicity phase (LPP), of which the latter only forms in the presence of long esterified (EO) CERs and is unique to the SC [1]. However, experimental techniques are unable to uncover the molecular-scale arrangement or the barrier mechanism of the lipids.

Atomistic molecular dynamics (MD) can be used to model SC lipids since they provide a 3D structure with atomic resolution. However, due to the low mobility of the gel phase SC lipids, atomistic simulations can be heavily biased by their preassembled initial configuration and not reach equilibrium over practical computation times. In addition, due to high computational cost, atomistic MD systems are typically single bilayers, rather than multilayers, which do not provide an accurate representation of the skin lipid lamella. Alternatively, simulations using coarse grained models can feasibly access the long timescales needed to study self-assembly from randomized configurations and achieve the large system sizes required for multilayer systems to provide a more realistic, albeit less detailed, structure. Here the development of a novel computationally efficient coarse-grained model of the CER EOS using multi-state iterative Boltzmann inversion (MSIBI) is presented [2]. Furthermore, the CG model is applied to examine the effect of cholesterol concentration on membrane structure and fluidity for self-assembled SPP and LPP systems.

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MTMS '21

MTMS '21, September 7 – 9, 2021

Keynote Lecture KL 05

Molecular Modeling of Supercapacitor Systems

Authors and affiliation

Peter T. Cummings*

Department of Chemical and Biomolecular Engineering, Vanderbilt University, USA

Key Word (3 words)

Electric double layer; supercapacitors; electrolyte

Abstract (less than 300 words)

Supercapacitors, also known as ultracapacitors or electric double layer (EDL) capacitors, are energy storage devices that store electrical energy in the form of charges adsorbed to the electrodes, which are typically micro- or mesoporous conducting materials to maximize the electrode surface area. The goal of supercapacitor research is to bridge the energy storage gap with batteries, while retaining high power density. This requires fundamental understanding of the properties of the EDL, the nanoscale layering of ions interacting with an electrode. We use molecular dynamics simulations to study the properties of electrolytes and electrodes, from which we obtain structural, transport, and electrochemical properties. We review some of our key work in this area, supported by collaborations with experiments and materials synthesis performed at Oak Ridge National Laboratory, Drexel University, and other institutions that belong to the Fluid Interface Reactions Structure and Transport (FIRST) Center, a U.S. Department of Energy-funded Energy Frontier Research Center [<https://web.ornl.gov/sci/first/>].

MTMS '21

Keynote Lecture KL 06

Kinetic viscosities prediction using ASOG-VISCO group contribution method for binary liquid mixtures

Authors and affiliation

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Key Word (3 words)

Viscosity, ASOG, Liquid mixtures

Abstract (less than 300 words)

A number of empirical correlations/ models, for the prediction of liquid mixture viscosities are available in the literature. A reliable and valid theory for the qualitative prediction of viscosities of liquid mixtures from the properties of pure components has not been established.

Group contribution models play a vital role in the prediction of viscosity data for liquid mixtures. Some of the best known group contribution based models for the prediction of viscosities of liquid mixtures are the UNIFAC-VISCO, ASOG-VISCO and Grunberg-Nissan model. [2-4]

In the present work, an attempt has been made for predicting the kinematic viscosities for 193 data sets of binary systems using ASOG-VISCO model based on Eyring's theory of absolute reaction rates and ASOG group contribution method. [1,5].

Close agreement is observed between the predicted and experimental viscosities for most of the systems studied. However, it is pointed out that ASOG-VISCO group contribution models give good estimates for mixtures viscosities as compared with ASOG-VLE.

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MTMS '21

Keynote Lecture KL 07

Prediction of vapor-liquid equilibria for multicomponent systems by a modified concentration dependent surface area parameter model

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Key Word (3 words)

CDSAP model, activity coefficient, vapor liquid equilibrium

Abstract (less than 300 words)

Our group proposed a new activity coefficient model which is based on the regular solution theory and composition-dependent surface area parameters. Surface area parameters, which account for the number of interactions between molecules, vary depending on partner molecules and the concentration of mixtures. This is called r-CDSAP model. r-CDSAP model can successfully describe an exceptionally high value or convex behavior of activity coefficient in the dilute region. r-CDSAP model also shows improved performances in correlating the liquid-liquid equilibria for ternary systems and the vapor-liquid equilibria for constituent binary systems with the same parameter sets [1,2].

r-CDSAP model is very flexible, but this flexibility is an obstacle in estimating the activity coefficients of multicomponent systems from the parameters determined with binary systems. Another obstacle is the restriction condition to make the surface area parameters of pure components common to multicomponent system.

In order to use r-CDSAP for estimating the activity coefficients of multicomponent systems, the following modifications have been made.

- (1) In r-CDSAP model, there is the restriction condition to make the surface area parameter of pure components common to multicomponent systems, which is removed.
- (2) When correlating the activity coefficients of binary systems, a limiting condition is added to the surface area parameters of pure components to avoid taking extreme values.
- (3) The surface area parameters of pure components determined by binary systems are used only for the corresponding term in excess Gibbs free energy.

As a result, it is possible to estimate the activity coefficients of multicomponent systems using the parameters determined from binary systems by a modified r-CDSAP model. This is called p-CDSAP model. The calculated results for several ternary and quaternary systems are good by p-CDSAP model.

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MTMS '21

Invited Lecture IL 01

Measurement of Vapor-Liquid Equilibria for Azeotropic systems

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Key Word (3 words)

vapor-liquid equilibria, azeotrope, equilibrium still

Abstract (less than 300 words)

It is known that about half of the binary vapor-liquid equilibrium (VLE) data available in the literature are azeotropic systems. There are generally two types of azeotrope of isobaric binary systems: the minimum boiling point azeotrope, where the boiling point is lower than that of the pure component at a specific composition, equal composition of vapor and liquid phases, and the maximum boiling point azeotrope, where the boiling point is higher. In addition, in very few cases, there are the double azeotrope that have both minimum and maximum boiling points at each specific composition. In isobaric ternary VLE, there are the minimum boiling point azeotrope and the saddle-type azeotrope.

In this study, the VLE of azeotropic systems measured using the original equilibrium stills with circulation of both the vapor and liquid phases, equipped with a Cottrell pump are shown [1,2,3,4]. For some systems, the VLE measured under pressurized conditions using a pressure-resistant equilibrium still [5,6] are shown to describing the trajectory of different of azeotropic points on elevated pressure from experimental data.

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MTMS '21

Invited Lecture IL 02

Methodology for Applying Equations of State to Phase Equilibrium Calculation for Mixtures

Authors and affiliation

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Key Word (3 words)

Equations of state, Mixing rules, Phase Equilibria

Abstract (less than 300 words)

Equations of state (EoS) are basically developed to represent the pressure-volume-temperature(PVT) behavior as well as the saturated properties of pure component. In applying such EoS to mixture property calculations, the effect of composition should be considered and several approaches have been proposed. Most popular approach is the mixing rules which defined the EoS parameters of mixtures by defining functional forms of the parameters in terms of composition. The mixing rules can provide very good performance for most cases, however the performance tends to decrease with asymmetric mixtures that consist of different size/polarity components. It would be noted that one possible reason is the difference in corresponding kinetic energy for asymmetric components even at same temperature. This indicates that, for a large asymmetric system, it is difficult to represent the PVT behaviors for both components by the same functional form of an EoS. It has been sometimes observed a singular PVT curve having multiple thermodynamic unstable regions in the case of virial type EoSs. The van der Waals mixing models, which combine the equation parameters as a function of composition, can be regarded as a mixing of the PVT curves of each pure component at the temperature. In other words, the model combines the stable and unstable PVT regions depending on the condition.

The corresponding state principle is a good methodology to calculate the mixture properties from pure component information with pseudocritical values. We can adopt this method to mix the thermodynamic properties of each component with confirming the values in stable state. By extending the Lee-Kesler method, a kind of mixing rule can be derived to combine the different type EoSs for each component of the mixtures^[1].

In the presentation, I will show the deviation of methodology and its possible extensions for some examples.

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MTMS '21

Invited Lecture IL 03

Application of Analytical Centrifugation to Chemical Systems for Measurement of Properties and Phase Equilibria

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Key Word

Sedimentation equilibrium, Distribution coefficients, Nanoparticles

Abstract

Analytical centrifugation applies a gravitational field to a sample solution and measures space-time extinction profiles (STEP) to determine the properties and stability of a colloidal system. In this work, we review measurements being made with analytical centrifugation for the determination of properties in chemical systems (diffusion coefficients, phase separation) and introduce our own studies on estimation of effective densities of nanoparticles in solution and consider two phase systems in which partition coefficients can be measured. Systems of interest and highlighted in the presentation are those in environmental (octanol-water), food (emulsions), chemical (nanoparticles) fields.

MTMS '21

Invited Lecture IL 04

Performance improvement on dynamic simulation for high pressure polyethylene synthesis by PC-SAFT

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Key Word (3 words)

Dynamic simulation, polyethylene synthesis, PC-SAFT

Abstract (less than 300 words)

High pressure polyethylene synthesis process requires advanced thermodynamic models such as PC-SAFT, and it is challenging to satisfy both computational reliability and performance, which are critical for dynamic simulation. In this work, two new computational techniques were developed and applied in our customer's projects. The first one is to improve the reliability by identifying a unique tangent point of the equation of state (EOS) [1]. The second one is to extend the squeeze theorem to functionals for performance improvement.

For any EOS there exists one tangent point which separates the vapor and liquid densities. With such tangent point, the computational effort solving the density roots can be significantly reduced. It also provides guarantee to avoid fake density root, so that complicated model like PC-SAFT can be reliably solved in high pressure region. Squeeze theorem states that if $f_L(x) \leq f(x) \leq f_U(x)$ for all x , then at some values of x (references) all three functions are equal. Such theorem can be extended into functionals $g_L(X_L)$ and $g_U(X_U)$ which replace $f_L(x)$ and $f_U(x)$ where both X_L and X_U are functions of x . Within a neighborhood of a reference ($x \pm dx$), the "squeeze"-relation still holds by those functionals, and the complicated $f(x)$ can be simplified by its first order Taylor expansion. The gap of the functionals would then be monitored to trigger necessary recalculation of $f(x)$ if value of x is moving away from the reference neighborhood. We call this squeeze functional as "super-linear" approach.

Both techniques are generally applicable to any EOS model. To keep the generality and best protect our customer's confidentiality, examples were extracted and generalized from projects as vapor-liquid phase equilibrium problems. The results were compared with literature data. Performance improvement by the squeeze functional were observed with double to triple magnitudes faster than benchmark results without using it.

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MTMS '21

Invited Lecture IL 05

Improvements on the Predictive COSMO-SAC Model and its Applications in Process and Product Design

Authors and affiliation

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Key Word (3 words)

COSMO-SAC; Molecular Design; Process Design

Abstract (less than 300 words)

Thermodynamic properties and fluid phase equilibria are crucial for the design and development of a chemical process. However, such data may not always be available, particularly for fine and specialty chemicals. Furthermore, in order to design new chemical products with desired functionalities, it is important to estimate their properties based on chemical structures. It is therefore desirable to have a reliable predictive method for the estimation of the thermodynamic properties. In this presentation, we will demonstrate how we develop accurate and reliable predictive models for thermophysical properties and fluid phase equilibria. In particular, we will introduce the COSMO-SAC model¹ for liquid activity coefficient, and its extension, the PR+COSMOSAC EOS², for fugacity of any fluid and fluid mixtures.

Equally important is to integrate the predictive methods with process simulators, such as AspenPlus, so that any chemical engineers can perform the routine design without the hassle of conducting the detailed property predictions. To this end, we have developed a new platform, T.E.A.M, that provides all the necessary thermodynamic information needed in a chemical process design in the format of AspenPlus file. The T.E.A.M has a web-based front-end, where the user can specify the chemicals involved in the process submit the request for determination of the all the variables needed for AspenPlus. If any of the needed properties are not available in the AspenPlus database, TEAM performs the needed calculations based on COSMO-SAC and PR+COSMOSAC equation of state. We will illustrate the use of T.E.A.M for the design of a process for converting CO₂ to high value chemicals³. This process involves 10 chemicals but about 20% of pure fluid properties and 85% of mixture properties are not available in AspenPlus. With the help of T.E.A.M we successfully developed a carbon-neutral and economically profitable process for utilization of CO₂.

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Invited Lecture IL 06

Mercury Solubility Measurements in Glycols and Amines for Natural Gas Processing Plant

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Key Word (3 words)

Elemental mercury, VLLE, equation of state

Abstract (less than 300 words)

Natural gas produced from in-situ reservoir sometimes contains small amount of mercury (Hg). The knowledge of Hg behavior is now an important matter on natural gas processing for proper handling of Hg. After oil and water contents are roughly separated from the natural gas at the separator, the natural gas is sent to acid gas removal and dehydration process. Then, amine and glycols have been widely employed as absorbents in these process. In this research, for the design of mercury removal units, solubilities of elemental mercury were measured in ethylene glycols (MEG), diethylene glycols (DEG), Triethylene glycols (TEG) and N-methyldiethanolamine (MDEA) under the atmospheric pressure at (303-333) K [1]. The solubilities were measured by an apparatus based on a static method. The sample was prepared under the nitrogen atmosphere to avoid the oxidation of elemental Hg, and it was in the vapor-liquid-liquid mercury equilibrium. The concentration of elemental Hg, in liquid, glycols and amine, was determined by a total Hg analyzer, which is based cold-vapor atomic absorption spectroscopy with the wavelength of 253.7 nm. The solubilities ranged from 5.64×10^{-8} to 6.34×10^{-7} in the mole fraction of Hg, and showed a temperature dependence followed van't Hoff equation with the dissolution enthalpies around 23 kJ/mol. The ratio of the mole fraction of elemental Hg was found to be the same as that of the numbers of carbon and oxygen in the main chain in the molecules at 303 K. The solubilities were also correlated with Peng-Robinson equation of states modified for elemental Hg in our previous research [2]. The calculation results will be described in the presentation together with those for Hg solubility in high pressure methane [2].

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MTMS '21

Invited Lecture IL 07

Solids Formation Risk in Natural Gas, LNG and Liquid Hydrogen Production

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Key Word (3 words)

Hydrogen, LNG, Gas Hydrates,

Abstract (less than 300 words)

Natural gas and hydrogen are emerging as the fuels of primary importance for the 21st century. A common threat to the reliable production, trade and utilization of these fuels is the risk of solids formation. For example, the production of natural gas often involves transporting high-pressure multiphase mixtures through pipelines hundreds of kilometers long, with temperature changes likely to trigger gas hydrate formation. To increase the volumetric energy density economically viable levels, natural gas and hydrogen are often liquefied by cooling them to 110 K or 22 K, respectively. Solid blockages can form in these liquefaction processes if multiple impurities are not removed to part-per-million concentrations for LNG and even lower for LH₂. Solids formation in any of these stages of the value chain can constitute a major technical and financial loss for the operators, yet the ability to quantitatively predict and/or monitor in real-time the risk of such an event represents a significant ongoing knowledge gap.

To address multiple aspects of this general problem we have developed several new apparatus with operating pressures as high as 30 MPa and operating temperatures as low as 80 K to acquire thousands of data points for both solid-fluid equilibrium and formation kinetics in key mixtures. These data have underpinned new predictive engineering models based on optimized equations of state for fluids and solids, as well as formation probabilities based on Classical Nucleation Theory. Online databases and free software packages, such as *ThermoFAST Web*, have been developed to implement and disseminate some of these results. Additionally a patented sensor for detecting solids freeze-out conditions in cryogenic liquefaction facilities has been demonstrated with samples from operating LNG plants. This talk will summarize the objectives and outcomes of this initiative to date and describe the challenges still to be addressed.

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Invited Lecture IL 08

Molecular Behavior of 1-Pentanol Guest in the NH₄F-doped Clathrate Hydrate

Authors and affiliation

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Key Word (3 words)

Clathrate Hydrate, Hydrogen Bonding, Ammonium Fluoride

Abstract (less than 300 words)

In pure water and even in the presence of help gases, 1-pentanol (1-PeOH) cannot form the clathrate hydrate structures both because of its size that is not appropriate for either the structure II $5^{12}6^4$ or structure H $5^{12}6^8$ cages and the presence of a hydrophilic OH group that tends to destabilize the clathrate hydrate framework. [1] Recently, the NH₄F doping in the clathrate framework was suggested to make the hydrate lattice more resistant to disruption by host-guest hydrogen bonding. [2,3] In this work, we report the synthesis of 1-pentanol + methanol binary structure II clathrate hydrate doped with NH₄F and demonstrate that the space filling of 1-pentanol as a guest molecule can be managed by the hydrogen bonding between doped NH₄F in the water framework and the hydroxyl group of 1-pentanol. The structural characterization of 1-PeOH + methanol hydrates was conducted by the powder X-ray diffraction (PXRD) pattern analysis and the solid state ¹³C NMR spectroscopy. The 1-PeOH guest conformations and molecular interactions in the clathrate cages and the guest conformations was also investigated by the solid state ¹³C NMR spectroscopy and molecular dynamics simulations. Additionally, the 1-PeOH hydroxyl group was observed to be incorporated in the clathrate hydrate water framework. The findings in this work show that doping the clathrate hydrate lattice with NH₄F and using methanol as a helper guest can be used for stabilizing heavier alcohol molecules which cannot be encaged in normal clathrate hydrates.

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Invited Lecture IL 09

Physical Chemistry of Amine-Based Carbon Dioxide Separation

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Key Word (3 words)

CO₂, Reaction mechanism, Solvation

Abstract (less than 300 words)

CO₂ capture and storage (CCS) technology is an effective CO₂ fixation technology. Today, this technology has become important due to the threat of global warming and climate change. Furthermore, the development of CO₂ capture and utilization (CCU) technology, which reuses the captured CO₂, has been prioritized in recent years. In this context, CO₂ separation is one of the key processes on a pathway to net zero emissions. Regardless of the maturity of various types of CO₂ separation technologies, amines are the most used chemical species in a variety of separation methods. This is because the moderate interaction between amines and CO₂ allows effective “catch and release [1, 2].” We have been studying physical and chemical properties of amines and amine-containing media for CO₂ separation. The physical properties including the boiling point, diffusion coefficient, and polarity are of vital information for understanding, designing, and optimizing amine-based CO₂-separation technologies [2, 3]. In those technologies, the central chemical reactions are carbamate formations and bicarbonate formations [4, 5]. The branching ratio of these reactions, which depends on the structure of amine molecule, greatly affects the CO₂-separation performance [6, 7]. The complicated molecular interactions, various elementary steps, by-products, and surrounding developments are involved in these reactions. Among them, the effects of substituents such as alkyl and hydroxy groups, hydrogen bond, and solvation are of paramount importance [8, 9].

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Invited Lecture IL 10

DDBST and LTP – Your Source for Reliable Thermophysical Properties

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Key Word (3 words)

Databanks, Software, Measurements

Abstract (less than 300 words)

The reliable knowledge about the real behavior of the pure compounds and their mixtures as a function of temperature, pressure and composition is of a great importance for the development and design of industrial processes. Since an experimental determination of all needed properties is nearly impossible, the process engineer depends on factual data banks or reliable predictive models.

With a view to the synthesis and design of separation processes, fitting and critical examination of model parameters used for process simulation and the development of group contribution methods, the compiling of a computerized data bank for phase equilibrium data was started 48 years ago by Gmehling and Onken at the University of Dortmund. Today, the Dortmund Data Bank is the worldwide largest factual data bank for thermophysical properties of pure components and their mixtures and contains nearly all worldwide available phase equilibrium data, excess-, transport- and pure component properties even for polymer and electrolyte systems. Besides the easily accessible thermophysical properties from scientific literature, DDB contains also a huge amount of data not available via the open literature. A powerful software package for the data handling, correlation, property estimation and process synthesis enables the user to get most out of the data.

If a certain property should still not be found, our affiliated Laboratory for Thermophysical Properties might be able to perform measurements for the requested systems. The LTP is very experienced in phase equilibrium measurements, also at high pressures over a broad temperature range. The laboratory works since many years on transport and calorific properties and PVT data at elevated pressures. With more than 40 set-ups for thermodynamic measurements LTP covers a broad temperature and pressure range.

MTMS '21

Invited Lecture IL 11

Association-based Activity Coefficient Models for Nonelectrolyte and Electrolyte Solutions

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Key Word (3 words)

Association theory; Fluid phase equilibria; Nonrandom Two-Liquid activity coefficient model

Abstract (less than 300 words)

The classical nonrandom two-liquid (NRTL) activity coefficient model for nonelectrolyte solutions [1] and the electrolyte NRTL model for electrolyte solutions [2] have been considered the most versatile and widely practiced molecular thermodynamic models to correlate and predict phase equilibrium behavior of multicomponent systems in support of process simulation, design, and optimization. Derived from the two-liquid theory, these NRTL models rely on the “binary interaction parameters” to account for the combined short-range physical interactions and chemical associations that dedicate the liquid structure and energetics of the system at a microscopic level. However, without explicitly accounting for specific chemical associations such as hydrogen bonding and ion hydration, these NRTL models fail to accurately correlate and predict phase behavior of highly associating nonelectrolyte systems such as methanol – alkanes binaries and aqueous electrolyte solutions with highly charged ionic species such as lithium and magnesium salts.

Extensively applied to equations of state such as Statistical Associating Fluid Theory and Cubic Plus Association, Wertheim’s perturbation theory has recently been integrated with the NRTL models to explicitly account for the associations. [3,4,5] Specifically, the association contribution is formulated with a water self-association reference term and species-specific association strengths for molecules and ions while the physical interaction contribution is captured with the NRTL binary interaction parameters. The resulting association NRTL models reduce to the classical NRTL models when the association strengths are negligible. With refined theoretical basis and superior accuracy over the classical NRTL models, the association models enable accurate correlation and prediction of fluid phase equilibria of multicomponent association systems with minimum numbers of adjustable parameters. This presentation shows the association NRTL models yield drastically improved correlative and predictive results for many highly associating multicomponent systems, electrolytes and nonelectrolytes.

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MTMS '21, September 7 – 9, 2021



Oral Presentations

OP 01

Phase diagram of ternary mixtures water + *n*-alkane + non-ionic surfactant

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Key Word (3 words)

Non-ionic Surfactant, Phase equilibria, Fish-shaped

Abstract (less than 300 words)

n-Alkyl polyglycol ethers $\text{CH}_3(\text{CH}_2)_{i-1}(\text{OCH}_2\text{CH}_2)_j\text{OH}$ (C_iE_j) are the most important class of non-ionic surfactants. They are widely used in many different industrial processes such as the surfactant flooding in tertiary oil recovery, production of herbicides, drugs, cosmetics, and nano particles. Understanding the phase behaviors of the ternary mixture water + alkane + C_iE_j is very crucial to choose a suitable surfactant and surfactant concentration for the flooding process [1]. It is also important in the fundamental research of critical phenomena and wetting transitions [2]. Phase diagram of water + *n*-alkane + C_iE_j has been reported to exhibit complex behavior called “Fish-Shaped” [1, 2], when the temperatures of phase transitions are plotted vs. the mass fraction of C_iE_j in the fixed water / alkane mass ratio. Especially, an intersection of the body and tail of the fish-typed phase diagram is called as “X-point”. One-liquid phase can be formed in the minimum concentration of the surfactant at X-point. Thus, it is important to choose a suitable surfactant and surfactant concentration in the processes using the surfactant.

The object of this work is an accurate determination of the phase diagram of ternary mixtures water + *n*-alkane + C_iE_j using a cloud point method with laser scattering technique [3, 4]. *n*-Octane and *n*-dodecane were selected as *n*-alkane. 2-butoxyethanol (C_4E_1) and 2-(2-hexyloxyethoxy)ethanol (C_6E_2) were selected as non-ionic surfactant. In the measurements of ternary mixtures, the C_iE_j free basis mass fraction of *n*-alkane “ α ” was changed from 0.1 to 0.9.

In the fish-type phase diagram, body is three-liquid phase, tail is one-liquid phase, and another region is two-liquid phase. An intersection of the body and tail is called “X-point”. Changes in the phase diagram and X-points with different *n*-alkane, C_iE_j , and the value of α were discussed from the experimental data.

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MTMS '21

OP 02

Measurement and correlation of diffusion coefficients of Cr(acac)₃ in high temperature supercritical carbon dioxide

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Key Word (3 words)

Diffusion coefficient, Supercritical, Organometallic compound

Abstract (less than 300 words)

Over the last 40 years, the chemical processes with supercritical carbon dioxide (scCO₂) has been intensively studied from the early stages in many applications such as supercritical fluid extraction, separation/fractionation, cleaning, supercritical fluid deposition, polymer dyeing, nano/micropore formation, atmosphere or solvent for chemical reactions, and mobile phase for supercritical fluid chromatography. As the applications have expanded, the data on both equilibrium and transport properties for supercritical fluids/mixtures have been required and vigorously measured. However, they are not yet sufficient [1], and the diffusivity data on organometallic complexes, especially in high temperature scCO₂, are not sufficiently enough and demanded for determining kinetics and designing processes for supercritical fluid deposition. In this study, extending to our previous study in which diffusion coefficients of Cr(acac)₃ in scCO₂ were measured up to 343K [2], the measurements were carried out at temperatures up to 423 K and pressures up to 20 MPa by the chromatographic impulse response (CIR) method, which provides diffusion coefficient and retention factor. The new D_{12} data more deviated at CO₂ viscosities lower than 40 μ Pa s from the hydrodynamic equation, in which D_{12}/T vs. CO₂ viscosity can be represented by a straight line in logarithmic plot, and is effective for many organic compounds measured in liquid-like density region of scCO₂ [1-4], and the deviation becomes more at lower CO₂ viscosities. To the contrary, retention factors were expressed by a single equation as a function of temperature and CO₂ density over at entire conditions studied. The accuracies for various predictive correlations are examined, and a modified Schmidt number correlation is proposed. As a result, the modified Schmidt number correlation was effective with average relative deviation of 6.10 % for 282 data points over an entire range of temperature and pressure studied.

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MTMS '21

OP 03

Vapor Pressure Prediction Method for Pure Substances

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Key Word (3 words)

Vapor pressure, Prediction, Boiling point

Abstract (less than 300 words)

In a newly proposed prediction method of vapor pressure, the parameters of the vapor pressure equation are directly determined using the parameter of the reference substance with one set of vapor pressure data, for example, boiling point data. A series of observed vapor pressure data of a substance shows linear relation between logarithm of measured vapor pressure and reciprocal value of its absolute temperature. In addition, the slope of the linear relation is almost same for homologous series. By using this slope of homologous substance, for the homologous substance of which vapor pressure is not observed, the intercept of the vapor pressure equation can be determined from the one set of vapor pressure data. As the vapor pressure equation, the Clapeyron and the Antoine equation are chosen. The method was applied for the following homologous substances; alcohols, acids, esters, ketones, organophosphors, pinenes, and silanes. The average absolute deviations (AAD) of these homologous substances were 0.615 and 0.709 kPa for the Antoine and the Clapeyron equations, respectively. The feature of the method is that it does not use any correlation, except that it uses a homologous substance as a reference substance. Therefore, unlike the other method, there is no error due to data correlation. The accuracy of the method depends on the difference in latent heat of vaporization between the substance to be estimated and the reference substance, that is, the difference in the slope of the vapor pressure expression equation. However, it depends on the selection of reference substance and temperature range to be used for prediction. Since this method is based on thermodynamically derived Clausius-Clapeyron relation, it is a widely and generally applicable method and there is no limitation by substance, temperature and pressure.

MTMS '21

OP 04

Prediction of solubility of organic compound for high-temperature water by machine learning

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Key Word (3 words)

Solubility, Machine learning, Subcritical water

Abstract (less than 300 words)

In recent years, high-temperature water has attracted attention for processes such as organic reactions and extractions due to its low environmental load and low waste. The experimental data of the solubility of organic compound for high-temperature water is important for designing the processes. However, the data on the solubility of organic compound for high-temperature water is limited due to the difficulty of the experiments. On the other hand, the data on the solubility of organic compound in water under ambient temperature and pressure is abundant. In this study, we developed a prediction model of the solubility by machine learning by combining the experimental data at ambient temperature with those at high temperature.

At first, the chemical structure of the organic compound was converted into descriptors using Python RDkit, which is an open source of chemical informatics and machine learning. Regression of the organic compound solubility was performed using the descriptors, temperature, and water density. As a result, it was found that the model obtained by the regression can predict the solubility of organic compound in high-temperature water.

MTMS '21

OP 05

Predicting the solubilities of acetylacetone-type metal precursors in supercritical CO₂: Thermodynamic modeling using PC-SAFT

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Key Word (3 words)

Supercritical CO₂, Solubility, PC-SAFT

Abstract (less than 300 words)

The deposition of metal particles on porous supports such as mesoporous silica using supercritical CO₂ has attracted much attention as a method for preparing supported catalysts because the metal particles can be dispersed in the pore structure [1, 2]. Prediction methodology of the solubility of metal precursors in supercritical CO₂ is important to efficiently design the supported catalyst using the supercritical CO₂ deposition method.

In this study, a thermodynamic model using the PC-SAFT (perturbed-chain statistical associating fluid theory) equation of state [3] was used to predict the solubility of various acetylacetone-type metal precursors in supercritical CO₂. The pure component parameters (the segments number, segment diameter, and dispersion energy) of the metal precursors were determined by considering the correlation with the solubility data of the metal precursors in various organic solvents that were newly measured in this study. The pure component parameters of the metal precursors determined using the correlations were applied to the prediction of the solubility data of metal precursors in supercritical CO₂ using PC-SAFT. The model could reproduce the solubility of various metal precursors over a wide range of temperatures and pressures in supercritical CO₂ without the binary interaction parameter (k_{ij}) for almost all conditions investigated.

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MTMS '21

OP 06

Controlling the CO₂-lipid liquid phase separation via process tuning and lipid structural design

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Key Word

Volume expansion, Supercritical CO₂, Thermodynamics modeling

Abstract

The volume expansion of organic solvent at near critical and supercritical CO₂ (ScCO₂) is a critical property for designing and optimizing ScCO₂-mediated process. The lipid expansion behavior in the ScCO₂ is found to be a dominant factor toward ScCO₂ anti-solvent precipitation process, liposome capsule production using ScCO₂, and ScCO₂ assisted lipid extraction process[1-5]. In this work, the oleic acid, linoleic acid, and 1-octadecene are selected to perform measurement of liquid volume expansion during CO₂ pressurization at a pressure–volume–temperature (PVT) cell with visible window, to investigate the role of carboxyl group and double bond to CO₂ dispersion behavior in the lipid at pressure range of 5 MPa to 20 MPa, temperature range of 308 K to 338 K.

It is found that the dispersion behavior of CO₂ in the liquid phase is dominated by the carboxyl group on the lipid. The temperature and pressure dependent liquid expansion in CO₂ environment is reasonably fitted by Peng-Robinson equation of state combining with Wong-Sandler mixing. From analysis of molecular σ -profile, carboxyl group and double bond shows strong and weak hydrophilic character, respectively. Both functional groups are disadvantage of CO₂ dispersion into liquid lipid, leading to CO₂-lipid phase separation at high pressure region ($P > 15\text{MPa}$).

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MTMS '21

OP 07

Development of CO₂-assisted dispersibility of organic-inorganic hybrid nanoparticles with expanded liquid solvent mixtures

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Key Word (3 words)

Solubility parameter, Solvent selection, Nanoparticles

Abstract

Applications of organic-inorganic hybrid nanoparticles (NP) require a suitable solvent to have high dispersibility in terms of target objectives. According to the literature [1], pure nonpolar solvents (e.g. cyclohexane and hexane) can be a suitable solvent to provide high dispersibility for decanoic acid-modified NP (homogeneous solution), while pure polar solvents (e.g. ethanol and water) caused turbid solution due to agglomeration in NP. The limitation of NP processing comes from a small number of suitable pure solvents due to attractive forces between the particles and the complicated interactions between surface chains of NP and solvent molecules. In this sense, the first objective of this work is to propose a method for selecting suitable solvents by extending the candidate into binary solvent systems. The second objective is to develop a CO₂-expanded liquid process for controlling NP dispersibility.

In this work, the literature data of NP and a solvent [1] were analyzed and were found that the dispersion solubility parameter (δ_d) and the van der Waals volume (V_{vdw}) are key parameters for defining suitable solvents, where favorable ranges were δ_d ($\approx 15 - 17 \text{ MPa}^{0.5}$) and V_{vdw} ($< 89 \text{ cm}^3 \cdot \text{mol}^{-1}$). To validate the favorable ranges, CO₂ was chosen to study because its δ_d ($\approx 15.6 \text{ MPa}^{0.5}$) and V_{vdw} ($19.7 \text{ cm}^3 \cdot \text{mol}^{-1}$) values are within the favorable ranges. In order to demonstrate the role of CO₂ in dispersion, the experiments were conducted by the addition of CO₂ into solutions. The studied conditions were 1wt% hybrid CeO₂ nanoparticles in solutions (decane solvent), the temperature of 40 °C and pressure from 2 to 6 MPa using a high-pressure observation. It was found that the addition of CO₂ could cause a change of turbid solution to clear solution, namely increasing the dispersibility. These results imply that the δ_d and V_{vdw} favorable ranges can be used to identify a suitable solvent and CO₂-expanded liquid solvent mixtures can be a suitable alternative solvent for NP processing.

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MTMS '21

OP 08

Surface modification of nano-TiO₂ with para-aminobenzoic acid in supercritical carbon dioxide for preventing aggregation of nanoparticles

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Key Word (3 words)

supercritical nanotechnology, supercritical carbon dioxide, nano titanium dioxide

Abstract (less than 300 words)

Post-modification amino acid modified titanium dioxide (TiO₂) nanoparticles syntheses were performed by the supercritical CO₂ method to prevent the aggregation of TiO₂ nanoparticles in the solvent systems. The results showed that the modification rate of TiO₂ nanoparticles with para-aminobenzoic acid (PABA) obtained by the supercritical carbon dioxide method was 2.24 times higher than the conventional solvent immersion method. From the results of FT-IR analysis and supported by TG-DTA, TEM, and elemental analysis, it can be concluded that the binding form of PABA molecules on the surface of TiO₂ nanoparticles produced through the chemically bridging reaction. XPS analysis confirmed that the carboxylate group is bound onto the TiO₂ surface and freely lets the amine group. The surface modification by PABA influenced the surface electrical property of TiO₂ nanoparticles to a positive charge and showed better dispersibility in water and alcohol compared to unmodified TiO₂ nanoparticles. A Supercritical CO₂ method is an environmentally friendly method and effectively be applied in the surface modification of nanomaterials.

MTMS '21

OP 09

Synthesis of decanoic acid-modified iron oxide nanocrystals using supercritical carbon dioxide as reaction medium

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Key Word (3 words)

Supercritical carbon dioxide, iron oxide nanocrystals, surface modification

Abstract (less than 300 words)

Nanoparticle synthesis in liquid phase, such as heat-up and hydrothermal methods, has been typically applied to the preparation of organic modified nanocrystals (NCs), however, these methods cause the large amount of the liquid waste for the synthesis and washing of NCs [1, 2]. In contrast to them, supercritical CO₂ can be one of the appealing candidates to fabricate organic modified NCs because supercritical CO₂ was used as not only synthesis but also washing and drying solvent for the particle production, which enables the simple fabrication process without the liquid waste. Moreover, solvation power of supercritical CO₂ for the starting and intermediate molecule can be tuned by operating temperature and pressure, where this characteristic is expected to control the reaction for the formation of organic modified NCs.

In this contribution, we report a synthesis using supercritical CO₂ as reaction medium for organic-modified NCs. To investigate the effect of supercritical CO₂, the synthesis was performed at N₂ atmosphere and at 30 MPa of CO₂ after introducing the starting materials of iron(III) acetylacetone, pure water and decanoic acid into the high pressure cell. The reaction time and temperature were set at 18 h and 100°C, respectively. As a result, the yield of the solid materials significantly increased by using supercritical CO₂ of 30 MPa compared with the test at N₂ atmosphere. Additionally, supercritical CO₂ medium gave the NCs of α -Fe₂O₃ and γ -Fe₂O₃ with the unimodal size distribution where the mean size was 7.8 ± 2.0 nm. Moreover, the FT-IR and TG analysis supported that decanoic acid do not physical absorb to the surface but chemically attach to the surface of iron oxide NCs obtained in supercritical CO₂.

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MTMS '21

OP 10

Production of spherical microparticles with Eudragit L100 by the PGSS process in supercritical CO₂-ethanol mixtures

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Key Word (3 words)

Microcapsule, pH responsiveness, Carbon dioxide

Abstract (less than 300 words)

Microencapsulation technology has attracted attention because it can add new functionality to the core substance [1]. In this study, we aim to form spherical microparticles coated with Eudragit L100, which is enteric polymer [2] and hard to dissolve in supercritical CO₂ (scCO₂), using the particles from the gas-saturated solutions (PGSS) process with scCO₂. In the PGSS process, it is necessary to saturate the polymer in a supercritical fluid, so the solubility of Eudragit L100 in mixtures of scCO₂ and ethanol as a cosolvent were determined by observing the cloud point visually with the experimental apparatus. Next, phenylalanine loaded CaCO₃ particles (adsorption amount: 26 mg/g, average particle size: 49.2 μm), Eudragit L100, and ethanol were charged into a high pressure cell, and the mixture was stirred. After 1 h, the system was depressurized through a nozzle ($\phi = 2.0$) into an atmospheric collector leading to formation of microparticles coated with Eudragit L100 by precipitation onto a Teflon sheet. The microcapsules (average particle size: 181.39 μm) were found to be completely covered with a smooth shiny surface and did not adhere to each other. The pH dependence of sustained release rate of phenylalanine from the microcapsules was confirmed using a UV-vis spectrophotometer. It was carried out with stirring using the Franz cell. We found that when the low pH was used, phenylalanine from microcapsules were released slowly. On the other hand, when the high pH was used, phenylalanine from microcapsules were released early.

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MTMS '21

OP 11

Application of direct sonication under high-pressure two-phase system

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Key Word (3 words)

Ultrasound, CO₂-expanded liquid, Phase separation

Abstract (less than 300 words)

The properties of supercritical fluids, in particular supercritical carbon dioxide (CO₂) are unique and have been well-established in the field of food, pharmaceutical, and cosmetic applications providing numerous opportunities in extraction, separation, fractionation, micronization, and encapsulation processes by acting as a solvent, co-solvent, or anti-solvent. Herein, we introduced a new technique of high-pressure CO₂-expanded liquid (CXL) system with a combination of direct sonication allowing rapid formation of liposomes or nanobubbles. Additionally, the application of direct sonication to the high-pressure CO₂ system has also been examined for the extraction of water soluble natural yellow pigments. Unlike ScCO₂, a gas phase may exist in the CXLs system in addition to the CO₂-expanded liquid phase; therefore, density change with pressure is negligible. As a result, excess solvent power sensitivity with the change of operation pressure can be avoided. The effects of different parameters including entrainers (water, or aqueous ethanol), temperature (5-25 °C), pressure (8-14 MPa), and sonication time (0-200 s) on the final product (liposome¹ or nanobubble or nanocellulose or extraction²) were examined. The efficacy of direct sonication was evaluated by analyzing particle size distribution (PSD), scanning electron microscope (SEM) and transmission electron microscopy (TEM).

Direct sonication to the water/CO₂ two-phase system caused rapid physical mixing between the water and CO₂ phases including micro-phase separation and cavitation which speed-up the mass transfer at lower frequencies, typically 20 kHz may be responsible for the production of high yielding liposomes or nanobubbles as well as facilitated the production of nanocellulose fiber for high or high yielding the natural pigment extraction.

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MTMS '21

OP 12

Analysis of the mechanism of hydrothermal carbon dioxide fixation into serpentine with estimation of equilibrium of chemical species

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Key Word (3 words)

Hydrothermal, Carbon dioxide, Serpentine

Abstract (less than 300 words)

Developing CO₂ storage technology is attracting attention as a reduction of the concentration of greenhouse gases. Serpentinite (Mg₃Si₂O₅(OH)₄) is widely distributed in the ground and one of the agents for CO₂ capture because CO₂ can be immobilized as magnesite (MgCO₃) in hydrothermal condition. In this study, we examined the fixation of CO₂ in serpentine under hydrothermal condition. The equilibrium composition of species in this system under hydrothermal condition was calculated and the effect of temperature and pH on CO₂ fixation is discussed [1].

CO₂ fixation experiment was conducted with batch type reactor by introducing the serpentine powder, water and pressurizing with CO₂. A certain concentration of nitric acid and sodium hydroxide aqueous solution was used for changing pH of solution. After the reaction, the recovered powder was analyzed with TG-DTA and XRD. The equilibrium composition was calculated using PHREEQC software with llnl.dat database [2]. The initial amount of gas, liquid (solvent) and solid species, initial temperature and pressure was given. Thermodynamically stable species were determined at each temperature to satisfy the mass balance. In the experiment, the yield of magnesite was below 15% based on magnesium atom and once decreased and increased with initial pH of solution at 7.1 MPa of initial pressure of CO₂ for 6 h. The reaction mechanism was proposed by the main species in the calculated equilibrium composition. The dissolution of serpentine was enhanced by the contribution of H⁺ in low pH region and synthesis of magnesite was enhanced by OH⁻ in high pH region based on the mechanism and these factors probably promoted the formation of magnesite.

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MTMS '21

OP 13

Ultimately large-scale *ab initio* molecular dynamics with effective fragment potential opens an era for predicting physicochemical properties of mixed liquids and supercritical fluids

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Key Word (3 words)

ab initio effective fragment potential molecular dynamics, functional liquids, supercritical fluids

Abstract (less than 300 words)

Predicting the fundamental properties of solutions is one of the essential aspects of chemical engineering. Although the design of liquid mixtures and supercritical fluids is an indispensable technology in chemical engineering, it has been impossible to simulate their kinetic behavior in detail. Of course, in the spirit of "quick and dirty" chemical engineering, it would be great if faster molecular simulations were possible, which would directly accelerate research and development. However, now that we have access to powerful computers, shouldn't we take full advantage of their capabilities and tackle chemical engineering simulations previously impossible in principle? The future of chemical engineering should be revolutionized to be "Quick and Clear" with the help of high-speed computers and first-principles molecular simulations that maximize their capabilities.

In this context, recently, we have established an accurate and efficient first-principles MD protocol (EFP-MD; Effective Fragment Potential-Molecular Dynamics [1-3]), which focuses on the apparent fact that the interacting molecules determine the nonlinear molecular interactions that govern condensed matter properties. In this talk, we will start from the basics of the EFP-MD method and introduce the application of the EFP-MD method to ionic liquids, mixed liquids, and supercritical fluids.

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MTMS '21

OP 14**High Throughput CO₂ Solubility Measurement in Amine Solution using HS-GC**

Authors and affiliation

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Key Word (3 words)

Carbon dioxide capture, CO₂ solubility, Head-Space GC

Abstract (less than 300 words)

CO₂ solubility is one of the key factors in evaluating the energy consumption of the CO₂ capture process from flue gas or air. High-throughput CO₂ solubility measurement techniques such as small samples, rapid equilibration time, automated sample change, and high reproducibility are important, especially in the amine screening phase. We have developed a measurement apparatus of CO₂ solubility in amine solutions using headspace gas chromatography (HS-GC). Measurements of CO₂ solubility by HS-GC were reported by Maurer et al [1]. We used a GC-3200 gas chromatograph (GL Sciences) with a Turbomatrix HS16 headspace autosampler (Perkin Elmer) and a thermal conductivity detector. The equilibrium time and calibration curve were checked first. Developed apparatus showed high reproducibility with reference CO₂ solubility data in amine solution. Using HS-GC system, we have been evaluating new type of CO₂ capture solution including phase separation solvent [2], water-lean solvent and polyamine solutions.

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MTMS '21

OP 15

A new approach to the study of amine-CO₂ system based on the absolute reaction rate theory

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Key Word (3 words)

Reaction Kinetics, Kinerator, CO₂ absorption

Abstract (less than 300 words)

Aiming for a carbon-free society, CO₂ capturing technologies are gathering attention. Amine solutions are well-known CO₂ adsorbents. Quantum mechanical reaction analyses can identify transition states to clarify adsorption mechanisms of amine solutions with obtaining free energies of reactions.

So far, we have been developing a reaction kinetics simulator; Kinerator [1]. This program simulates the rate of reaction progress using those free energies. However, in case of solving a complicated system in which the reaction rates are significantly different and some reactions sharing same substrates exist, there is a problem that the computational time to carry on numerical integration becomes huge.

In this study, we made a second visit to the reaction kinetics and devised simultaneous ordinary differential equations to efficiently solve these complicated systems using numerical solutions. We also implemented them into our Kinerator. For applications, we applied this to some amine solutions represented by AMP(2-amino-2-methyl-1-propanol) and PZ(piperazine) due to clarify detailed reaction profiles in a short time range depending on CO₂ concentration and temperatures. Especially for AMP, we were able to reproduce actual measurement values [2] with extremely high accuracy using free energies obtained by SMD/B3LYP/6-311++G(d,p)//SMD/B3LYP/6-31G(d) level of theory based on the mechanism of Yamada *et al.* [3].

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MTMS '21

OP 16

Temperature dependent of absorption heat in phase-change solvent in carbon dioxide capture

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Key Word (3 words)

Absorption heat, Carbon dioxide capture, Phase-change solvent

Abstract (less than 300 words)

Capturing carbon dioxide using amine solvents has been a mature method. However, the energy penalty is the disadvantage of this chemical method. The homogeneous solvents that separate into liquid-liquid or solid-liquid phases after CO₂ absorption are named phase-change solvents (LLPS and SLPS solvents, respectively). Regeneration only the CO₂-rich phase or regeneration based on the properties of CO₂-rich and -lean phases is expected to overcome the energy consumption in the regeneration process [1, 2]. The absorption heat is an important property in evaluating the efficiency of solvent in CO₂ capture. In this study, LLPS solvents were investigated with 2-(ethylamino)ethanol (EAE) in organic solvent (Diethylene Glycol Diethyl Ether, DEGDEE) with/without water presence (named as EAE/DEGDEE 30/70 and EAE/DEGDEE/water 30/60/10 (weight base), respectively). In these solvents, the product of EAE and CO₂ – carbamate – has low affinity to the hydrophobic DEGDEE; therefore, it forms a new phase. Aqueous solution of 2-amino-2-methyl-1-propanol (AMP) at 50 wt% was used as SLPS solvent. The absorption heat of 100g of each solvent was examined with absorption temperature range of 25 - 80°C with 1 L/min of N₂:CO₂ mixture (4:1 ratio). The amount of CO₂ absorbed was measured by the total organic carbon as well as the difference between the CO₂ concentration of the inlet and the outlet gases. EasyMax102 (Mettler Toledo, Inc.) was used to continuously measure the generated heat and to maintain the isothermal condition during CO₂ absorption.

The obtained absorption heat curves exhibit the loading point – the ratio of the moles of CO₂ absorbed to that of amine in solvent – where the solvent changes its phase. The LLPS solvent with water presence separates at lower loading than that of LLPS solvent without water. The absorption heat of those phase change solvents and the loading point of solvent change are independent to the absorption temperature.

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MTMS '21

OP 17

Prediction of CO₂ solubility in ionic liquids and glymes with modified generalized BWR Eos

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Key Word (3 words)

Prediction, CO₂, Ionic liquid

Abstract (less than 300 words)

When the critical properties of a pure substance are known, it is possible to predict thermodynamic properties based on the corresponding states principle with an equation of state EoS. However, we can hardly find experimental values of critical properties of complex molecules such as ionic liquids. In this work, the extended Joback method is used to obtain the critical properties of ionic liquids or glymes.

To calculate a mixture property precisely, a binary interaction parameter, m_{ij} , should be determined. Based on other researcher's work and our own experimental data containing phosphorous ionic liquid, we determined optimal m_{ij} values to fit CO₂ solubility in ionic liquids and glymes.

In 1977, using a modified generalized BWR EoS, one of author (Nishiumi) showed that m_{ij} values for the system CO₂ + non-polar substances is expressed as a simple function of the ratio of critical volumes [1]. In this paper, we found that m_{ij} values for these CO₂ + non-volatile mixtures could be useful for the prediction of CO₂ + ionic liquid mixture or glymes, although they are polar mixtures. The result in this work is expected that predictability of CO₂ solubility in ionic liquids will enable to give a prompt choice of a non-volatile solvent for CO₂ capture.

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MTMS '21



Poster Presentations with Flash Talk

PA 01**Measurements and Modeling of Vapor-Liquid Equilibrium Properties for Low GWP refrigerants R1123/R1234yf/R32 Ternary Mixtures****Authors and affiliation**

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Key Word (3 words)

HFO refrigerant, Measurement, Modified Peng-Robinson Equation of State, Vapor-Liquid Equilibrium

Abstract (less than 300 words)

There is an immediate need to replace existing refrigerants that have significant greenhouse effects with next-generation, low-GWP type refrigerants. While preserving refrigerant performance, to reduce flammability and / or toxicity and to improve compatibility with lubricating oils, various multi-component refrigerant mixtures are potential candidates. In this study, regarding the HFO1123/HFO1234yf/HFC32 ternary mixtures, we performed precise measurements of vapor-liquid equilibrium properties and tried to verify the reliability of two kind of thermodynamic property models. Measurements were conducted at temperatures from 303.15 to 328.15 K and at saturation pressures up to 3.7 MPa. The expanded uncertainties ($k = 2$) in temperature, pressure, and component measurements were estimated to be less than 0.03 K, 1.4 kPa, and 0.43 mol%, respectively. One of the models used is the Helmholtz-type equation of state with the latest parameters. We used this equation of state to predict the VLE data for the ternary mixtures. Another model is the Peng-Robinson equation of state modified by Mathias and Copeman. We used the optimized parameters of pures and binary mixtures published by the present authors, for the present calculations of each ternary mixtures without any additional parameters specified to the ternary mixtures. Systematic comparisons between the predicted values and the present measurement results for the ternary mixtures will be discussed.

MTMS '21

PA 02

Phase Behavior of CO₂/Toluene/PMMA ternary system

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Key Word (3 words)

Phase equilibrium, Carbon dioxide, Polymethyl methacrylate

Abstract (less than 300 words)

Supercritical fluids, especially the combination of supercritical carbon dioxide (scCO₂) and polymers, has been attracting much attention as an inexpensive, safe, and environmentally friendly processing process. Furthermore, attempts have been made to add organic solvents as third components to improve the solvent properties of the CO₂. In that regard, reports have been published indicating that performance can be changed more broadly with the addition of the organic solvents. It is thought that the change in physical properties, especially the change in the phase behavior, is a major factor for the enhancement of the solvent properties. However, phase equilibrium data for carbon dioxide (CO₂)/organic solvent/polymer ternary systems are rare. In this work, the phase diagram of a CO₂/Toluene (Tol)/Polymethyl methacrylate (PMMA) ternary system was measured using a synthetic method. In this system, the vapor-liquid equilibrium and vapor-liquid-liquid equilibrium (bubble point, BP) and the liquid-liquid equilibrium (cloud point, CP) were confirmed as the phase separation points. The BP was measured by the method combined with a laser rangefinder, and the CP was measured by the method combined with a laser turbidimetry. The phase boundaries were measured at temperatures of 313.2 K and 353.2 K, and CO₂ weight fractions ranging from 0.10 to 0.48.

The homogeneous phase area decreased with the increase of the concentration of PMMA or the temperature. These changes were expected to be related to the mutual solubility between the components. Therefore, the changes in the homogeneous phase area were evaluated using the solubility parameters. In addition, the phase diagram of the triangular prism was constructed from the obtained phase diagram, and the overall picture of the phase behavior of the ternary system was confirmed.

MTMS '21

PA 03

Thermodynamic properties of tetra-*n*-butylphosphonium dicarboxylate semiclathrate hydrates

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Key Word (3 words)

Phase equilibria, Dissociation enthalpy, Semiclathrate hydrate

Abstract (less than 300 words)

Semiclathrate hydrate (SCH) is a crystalline inclusion compounds which consists of host water molecules and guest substances. SCH has been investigated for a thermal storage material by using enthalpy of phase change (around 200 J/g), since the equilibrium temperatures are in the range of 273-300 K. One of the advantages of using SCH is a designability of the thermodynamic properties by selecting the guest substances. Conventional SCHs consists of halide anions, but in recent years, a number of reports on SCHs including monocarboxylate anions from environmental and biocompatibility reasons [1,2] have been reported. In this study, various tetra-*n*-butylphosphonium dicarboxylate (TBP-DC) SCHs in which the dicarboxylate species were oxalate, malonate, succinate, glutarate, maleate, and fumarate, were prepared to investigate the effects of polyvalent ions and steric structures on the thermodynamic and crystallographic properties.

The equilibrium temperatures of TBP-DC SCHs depended on the structure of guest substance, and located in the range of 282.9-290.3 K. The highest equilibrium temperature and the largest dissociation enthalpy, which were observed in TBP-Maleate SCH, were 290.3 K and 206 J/g, respectively. In the presentation, how the dicarboxylate anions affect thermodynamic properties and crystal structure of SCHs will be discussed.

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MTMS '21

PA 04

Gas separation properties of semiclathrate hydrates for CH₄+CO₂ mixed gas

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Key Word (3 words)

Gas separation, Mixed gas, Semiclathrate hydrate

Abstract (less than 300 words)

In recent years, the usage of several semiclathrate hydrates is expected for gas storage, separation, and transportation. It has been reported that the structure of the cage changes depending on the gas contained in the semiclathrate hydrate, and the ease of entering the cage differs depending on the kind of the guest gas. In this study, semiclathrate hydrates were created using four types of ionic substances (tetra-*n*-butylammonium bromide, tetra-*n*-butylammonium chloride, tetra-*n*-butylphosphonium bromide, and tetra-*n*-butylphosphonium chloride) and separation properties of CH₄ + CO₂ mixed gas were acquired. Measurements were made at three different concentrations (10wt%, 20wt% and 30wt%) and two different pressures (3 MPa, 5 MPa). The gas phase before and after hydrate formation were collected, and the composition was analyzed using a gas chromatograph. The results showed that at a gas pressure of 5 MPa, the gas incorporated into the TBA-based hydrate had a higher CO₂ composition than the TBP-based hydrate at any concentrations. It was also shown that the hydrates with low-concentration of ionic substances have a higher CO₂ composition than that with high concentration of ionic substances.

MTMS '21

PA 05

Host-guest chemistry of antibacterial molecular crystal in supercritical CO₂ with solvent

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Key Word (3 words)

host-guest chemistry, supercritical CO₂, COSMO-SAC

Abstract (less than 300 words)

There are several techniques to improve the properties of a medicine, such as polymorphs of crystals, amorphization, salts, and co-crystals [1]. In particular, host-guest chemistry, which means fixing CO₂ molecular inside of drug molecular crystal, is expected to enhance drug solubility and improve drug dissolve behavior, because released CO₂ in water can lower pH locally. In addition, this technique would achieve the advantages of easy handling, safety in terms of less harmful solvents, and high yields compared to the other methods.

In this work, we focus on the mechanism of host-guest chemistry for drug molecular crystal with CO₂ by conducting both experimental and computational approaches on "how much the host-guest chemistry accelerated by a cosolvent in supercritical CO₂".

We choose Enoxacin as target medicine, which has low solubility (< 0.1 mg/ml in water at 25°C)[2]. For the experiment, Enoxacin was placed in a container and contacted with scCO₂ at 80°C and 20 MPa for 2 h in the presence of some solvents (EtOH, 1-PrOH, 1-BtOH, Acetone, Ethyl acetate). As a result, the solvents with hydroxy groups accelerates host-guest chemistry, which means Enoxacin can capture more CO₂ inside of its crystal. For the computational calculation, using quantum chemistry and thermodynamic calculations, we constructed a model to describe the host-guest chemistry for drug molecular crystal with CO₂, which has 2 steps: (1) relaxation of crystal structure pairing with CO₂, (2) recrystallization while retaining CO₂ inside. As a result, the experimental result is well explained by enthalpy change in the process (1) in the model. That is the solid dissolution of scCO₂ at the interface is an important process on the formation of host-guest drug molecular crystal with CO₂.

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MTMS '21

PA 06

Itraconazole cocrystallization in fatty acid under high-pressure CO₂

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Key Word (3 words)

cocrystallization, itraconazole, high-pressure CO₂

Abstract (less than 300 words)

Itraconazole, which is an antifungal drug with a low solubility, has been focused on as one of the model molecules in the investigation of processing technologies to improve solubility in human body [1]. Some studies have reported improved solubility of itraconazole by the formation of the cocrystal which is a new crystal structure composed of active pharmaceutical ingredients (APIs) and additives called as coformer (CF) [2, 3]. The cocrystallization processes need multi-steps using organic solvent to dissolve API and coformer. Therefore, in order to solve these disadvantages, we suggest a single step method for the formation of cocrystal with liquefied fatty acids under high pressure CO₂ in terms of their melting point depression by high pressure CO₂. In this study, we investigate the cocrystal composed of itraconazole as API and succinic acid as CF, using liquefied fatty acid under high pressure CO₂.

As the result, the cocrystals of itraconazole can be formed under high pressure CO₂ with linoleic acid, oleic acid and stearic acid used as fatty acid. Itraconazole cocrystals cannot be formed by the cocrystallization with hydrocarbon, ontadecane and 1-octadecene and without the fatty acid. These results show that cocrystal formations is promoted in the media of the fatty acid under high-pressure CO₂. For the purpose of clarifying the role of the fatty acid and the mechanism of the cocrystallization, we also focused on the molecular interaction energies among the fatty acid, itraconazole and succinic acid by thermodynamic relationships and molecular information from quantum chemical calculations. The calculated results give that the molecular interaction of cocrystal compounds with the fatty acid are stronger than those with hydrocarbons. The experimental and calculated results could suggest that the strong molecular interaction with fatty acids achieve the promotion of the itraconazole cocrystallization.

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MTMS '21

PA 07

Volumetric behavior of HFO-1234ze(E) + acetone liquid mixture at 303.2 K.

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Key Word (3 words)

Density, Hydrofluoroolefin, Binary mixture

Abstract (less than 300 words)

Hydrofluorocarbons (HFC) have been widely used as refrigerants, forming agents and spray propellants. However, hydrofluoroolefins (HFO) are now considered to be an alternative for HFC because of zero ozone depletion potential (ODP) and its quite low global warming potential (GWP) [1]. The authors have investigated bubble point pressure [2,4], liquid density [3] and dielectric constant [4], for the mixtures of conventional propellant, propane or dimethyl ether (DME) with some organic solvents. However, there are few experimental data for the mixtures containing (E)-1,3,3,3-Tetrafluoropropene (HFO-1234ze(E)) except for the bubble point pressure reported previously [2].

In this study, the density was measured for a liquid mixture of HFO-1234ze(E) + acetone at 1.0 MPa and 303.2 K, and the volumetric behavior of mixture was investigated for the mole fraction dependence of the excess molar volume.

Density of mixture was measured by oscillation of U-shaped tube densimeter (Anton Parr 512P). The density of mixture was estimated by Oscillation period of U-shaped tube filled with liquid mixture. The densimeter was calibrated with butane[5] and water[6] at 1.0 MPa and 303.2 K.

The density of liquid mixture for HFO-1234ze(E) + acetone studied monotonously increased with increasing mole fraction of HFO-1234ze(E) at 1.0 MPa and 303.2 K. The excess molar volume of this liquid mixture studied showed to be negative in the whole range of mole fraction of HFO-1234ze(E), and a minimum was seen around 60 mol% of HFO-1234ze(E). This may suggests that an attractive force among HFO-1234ze(E) and acetone will be important role of volumetric behavior in liquid mixture of HFO-1234ze(E) + acetone at 1.0 MPa and 303.2 K.

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MTMS '21

PA 08

Measurement of the Density of Carbon Dioxide/Methanol and Dioxide/Ethanol Homogeneous Mixtures and Correlation with Equations of State

Authors and affiliation

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Key Word (3 words)

Equation of state, carbon dioxide, alcohol

Abstract (less than 300 words)

Equations of state (EoS) can be used to estimate a wide variety of physical properties. They are mainly of the van der Waals-type, the lattice-fluid type (the Flory-Huggins theory), and the SAFT type (the perturbation theory). They should be used according to the target system and property. However, the relationship between the physical properties and the validity of the EoS have not been studied much. The densities of homogeneous phase fluid mixtures of the carbon dioxide (CO₂)/Methanol (MeOH) and CO₂/Ethanol (EtOH) binary systems were measured and correlated to three equations of state. The density measurements were performed using a high-pressure vibration-type density meter equipped with a circulation pump and variable-volume viewing cell, which guaranteed the homogeneity of the mixtures. The densities were measured at temperatures ranging from 313 to 353 K, pressures up to 20 MPa, and CO₂ concentrations from 0 to 80 mol%.

The experimental data obtained were correlated to three typical EoS, namely Peng–Robinson (PR), Sanchez–Lacombe (SL), and Perturbed Chain statistical associating fluid theory (PC-SAFT) EoS. As the result, it was not possible to correlate the density of binary systems using the three EoS, presumably due to heterodimers were formed [1,2] when CO₂ and alcohol are mixed. Of the three, PC-SAFT gave the best correlation of densities, because it had the advantage of considering the association of alcohols compared to the other two equations. Similarly, the vapor liquid equilibrium (VLE) of the CO₂/MeOH and CO₂/EtOH mixtures was correlated but the accuracy of them were not sufficient for the same reason. These results suggest that it was difficult to correlate the density and VLE in the CO₂/MeOH and CO₂/EtOH systems using the equation of state, and that an approach using heterodimers of CO₂ and alcohols was necessary for accurate property correlation.

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MTMS '21

PA 09

Measurement and correlation of PVT for organic-inorganic hybrid nanoparticles

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Key Word (3 words)

Organic-inorganic hybrid nanoparticles, PVT, Equation of state

Abstract (less than 300 words)

Organic-inorganic hybrid nanoparticles (HNPs), which are composed of inorganic core nanoparticles and organic surface modifiers, have been expected to be used as fillers in polymer functional materials. HNPs are usually single-nanometer in size and their behaviors in polymer materials have been occasionally recognized as those of molecules as well as solids. This might be attributed to the small size of HNPs.

In our research, we have attempted to apply molecular thermodynamics to the HNPs. The features of surface modifiers and core parts are quite different, and it is very important to characterize quantitatively their influence on properties. One possible method for the functional evaluation of HNPs is PVT measurement. However, there have been reported no data and useful approaches in the literature.

In this work, carboxylic acid-modified ceria nanoparticles are adopted as a model HNP. The PVT was measured with the bellows type apparatus originally developed by Y. Sato *et al*^[1]. The validity of the experimental apparatus and procedure were firstly demonstrated by measuring the PVT of decane. The obtained experimental PVT data were correlated with the Tait equation^[2] and the Sanchez-Lacombe equation of state (S-L EoS)^[3], which are widely applied to thermodynamic property calculations of polymer systems. PVT measurement data indicated that the specific volume increases with increasing temperature and decreases with increasing pressure. Such PVT behaviors were well correlated with the above equations. In correlating with S-L EoS, the EoS parameters were determined by assuming the HNP as a pseudomolecules and the density reflects the contributions of core and surface modifier.

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PA 10

Micro-flow process of emulsification and supercritical fluid extraction of emulsion for stearic acid lipid nanoparticle production

Authors and affiliation

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Key Word (3 words)

Supercritical carbon dioxide, Solid lipid nanoparticle, Microfluidic system

Abstract (less than 300 words)

Solid lipid nanoparticles (SLN) represent as an active ingredients carrier that gives the attractive advantages such as controlled release and degradation protection of active compounds [1]. Supercritical fluid extraction of emulsion (SFEE) has been applied for fabrication of SLN. Utilization of supercritical carbon dioxide (scCO₂) can remove organic solvent at the mild processing temperature while conventional evaporation method at high temperature leading to the degradation of active compounds [2]. Furthermore, introduction of microfluidic system for SFEE allows the reduction of costs and time of the operation [3].

In this study, emulsification by micro-swirl mixer and SFEE in microchannel (inner diameter of 500 μm) are combined in micro-flow system for the formation of stearic acid lipid nanoparticles dispersed in aqueous solution. The effect of the surfactant species, surfactant concentrations and pressure on the size of stearic acid nanoparticles and extraction efficiency of ethyl acetate (EA) from the ethyl acetate in water (EA/W) emulsion are investigated. Tween 80 as hydrophilic surfactant was dissolved in water (0 to 3.0 wt%). Stearic acid (0.5 wt%) as lipid and egg yolk lecithin (0 to 1.5 wt%) as hydrophobic surfactant were dissolved in EA. The feeding flow rates of water and EA were 1.6 and 0.4 ml min⁻¹, respectively. The operating temperature was 40 °C. Ethyl acetate in water emulsion was formed by using micromixer. Supercritical carbon dioxide was applied for EA extraction from EA/W emulsion in microchannel. Increasing amount of lecithin results in higher uniformity of SLN size distribution. Variation of pressure has no significant effect on the extraction efficiency and all pressure conditions gave the high efficiency over 97%. However, higher pressure leads to larger average size and aggregated form of SLN. This phenomenon can be explained by the aggregation of SLN due to the loss of lecithin by the extraction into scCO₂ phase.

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PA 11

Study for hydration structure through the refractive index during microwave irradiation

Authors and affiliation

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Key Word (3 words)

Microwave; refractive index; hydration

Abstract (less than 300 words)

Generally, several solvent molecules are bound around solute molecules and ions in a solution. For example, solute molecules and ions in a solvent form a weak bond with the solvent molecule due to electrostatic interaction with the solvent molecule, and the solvent molecule is oriented around the bond. At this time, the state is called solvation. In particular, when the solvent is a water molecule with a large dipole moment, this hydration becomes a factor that determines the rate of chemical reaction in the solution and precipitation of crystals.

On the other hand, it is known that the reaction rate is drastically improved by microwave irradiation in the process of chemical synthesis. We thought that since the reaction rate is related with solvation. In this study, the refractive index was considered as an index for observation of the solvation because the value depends on the speed of light in the medium. For example, water shows relatively a large refractive index because of the strong hydrogen bonds. According to the data for refractive index during microwave irradiation, it was predicted that the solvation temporarily collapses due to rotation of water molecules caused by the irradiation. The behavior strongly depends on microwave power.

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PA 12

Development of a predictive Dimensionless Distribution coefficient (pDD) model for fractionation of Hops extracts

Authors and affiliation

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Key Word (3 words)

Ethanol, Water, Partition coefficient

Abstract (less than 300 words)

Measurements of vapor-liquid distribution coefficients (K-values) of compounds contained in hops-extract ethanol or ethanol aqueous solution in high pressure CO₂ systems were carried out at temperatures of 313–373 K and pressures of 5–14 MPa with a continuous counter-current fractionation apparatus. Using the measured K-value data, a correlation for the vapor-liquid distribution coefficients of 7 solutes in hops-extract was constructed based on entropy-based solubility parameter (eSP)^[1]. The correlation was generalized as a dimensionless form, named as predictive Dimensionless Distribution coefficient (pDD) model, by modifying the equation developed in the previous work^[2] with keeping eSP concept and by introducing new mathematical approaches. From this eSP concept, eSP distance of solute and fluid (vapor or liquid) is considered as a key factor to predict K-values of solutes. In the calculation with the pDD model, it was assumed that mutual interaction of solutes was neglected due to the dilute solution.

The pDD model was then applied to the counter-current extraction simulation, which shows that flavor compounds can be highly fractionated and selectivities can be advantageously manipulated with temperature and pressure. Resin components were found to concentrate in the raffinate phase. From these results, highly effective separation of hops-extract can be consistently demonstrated in the experimental system and in the predictive simulations.

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PA 13

Evaluation of solid-liquid equilibria for drug + water + cyclodextrin derivatives systems using activity coefficient model

Authors and affiliation

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Key Word (3 words)

Drug, solid-liquid equilibria, activity coefficient model

Abstract (less than 300 words)

Drug candidates with strong pharmacological activity have increasingly been developed using combinatorial chemistry and high-throughput screening. As a result of these screening methods, the number of drugs with decreased water solubilities has increased due to higher molecular weights and more complicated chemical structures. Therefore, the co-solvents are commonly used in the pharmaceutical industry in order to increase the solubility of relatively water insoluble drugs. The solid-liquid equilibria for systems containing drugs and co-solvents have been measured [1, 2].

Some predictive method in order to predict the solubility of drugs using activity coefficient models have been proposed [3]. But the co-solvents are liquids. Recently we have the interests to cyclodextrins as co-solvents.

This paper deals with evaluation of solubility for drug + water + solid co-solvent system using activity coefficient models. The drugs treated in this paper are etodolac, famotidine, naringin, and the co-solvents are cyclodextrin derivatives (α -CD, β -CD, 2-HP- β -CD, 2-HE- β -CD, M- β -CD, DM- β -CD, SBE- β -CD). The activity coefficient models used in this study are Wilson and Wilson + Porter equations.

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MTMS '21

PA 14**Prediction for modification of liquid-liquid interface by energy concentration of microwave heating**

Authors and affiliation

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Key Word (3 words)

Microwave; Interfacial tension, Dimensionless number

Abstract (less than 300 words)

In previous study, surfactant at liquid-liquid interface is desorbed by microwave because microwave can pass through oil phase and approach water phase directly. However, the mechanism has not been clear perfectly. In this study, tension of oil-water interface was measured during and after microwave irradiation for the different surfactant concentration in water phase. The profiles of interfacial tension shows that the quick response was observed due to the thermal energy concentration by microwave absorption at the interface. The degree of interfacial modification could be predicted through our dimensionless number, which was proposed as an index for the energy concentration of microwave local heating. Moreover, surfactant desorption was caused by rotation/vibration of both water molecules and polar substituent of surfactant. In the future, microwave heating can be expected as a new demulsification method.

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PA 15

Dielectric properties of Liquefied Dimethyl Ether + Ethanol + Water Mixtures at 303.2 K

Authors and affiliation

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Key Word (3 words)

Dielectric constant, Dielectric relaxation time, Dimethyl ether,

Abstract (less than 300 words)

To investigate the separation process with controlled volatility and polarity, we have previously reported dielectric properties of liquid mixture for dimethyl ether (DME) + ethanol and propane + ethanol system [1, 2]. The static dielectric constant of water is about 78.5 at 298 K and water has a solubility of 7 mass% in DME [3]. Ethanol aqueous solution is well miscible with DME over a whole composition at 303.2 K. By using liquefied DME + ethanol + water mixture, it is expected that the range of polarity control depending on the composition can be expanded. In this study, complex dielectric spectra of liquefied DME + ethanol + water mixture were measured at 303.2 K and composition dependence of dielectric constant and dielectric relaxation time for DME + ethanol + water mixture was examined.

Complex dielectric spectra of liquefied DME + ethanol + water mixture liquid mixture studied were measured by frequency domain method with the network analyzer in the frequency range of 0.5 – 15 GHz. Frequency dependence of the complex dielectric spectra was fitted by single-phase Debye equation, and the static dielectric constants and the dielectric relaxation times of liquefied DME + ethanol + water mixture at 303.2 K were determined.

The static dielectric constants of liquefied DME + ethanol + water mixture studied decreased with increasing DME and increased with water at 303.2 K. The dielectric relaxation times of mixture studied showed minima around 0.8 mole fraction of DME, and DME composition of dependence the dielectric relaxation times studied became smaller in DME-rich region at 303.2 K. Excess dielectric constants of liquefied DME + ethanol + water mixture liquid mixture studied were negative over a whole composition of DME and increased with increasing ethanol. Excess values of reciprocal dielectric relaxation time showed maxima around 0.8 mole fraction of DME.

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PA 16

Prediction of thermal conductivities for liquid mixture using ASOG-ThermConduct model

Authors and affiliation

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Key Word (3 words)

Thermal Conductivity, Group contribution, ASOG-TC

Abstract (less than 300 words)

Thermal conductivity is one of transport properties relating to heat transfer required for designing chemical process [1]. The authors have proposed the model for calculating liquid mixtures using excess thermal conductivity [2]. The thermal conductivity for ternary system can be predicted using binary Wilson-TC parameters.

This paper deals with the prediction of thermal conductivity for liquid mixture using ASOG group contribution method [3-5]. The group pair parameters for CH₂, ArCH, CyCH, H₂O, OH and CO groups have been determined using the observed thermal conductivity data. The average deviations for binary systems discussed in this paper are 0.3 % and 2.1 % for non-aqueous and aqueous systems, respectively. The overall average deviations for 3 ternary systems is 1.25 %.

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MTMS '21

PB 01

CO₂ solubility of deep eutectic solvent consisting of choline chloride and ethylene glycol

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Key Word (3 words)

Deep eutectic solvent, Choline chloride, Ethylene glycol

Abstract (less than 300 words)

Deep eutectic solvents (DESs) are now widely acknowledged as a new class of solvents like ionic liquids (ILs) because they share many characteristics and properties with ILs [1]. DESs generally have low vapor pressure and non-flammability, and their physicochemical properties are optimized. Then, DESs can be conveniently prepared by simply mixing a hydrogen bond donor (HBD) and acceptor (HBA) with a suitable composition. In the previous work [2], we have investigated CO₂ solubilities of DES, consisting of choline chloride (ChCl) and ethylene glycol (EG) at a 1 : 2 molar ratio (ChCl2EG) at 313.15 K. CO₂ solubilities of ChCl2EG were lower than Leron *et al* [3], however, the reason is not still known.

In the present study, CO₂ solubilities and their saturated densities of EG or ChCl2EG were measured at 298.15, 313.15, and 333.15 K and the pressure up to 10 MPa by a static-circulation type apparatus [4]. The saturated densities of liquid phase (ρ_L) slightly increases with increasing pressure. The saturated density of vapor phase (ρ_V) remains almost the same as that of pure CO₂ density calculated by Span-Wagner equation [5] at each pressure. CO₂ solubilities of EG or ChCl2EG decreased with increasing temperature. CO₂ solubilities of ChCl2EG were slightly higher than that of EG, on the other hand, that of ones were lower than Leron *et al* [3]. Furthermore, the molarity scaled solubilities were calculated from the experimental solubility data. The volumetric concentration for CO₂ in ChCl2EG were slightly lower than that in EG, however, the volumetric concentration of ChCl2EG were greatly lower than EG; therefore, ChCl2EG can absorb CO₂ with fewer molecules than EG.

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PB 02**CO₂/hydrocarbon selectivity of phosphonium based ionic liquids**

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Key Word (3 words)

Ionic liquid, Carbon dioxide, Hydrocarbon

Abstract (less than 300 words)

Carbon dioxide (CO₂) separation is critical in the petrochemical industry for natural gas purification and coal gasification. Chemical/physical absorption, adsorption, and membrane separation have been attempted for CO₂ separation from CO₂-hydrocarbon gas mixtures. The conventional physical absorbents such as Selexol and Rectisol absorb a large amount of CO₂ and a significant amount of hydrocarbons such as methane (CH₄), therefore, their CO₂/hydrocarbon selectivities are not so high. Ionic liquids (ILs) are expected to be a promising alternative to the conventional physical absorbents because of their comparable CO₂ solubilities and high CO₂/CH₄ selectivities ranging from 10 to 20 [1].

In the previous study, trihexyl(tetradecyl)phosphonium bis(trifluoromethanesulfonyl)amide ([P₆₆₆₁₄][TFSA]) and trihexyl(tetradecyl)phosphonium perfluoroctanesulfonate ([P₆₆₆₁₄][PFOS]) were chosen as the ILs with superior CO₂ absorption by predicting Henry's law constants of CO₂ in 68775 ILs using conductor like screening model for realistic solvation (COSMO-RS) method [2]. Based on the prediction results, CO₂ solubilities of the selected phosphonium based ILs were measured at 313.15 K and 333.15 K [3].

In the present study, hydrocarbon such as CH₄, ethane (C₂H₆), and ethylene (C₂H₄) solubilities in [P₆₆₆₁₄][TFSA] or [P₆₆₆₁₄][PFOS] were measured at 313.15 K and 333.15 K by using a magnetic suspension balance. Henry's law constants of CO₂ or hydrocarbon were calculated from the experimental solubility data at pressures lower than 0.4 MPa. Furthermore, CO₂/hydrocarbon selectivities of ILs were obtained from the ratio of CO₂ and hydrocarbon experimental solubility data.

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MTMS '21, September 7 – 9, 2021

PB 03**Thermodynamic study of extraction behavior for precious metals using phosphonium-based ionic liquids**

Authors and affiliation

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Key Word (3 words)

Ionic liquids, Precious metals, Solvent extraction

Abstract (less than 300 words)

Room temperature ionic liquids (ILs) have unique physicochemical properties such as negligible vapor pressure, high ionic conductivity and wide electrochemical window. Compared to general organic solvent, the use of hydrophobic ILs is advantageous for operations at variable temperatures. On the other hand, it is important to develop the separation and recovery processes for platinum group metals such as platinum (Pt), Palladium (Pd), iridium (Ir) and ruthenium (Ru), and noble metals such as gold (Au). We had demonstrated that the recovery of Pt [1] and Ir [2] metals from phosphonium-based ILs and amine extractant by solvent extraction and direct electrodeposition so far.

In this study, several types of ILs consisting of triethyl-*n*-pentyl phosphonium; $[P_{2225}^+]$, triethyl-*n*-octyl phosphonium; $[P_{2228}^+]$, triethyl-*n*-dodecyl phosphonium; $[P_{22212}^+]$, the other type of cations and bis(trifluoromethylsulfonyl)amide; $[NTf_2^-]$ anion without extractant was applied for the solvent extraction of Au(III), Pt(IV), Pd(II), Ir(IV) and Ru(III). Under the experimental conditions, many phosphonium-based ILs exhibited a high extractability for Au(III). The extraction mechanism would be considered as anion exchange reaction; $[AuCl_4^-]_{aq} + [P_{2225}][NTf_2]_{IL} \rightleftharpoons [P_{2225}][AuCl_4]_{IL} + [NTf_2^-]_{aq}$.

Moreover, thermodynamic results help predict the complexation behavior of the metal with extractants. In order to investigate the temperature effect on the extraction for Au(III), Pt(IV), Pd(II), Ir(IV) and Ru(III), the thermodynamic characteristics were evaluated at different operating temperatures (298–358 K). As a result, the Van't Hoff plot yielded a slope proportional to the enthalpy (ΔH) for Au(III), Pt(IV) and Pd(II) extractions. The complexation state of the extracted species would be also investigated by Raman spectroscopic analysis.

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MTMS '21

PB 04**Thermodynamic study of W(VI) extraction using amine-based extractant and phosphonium ionic liquids**

Authors and affiliation

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Key Word (3 words)

Ionic liquids, Solvent extraction, Tungsten

Abstract (less than 300 words)

Recently, the development of a process to separate W(VI) component from spent tungstophosphate catalyst has become important. We had demonstrated that a novel hydrometallurgical process involving the following steps; leaching, precipitation, solvent extraction using ionic liquids (ILs) and crystallization-stripping. First, the spent catalyst was completely leached in a distilled water at 343 K for 24 h. The leaching reaction; $H_3[PW_{12}O_{40}] + 27[OH^-] \rightarrow 12[WO_4^{2-}] + [PO_4^{3-}] + 15H_2O$ smoothly proceeded in leachate. After leaching, the $[PO_4^{3-}]$ component was separated by the precipitation reaction using the precipitation agent; $Fe(NO_3)_3 \cdot 9H_2O$. The separation percentage of $[PO_4^{3-}]$ was 90.78% at pH=8.11 according to IC analysis.

Solvent extraction was performed using triethyl-*n*-pentyl phosphonium bis(trifluoromethylsulffonyl)amide as the IL, and Alamine 336 was employed as the extractant for the selective separation of W(VI). The extraction percentage (*E*) of W(VI) was 94.6% at pH=1.03 and the separation factor of W/P was 100.8. The extraction mechanism of W(VI) was based on the ion association reaction; $[H_xW_yO_z]_{aq} + n[R_3NH^+Cl^-]_{IL} \rightleftharpoons [(R_3NH)_n(H_xW_yO_z)]_{IL} + [Cl^-]_{aq}$, where *x*, *y*, *z*, and *n* are the stoichiometric coefficients related to the complexation state and are dependent on the pH. The Van't Hoff plot of the different operating temperatures (298-358 K) yielded the linear relation. Thermodynamic result indicated the positive enthalpy ($\Delta H=18.32\text{ kJ mol}^{-1}$) for W(VI) and favored the endothermic nature of the extraction reaction. This tendency was consistent with the reference [1].

The stripping percentage of W(VI) reached to be 100 % on the condition of 8< pH by the stripping reaction; $[(R_3NH)_n(H_xW_yO_z)]_{IL} + n[NH_4OH]_{aq} \rightleftharpoons [(NH_4)_n(H_xW_yO_z)]_{aq} + n[R_3NH^+OH^-]_{IL}$. Finally, the crystallization reaction occurred at pH~5 and the obtained precipitates were identified as the ammonium paratungstate by XRD. A series of novel hydrometallurgical process using ILs enabled us to conclude that W(VI) component was efficiently recovered from spent tungstophosphate catalyst.

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PB 05

Effects of Water in the Decarboxylation of Aromatic Carboxylic Acids in Supercritical Water

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Key Word (3 words)

Supercritical water, Decarboxylation, Effect of Water

Abstract (less than 300 words)

Organic solvents, although indispensable in organic syntheses and chromatography, are mostly toxic to the environment, urging the search for greener alternatives. Supercritical water (SCW), able to dissolve many organic compounds, has become a popular candidate. However, despite the decades-long investigation of SCW, there is still lacking information about the processes occurring in SCW, thereby limiting its applications. In this research, decarboxylation reaction, a ubiquitous reaction both in degradation and synthesis, was investigated to study the effects of water. Utilizing a flow reactor, water density was varied by changing the pressure, which simultaneously affects other water properties. Phthalic acid decarboxylation was chosen as the model reaction due to its ease of dissolution and higher reactivity compared to other carboxylic acid derivatives.

Kinetic studies revealed that the reaction is in first-order. The resulting rate constants were plotted against pressure, which revealed a rather half-parabolic decrease in rate when pressure was increased. In an attempt to explain the trend, solvation effects were considered. For a nonionic reaction like decarboxylation, the rate increases with density when the transition state is more polar than the reactant(s). [1] The observed inverse relationship between rate and density suggests that the conversion of phthalic acid to benzoic acid passes through a transition state that is less polar than the reactant. Kirkwood's expression was employed to investigate a possible relationship between the rate and solvent dielectric constant which varies with density. Plotting the $\log k$ and the Kirkwood dielectric function, $(\varepsilon - 1)/(2\varepsilon + 1)$ using the rate constants and literature values of the dielectric constants, ε , of SCW at different pressures at 400 °C, an inverse relationship was observed. Good linear dependence between the two constants was observed, supporting the conclusion that the effect of water is through solvation.

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MTMS '21

PB 06

Calculation of Solubility of Organic Compounds in Supercritical Carbon Dioxide Using Machine Learning with Molecular Descriptors

Authors and affiliation

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Key Word (3 words)

Solubility, Machine learning, Molecular descriptors

Abstract (less than 300 words)

The solubility of target substances in supercritical CO₂ (scCO₂) is essential as a basic knowledge for designing the processes and finding the optimum conditions of industry processes [1]. The solubility can generally be determined by experimental measurements or calculations. However, experimental measurements are very time-consuming and costly. In addition, the thermodynamic calculation methods, which are widely used nowadays, require various physical properties and interaction parameters of solutes and solvents, leading it difficult to calculate the solubility easily.

In this study, the solubility of 29 organic compounds in scCO₂ was calculated using neural network based on the Quantitative Structure-Property Relationship (QSPR) model [2]. We used 886 solubilities of 29 organic compounds in scCO₂ under various temperatures and pressures. The solubility data of organic compounds were randomly divided into training, validation and test sets. The training data and the validation data each contain data of the same compound under different conditions. Test data is new data that was not used for training and evaluation data. A large number of molecular descriptors were calculated using RDKit [3]. The descriptors for all compounds with the same or zero data values and those with pair correlation greater than 0.9 were eliminated. In the calculations, we used four parameters such as temperatures, pressures, 99 descriptors for the organic compounds, and the density of CO₂. Modeling of the relationship between the parameters and solubility data was achieved by artificial neural network method. The artificial neural network architectures and hyper-parameters were optimized empirically.

The calculation results showed that the solubility of many compounds could be expressed qualitatively and quantitatively relatively well. However, there were some compounds whose solubility was difficult to express quantitatively. These may be improved by considering the interactions between the compounds and CO₂.

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MTMS '21

PB 07**Simultaneous correlation of liquid-liquid equilibria for ternary systems and phase equilibria for constitutive binary systems by modified new activity coefficient model**

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Key Word (3 words)

Activity coefficient model, Vapor-liquid equilibrium, Liquid-liquid equilibrium

Abstract (less than 300 words)

In the previous study, new activity coefficient models, Concentration Dependent Surface Area Parameter (CDSAP) model [1] and r-CDSAP model [2,3], were proposed. CDSAP model is based on the quasi-chemical theory, and assumes that the surface area parameters depend on partner molecules and their concentrations. CDSAP model requires iterative calculations for more than 3 component systems. r-CDSAP model is obtained by Taylor expansion at $\Delta E = 0$ for excess Gibbs energy of CDSAP model. The calculated results by r-CDSAP model are very good for binary vapor-liquid and ternary liquid-liquid equilibria. However, the surface area parameter of pure component q_i^0 is assumed to be common to multicomponent systems in r-CDSAP model. This restriction is slightly inconvenient to use r-CDSAP model for multicomponent systems.

In this study, a modified r-CDSAP model, which is called f-CDSAP model, was applied to simultaneous correlation of liquid-liquid equilibria for ternary systems and phase equilibria for constitutive binary systems with the same parameter sets. In f-CDSAP model, the restriction condition that q_i^0 is common to multicomponent systems is removed, and q_i^0 is determined for each binary system ($i + j$ system) as follows.

$$q_i^0 = q_{ji}^*$$

q_i^0 is expressed as follows for more than 3 component systems.

$$q_i^0 = \frac{\sum_{j \neq i} q_{ji}^* x_j}{\sum_{j \neq i} x_j}$$

For isothermal systems, the correlated results by f-CDSAP model are in good agreement with the experimental data for both vapor-liquid and liquid-liquid equilibria with the same parameter set, and better than those by NRTL and UNIQUAC models. By introducing temperature dependence parameters to f-CDSAP model, ternary liquid-liquid equilibria and constitutive binary phase equilibria with different temperatures are simultaneously correlated well with the same parameter set.

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MTMS '21, September 7 – 9, 2021

PB 08

Anionic States play more important role: Electronic Structure Informatics of Gas-Phase Acidity Toward Fast and Precise Acids Design for Engineering

Authors and affiliation

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Key Word (3 words)

Acids design, materials informatics, conjugate anion

Abstract (less than 300 words)

In semiconductor processing, it is necessary to design super acids having desired physicochemical properties according to the situation where they will be applied. In acid engineering, there is a growing momentum breaking away from the traditional experiment-driven molecular design in which whole candidates are synthesized. Since the synthesis of superacid is dangerous, it has been considered necessary to design the target superacid molecule safely with enough quickness and precision before experiments. For this purpose, there is a need to develop a new theoretical molecular design method based on quantum chemical calculations that can predict the acidity of unknown compounds. Acid pK_a values can be calculated by quantum chemical methods with an error of about 1 pK_a from the experimental value. However, previous methods require manual classification of the acidity functional group for each compound species [1], and there is no highly accurate and efficient method for predicting the acidity of arbitrary compounds.

We have performed a set of *ab initio* molecular orbital calculations to predict the gas phase acidities of various organic substances, which is the basis of superacid design. We confirmed the necessity of high-precision quantum chemical calculations that can accurately calculate the anions. In general, the high-precision molecular orbital method has been considered unsuitable for the industrial exploration of new super-acidic materials due to its high computational cost. In this study, we report on developing a method for fast prediction of gas-phase acidity (calculation time/molecule: 1 day → 1 min) using machine learning models with the results of the high-precision molecular orbital method as the correct answer information. This method quantitatively suggests that it is necessary to consider the anionic state to explain acidity and that accurate prediction cannot be expected from the neutral state only.

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MTMS '21

PB 09

Optimization of an Artificial Neural Network for Pure Component Parameters based on a Group Contribution Method of PC-SAFT EoS

Authors and affiliation

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Key Word (3 words)

PC-SAFT equation of state, Artificial neural network, Group contribution method

Abstract (less than 300 words)

In recent years, the perturbation theory-type equation of state (EoS), such as perturbed chain statical associating fluid theory (PC-SAFT) EoS [1], has been attracting attention owing to its applicability for wide molecular families including polymers and ionic liquids. The pure component parameters of the PC-SAFT EoS are generally obtained from liquid density and saturated vapor pressure. Unfortunately, these properties do not often exist. Therefore, a group contribution method (GCM) is used as one of the methods to obtain the pure component parameters. GCMs for parameters of the perturbation theory-type EoS have been reported [2, 3], whose high reliability was confirmed by numerous studies. However, the number of atomic groups covered is limited. Furthermore, it is impossible to predict when it comes to complex molecular structures. We introduced an artificial neural network (ANN), which can represent objects that are difficult to formulate, rather than the model of the GCM, because the model in the existing GCM is no longer able to manage enormous diversification of substances. Hence, a model to estimate the pure component parameters m , σ , and ε of the PC-SAFT EoS was developed. Furthermore, we tried to improve the estimation accuracy by optimizing the network structure and changing the input data. The results confirm that the model can determine the pure component parameters of PC-SAFT, which can estimate the liquid density, saturated vapor pressure, and critical properties. Furthermore, in each pure component parameters of the PC-SAFT EoS estimated using ANN, the estimation accuracy of the number of segments was lower than that of the other two parameters. We discussed this from several points of view and tried to improve the estimation accuracy of the number of segments.

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MTMS '21

PB 10**Screening of phase-separation CO₂ absorbent using machine learning combined with molecular information**

Authors and affiliation

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Key Word (3 words)

CO₂ capture, phase-separation absorbent, machine learning

Abstract (less than 300 words)

Carbon dioxide capture technologies have been focused to overcome global warming. A chemical absorption process using an aqueous amine solvent is one of the most established technologies of CO₂ capture because of the high absorption rate and high reactivity with CO₂. However, this process operation needs a large amount of energy, causing high regeneration costs. Recently, to reduce energy consumption, phase-separation absorbents have been reported. The phase-separation absorbents are mainly composed of mixed solvents of alkanolamine and organic solvents like glycol ether or alcohol. When the absorbent reacts with CO₂, a single liquid phase of the phase-separation absorbent transforms into two liquid phases, CO₂-rich and -lean phases. This absorbent can reduce the temperature difference between the absorption and desorption operations from 80 °C of the conventional chemical absorption process to 40 °C [1]. However, it is difficult to know phase behaviors of mixed-solvent absorbents, resulting in the necessity of screening experiments to find phase-separation absorbents [2, 3].

In this work, we developed a screening method of the phase behaviors of the mixed-solvent absorbents using supervised machine learning models: random forest, logistic regression, and support vector machine. There are 61 mixed-solvent absorbents containing alkanolamine/glycol ether or alcohol in a dataset. The dataset was split into a training set and test set, which contains 31 and 30 data of the absorbents, respectively. Extended-connectivity fingerprint [4] or molecular surface charge distributions calculated from a COSMO calculation [5] are used as molecular descriptors in the machine learning models. The machine learning models successfully predicted phase states of the mixed-solvent absorbents before and after CO₂ absorption with accuracies of more than 90 %. Furthermore, we analyzed contributions of explanatory variables to predict the phase states using the learned model.

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MTMS '21

PB 11**Prediction of Melting Point and Fusion Enthalpy of Cocrystal by Machine Learning combined with molecular informatics**

Authors and affiliation

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Key Word (3 words)

Cocrystal, Machine Learning, Chemical Calculation

Abstract (less than 300 words)

In the past decades, the solubility of the pharmaceuticals become lower. To solve this problem, the cocrystal have been considerate. By forming a new crystal structure with an additive which is called as coformer (CF), the thermodynamics property like melting point, fusion enthalpy of the pharmaceutical crystal can be modified. But by now, the melting point, fusion enthalpy of the cocrystal is mostly collected by experiments. So, in this research, we will try to build a machine learning model which can predict melting point and fusion enthalpy of cocrystal only from the molecular information of pharmaceutical (API) and coformer.

To make the molecular understandable for computer, we use the statistical charge distribution calculated by quantum calculation based on Conductor-like Screening Model (COSMO) as the descriptor for API and coformer. In additional, because the fusion enthalpy and melting is strongly related with energy, the sigma-profile of the API and coformer is input as a heat map matrix. The routable bond number, fusion enthalpy and melting point of the API and coformer are also inputted. For machine learning, least absolute shrinkage and selection operator with cross validation (LassoCV), support vector regression model with linear kernel (SVR-linear) is applied.

About 55 data sets are collect from the published paper. As the final result, the R² score, the mean relative error (MRE), and mean absolute error (MAE) for each test datasets are as below. For the melting point prediction, LassoCV model gives out the best result, while R² = 0.669, and the MRE = 3.9 %, MAE=16 K. And for fusion enthalpy prediction, SVR-linear model shows best performance, give out a R² = 0.625, MRE = 12.4% and the MAE=8.5 kJ mol⁻¹. For both cases, the R² is higher than 0.6 which indicating strong correlation between prediction and experiment, and the error is acceptable.

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PB 12

Cation effects on physical properties of acetate-based ionic liquids

Authors and affiliation

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Key Word (3 words)

Ionic liquid, Acetate, Physical property

Abstract (less than 300 words)

Ionic liquids (ILs) are salts with melting points being at or below ambient temperature. There are various ionic species, and thus, the natures of ILs can be optimized for individual applications by the combination of ions and chemical modification. Because ILs have unique characteristics like negligibly vapor pressure, non-flammability, and miscibility with various chemicals, they have attracted much attention as potential solvents in various fields. Here, we report the cation effects on the physical properties of acetate ($[AcO]$) based ILs before and after the CO_2 absorption. The cations of $[AcO]^-$ ILs were 1-ethyl-3-methylimidazolium ($[emim]^+$), N,N -diethyl- N -methyl- N -heptyl-ammonium ($[N_{1227}]^+$), N,N -diethyl- N -methyl- N -(6-hydroxyhexyl)-ammonium ($[N_{1226OH}]^+$), and dodecyltributylphosphonium ($[P_{444,12}]^+$). The physical properties of 1-ethyl-3-methylimidazolium 2,2-dimethyl-3-hydroxylpropionate ($[emim][OH-Piv]$) were also examined to elucidate the effect of the hydroxy-functionalized carboxylate.

The densities of $[P_{444,12}][AcO]$, $[N_{1227}][AcO]$, $[N_{122,6OH}][AcO]$, $[emim][AcO]$, and $[emim][OH-Piv]$ increased in this order at certain temperatures. The cations with the longer alkyl chains tended to decrease the densities of ILs. The hydroxy-functionalized ILs were denser than the corresponding non-functionalized ILs. $[N_{122,6OH}][AcO]$ has the highest viscosity followed by $[emim][OH-Piv]$, $[N_{1227}][AcO]$, $[P_{444,12}][AcO]$, and $[emim][AcO]$ over the present temperature range. This order is attributed to the cation size and the hydrogen bond via the hydroxyl group, except for $[P_{444,12}][AcO]$. The densities of the IL + CO_2 mixtures were slightly higher or comparable to those of the corresponding neat ILs. The ratios of the densities between before and after CO_2 absorption tended to be largely dependent on the CO_2 solubility: $[emim][AcO] > [N_{122,6OH}][AcO] > [P_{444,12}][AcO] > [N_{1227}][AcO]$. The CO_2 -saturated $[N_{1227}][AcO]$ and $[N_{1226OH}][AcO]$ were more viscous than the neat ILs. The viscosity increment is typically observed for the CO_2 chemical absorbent. In contrast, the viscosities of $[emim][AcO]$ and $[P_{444,12}][AcO]$ showed no appreciable change after CO_2 absorption. This difference in viscosity change would arise from the kind of CO_2 adducts.

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PB 13**Thermodynamic stabilities of clathrate hydrates including tetrahydrofuran and quaternary onium salts**

Authors and affiliation

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Key Word (3 words)

Clathrate hydrate, Phase change material, Dissociation enthalpy

Abstract (less than 300 words)

Tetrahydrofuran (THF), one of the most popular clathrate hydrate formers, forms the structure-II (sII) hydrate at temperatures below 277.5 K and atmospheric pressure. The sII unit lattice consists of 16 small cages (S-cages) as well as 8 large cages (L-cages). A THF molecule occupies the L-cage, whereas the S-cage remains vacant. The application of vacant S-cages, that is, the enclathration of another guest species into S-cages, has been investigated in the fields of gas separation or storage media. Considering the application of clathrate hydrates as latent heat storage materials, the enclathration of another guest species into vacant S-cages would be essential because it should lead to the increases in decomposition temperature and decomposition enthalpy of clathrate hydrates. It has been reported that, as a guest species other than small gas molecules, tetra-*n*-propylammonium fluoride (N3333F) can be enclathrated in the sII clathrate hydrate with THF (Manakov *et al.*, *J. Incl. Phenom. Mol. Recogn. Chem.*, vol. 17, pp. 99-106 (1994)). In the present study, we investigated thermodynamic stabilities of (THF + quaternary onium salt) mixed hydrates. The characterization of the (THF + quaternary onium salt) mixed hydrates was done with differential scanning calorimeter, Raman spectrometer, and powder X-ray diffractometer.

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PB 14

Measurements of diffusion coefficient for triolein in various pressurized fluids with different viscosities

Authors and affiliation

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Key Word (3 words)

diffusion coefficient, triolein, pressurized fluid

Abstract (less than 300 words)

As it is well known, mass transfer, which is one of the unit operations in chemical engineering, can roughly be divided into molecular diffusion and convection. Once solute concentration has become uniform, the molecules are all still in motion in different, random directions; as a result, there is no net flux or change in concentration and the solute molecules are never at rest at temperatures above absolute zero. Triolein is a symmetrical triglyceride derived from glycerol and three units of the unsaturated fatty acid oleic acid. Triglyceride can be employed to produce biodiesel fuel by transesterification process. Triglyceride can be extracted from biomass such as rice bran or olives by the fluids such as pressurized organic solvent and supercritical carbon dioxide. To design and optimize exactly a new process using pressurized fluids, physical properties are demanded, in particular, diffusion coefficient, D_{12} , is indispensable to accurately understand the amount of mass transferred in the system when molecular diffusion is the bottleneck of the mass transfer [1]. However, it is difficult to measure D_{12} in the pressurized fluids. In fact, there are very few reports on triolein in pressurized fluids [1,2].

Herein, the diffusion coefficients of triolein in the pressurized fluids such as carbon dioxide, hexane, methanol and ethanol were measured by the CIR method [3] and Taylor dispersion method [4] as a function of pressures from 1.0 to 31.0 MPa and temperatures from 298.15 - 333.15 K. The measured D_{12} in this study were well represented by the hydrodynamic equation over a wide range of fluid viscosity.

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PB 15

Molecular dynamics study on nucleation process for supersaturated ZnO solutions in hydrothermal conditions

Authors and affiliation

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Key Word (3 words)

Hydrothermal, Molecular simulation, Nucleation

Abstract (less than 300 words)

Molecular dynamics simulations were performed to investigate homogeneous nucleation mechanism of zinc oxide in ambient and hydrothermal conditions. Water model used in this work was the three-site flexible-SPC model proposed by Honma [1]. Atomic models for zinc and oxygen ions were constructed with Lennard-Jones and Coulomb potentials. The snapshot analysis of zinc oxide aqueous solution showed the two-step nucleation process, in which ions and water aggregate to form disordered clusters, followed by the crystallization of ions and solvent ejection. In case of ambient condition, the nucleation process of aqueous zinc oxide solution should be followed the two-step process, however, our simulation could not simulate the crystallization process as latter step due to slow nucleation process.

Radial distribution function of Zn^{2+} - O^{2-} revealed crystallization occurred at high zinc oxide concentration ($N_{ion}=40$), because sharp first and second peaks of $g(r)$ were observed in all temperature conditions. This trend was more significant at high temperature conditions. In case of low zinc oxide concentrations ($N_{ion}=5$), the broad peak on $g(r)$ were located around 6 Å up to 333 K. Zn^{2+} and O^{2-} ions would be solvated and moved independently. However, as increasing temperature, first peak of $g(r)$ at low zinc oxide concentrations observed shorter and higher. This trend indicates nucleation rates at hydrothermal condition was faster than rates at ambient conditions. Therefore, the molecular dynamics simulation would be represented the difference of nucleation rate in temperature, and it may be determined the nucleation rate and critical nucleus size. The critical nucleus size and free energy analysis is in progress, which will be discussed in the presentation.

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PB 16

Correlation of Solubilities in Mixed-Solvents with Local-composition-Regular Solution Theory

Authors and affiliation

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Key Word (3 words)

correlation model, active pharmaceutical ingredients, solid-liquid equilibria

Abstract (less than 300 words)

The dissolution of a solute in solvent is a common protocol in industries that process food and active pharmaceutical ingredients (API). Therefore, there is great demand to improve the processing of active components with desirable solvents and to reduce the use of organic solvents that can contaminate the product. Solid-liquid equilibrium data are necessary for addressing the forementioned challenges. However, determination of suitable solvent systems can complex because processing requirements involve multicomponents. In a previous study [1], local-composition-regular solution theory (LC-RST) was developed to correlate the solubility data of API in mixed-solvents for ternary systems. LC-RST can be extended to predict the phase behavior of non-polarity or non-specific interactions solutions [2, 3]. The objective of this study was to correlate solubility data of active pharmaceutical ingredients in mixed-solvents with LC-RST model and to study its generalization. The selected mixed-solvent were water-acetone, water- isopropanol and water- ethanol at 273 K to 313 K. In this study, the number of fitting parameters for ternary solid-liquid equilibrium data could be reduced from 12 to 6 with the sum of the solubility errors being in the range of 1.62×10^{-4} to 7.85×10^{-4} . Fitting parameters could be generalized with the properties of paracetamol and mixed-solvent systems. In the model two parameters had a linear relationship with the molecular weight of system; two parameters were related to the number of hydrogen donors and heat of fusion of the system; one parameter was related to the number of hydrogen acceptors and donors of system; and one parameter was related to the solubility parameters of compounds in system. The potential application of correlation is for selection of vegetable oil based mixed-solvents for a separation process in supporting green and sustainable development.

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