

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

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ABSTRACT

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. In 1977, using a modified generalized BWR EoS, one of authors (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. In this paper, we found that m_{ij} values for these CO₂+ non-volatile mixtures could be used 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. .

1. Introduction

To balance the rapid increase of carbon dioxide emission in the atmospheres, ‘carbon capture and storage’ (CCS) techniques are strongly required. Non-volatile solvents such as ionic liquids or glymes are believed to be excellent solvents for carbon capture, because they don’t soluble in gas phase in the recovery process of carbon dioxide [1].

As an ionic liquid is a complex salt, manufacturing it takes much time and cost. If we can even roughly predict the solubility of CO₂ in non-volatile solvents, it will be useful to plan an experimental schedule.

Based on the corresponding state principle, properties are calculated with an equation of state (EoS). To calculate thermodynamic properties with a generalized EoS, the basic properties such as critical ones for a pure substance are necessary, But, no experimental critical data on non-volatile solvents are reported. To predict them, we employed the Joback method [2]. Once the structure of an ionic liquid is known, we can calculate critical properties (T_c , P_c , V_c , ω). So, obtained element values may be called as the basic parameters for a generalized EoS rather than the critical properties..

One of authors (Nishiumi) already proposed that for a CO₂+non-polar system, binary interaction parameters m_{ij} are expressed as a function of the critical volume ratio $V_{ci}/V_{C,CO_2}$ [3]. As ionic liquids are polar substances, m_{ij} for the CO₂+ionic liquid will be affected by temperature. In this work, the m_{ij} relation between for CO₂+non-polar system and for CO₂+ionic liquid or glyme polar system was investigated. In this work, we would like to propose a new prediction method how much CO₂ will solve into an unknown an ionic liquid.

2. Critical properties calculation of ionic liquids and glymes

2.1 Joback method

Group contribution method gives the basic properties such as the critical properties of a pure substance. In this work, we used the following Joback method [2] :

$$T_c [K] = T_b \left[0.584 + 0.965 \sum \Delta_T - \left(\sum \Delta_T \right)^2 \right]^{-1} \quad (1)$$

$$T_b [K] = 198 + \sum \Delta_b \quad (2)$$

$$P_c [\text{MPa}] = 0.1 \times \left(0.113 + 0.0032 n_A - \sum \Delta_P \right)^{-2} \quad (3)$$

$$V_c [\text{cm}^3/\text{mol}] = 17.5 + \sum \Delta_V \quad (4)$$

Sum of structural elements Δ_T etc. gives the critical properties. Comparison of about 400 substance data in the famous book , “The Properties of Gases and Liquids” [4] with the Joback method shows that deviations are 5.9, 6.1 and 8.0 % for T_c , P_c and V_c each,

2.2 Critical properties of glymes

Examples of structural formulae of glymes and ionic liquids are shown in Table 1. For example tetraglyme (TETRAethylene GLYcol diMethyl ether) are composed of two CH₃-, eight -CH₂- and five -O- elements of the Joback method. The values of each element Δ_T , Δ_b , Δ_P and Δ_V are listed in the Joback method. Giving sum of element values $\Sigma \Delta_T=0.2634$, $\Sigma \Delta_b=540.3$, $\Sigma \Delta_P=0.0051$, $\Sigma \Delta_V=668.0$, the critical temperature T_c , critical molar volume V_c , and critical pressure P_c are calculated. Moreover, the molecular weight M.W. and acentric factor ω are listed in Table 2.

The value of ω can be obtained as follows: applying the Clausius-Clapeyron equation[4] for the critical point and vapor pressure P^s gives,

$$\log_{10} \left(\frac{P^s}{P_c} \right) = \frac{\log_{10} (1/P_c)}{1 - 1/(T_b/T_c)} \left(1 - \frac{1}{T/T_c} \right) \quad (5)$$

From the definition of ω [5–7] at $T/T_c = 7/10$

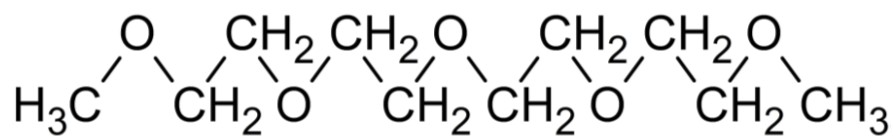
$$\omega = -\log_{10} \left(\frac{P^s|_{T/T_c=0.7}}{P_c} \right) - 1 = -\frac{3 \log_{10} P_c [\text{in atm}]}{7 \cdot 1/(T_b/T_c) - 1} - 1 \quad (6)$$

The value of T_b/T_c is given by Eq.(1) as a function of $\Sigma \Delta_T$.

Table 1. Structural formulae for Joback method in this work

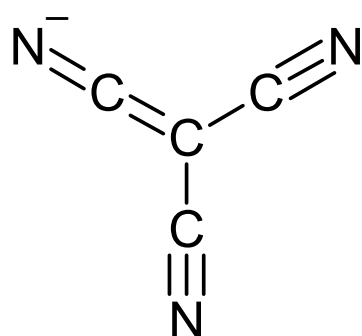
1. glyme

tetraglyme

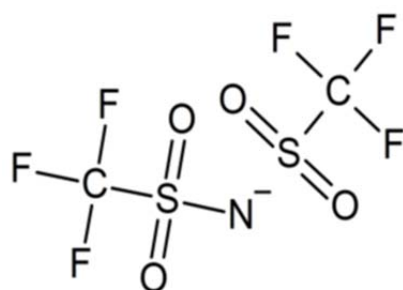


2. anion

TCM (TriCyanoMethanide)

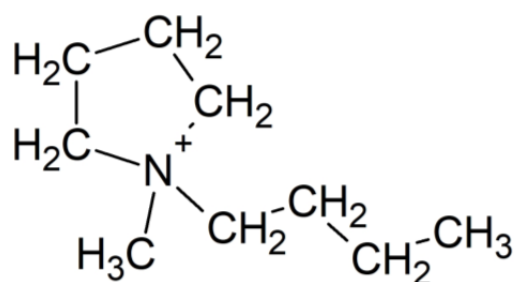


Tf2N (bis(trifluoromethylsulfonyl) imide)

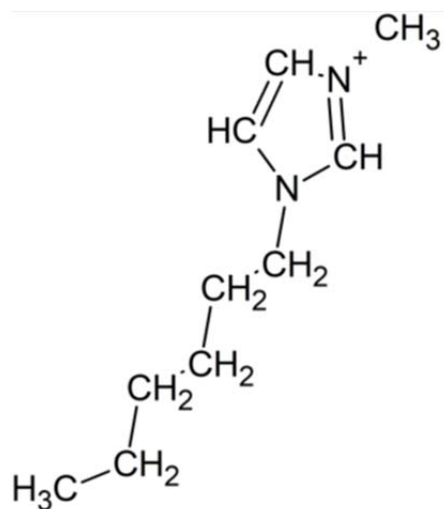


3. cation

4mPYR (1-butyl-1-methyl PYRrolidinium)



6mIM (1-hexyl-3-methyl IMidazolium)



4mPY (1-butyl-4-methyl PYridinium)

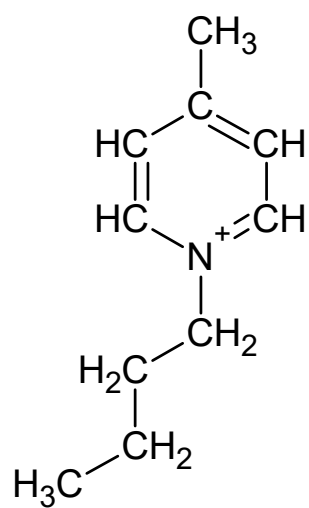


Table 2. Pure component and optimal mij for CO₂ solubility in glymes or ionic liquids

	component*	M.W.	$T_c(K)$	$V_c(L/mol)$	$P_c(MPa)$	$\omega(-)$
glyme						
	Diglyme	134.18	569.71	0.4255	2.938	0.557
	Triglyme	178.23	636.37	0.5555	2.370	0.687
	Tetraglyme	222.28	702.78	0.6855	1.953	0.831
ionic liquid						
cation	anion					
4mIM	TCM	229.30	818.54	0.6575	3.404	0.895
4mPY	TCM	240.30	877.12	0.7215	2.976	0.809
4mPYR	TCM	232.00	775.11	0.6930	2.820	0.787
3mPYR	Tf2N	408.38	707.94	0.9375	2.490	1.161
5mPYR	Tf2N	436.43	754.48	1.0495	2.074	1.194
6mPYR	Tf2N	450.46	778.25	1.1055	1.904	1.202
7mPYR	Tf2N	464.49	802.43	1.1615	1.754	1.199
8mPYR	Tf2N	478.51	827.09	1.2175	1.621	1.189
9mPYR	Tf2N	492.54	852.27	0.6922	1.502	1.170
2mIM	Tf2N	391.31	725.22	0.8465	3.307	1.219
6mIM	Tf2N	447.42	816.43	1.0705	2.219	1.290
3mPY	Tf2N	416.36	767.86	0.9385	2.685	1.050

* Shortened symbols are referred to Table 1

Similarly, the critical values of diglyme (DIethylene GLYcol diMEthyl ether) and triglyme (TRIethylene GLYcol diMEthyl ether) and ionic liquids can be obtained as shown in Table2. Obtained critical values are expected within deviation as stated.

When the critical properties of a pure substance, it is possible to predict thermodynamic properties of a pure substance based on the corresponding states principle with an equation of state. In this paper, a modified generalized BWR EoS is used for each calculation [8-12].

Fig.1 shows density calculation of glymes at 0.1 MPa [13]. The deviations are 1.8, 6.4 are 10.9 % for diglyme, triglyme and tetraglyme. The vapor pressure deviation of diglyme was 3.9 % with NIST data [14, 15]

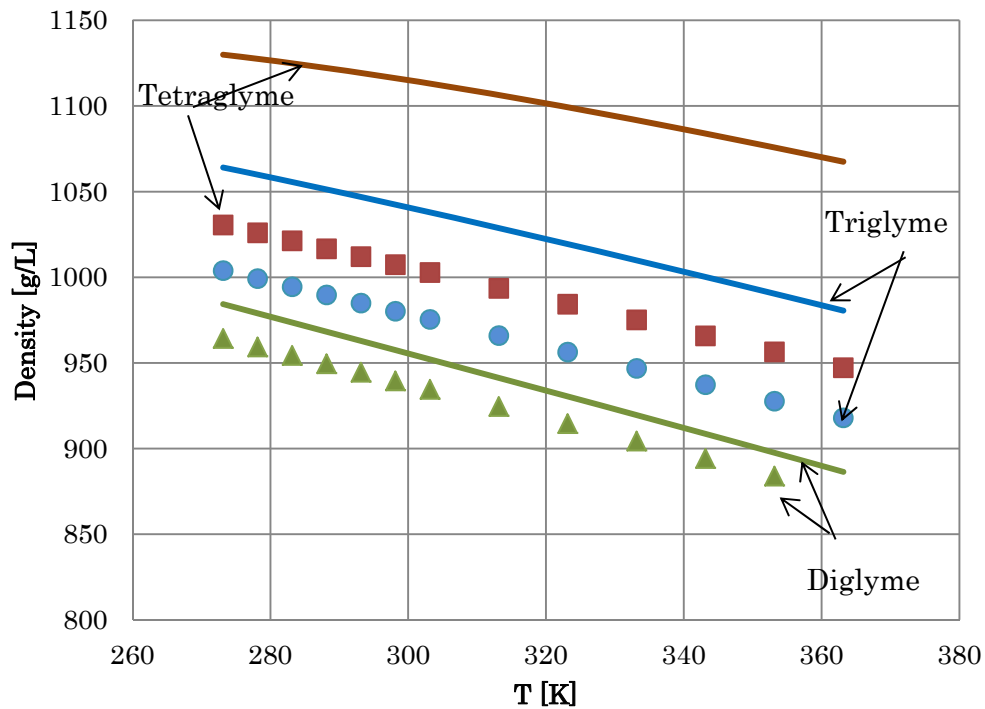


Fig.1 Density comparison of calculation with experiments of glymes at 0.1 MPa [13]

2.3 Critical properties of ionic liquids

There is no description about ionic elements in the Joback method. So, we set approximations as follows:

For anions, as shown in Table 1-2, center carbon of tricyanomethnaide (TCM) or center nitrogen of bis(trifluoromethylsulfonyl) imide (Tf₂N) one bond is added each. For cations in Table 1-3, center nitrogen of 1-butyl-1-methyl PYRrolidinium (4mPYR) or 1-hexyl-3-methyl IMidazolium (6mIM) or 1-butyl-4- methyl PYridinium (4mPY), one bond is removed each.

Ionic liquids in this work are given in combination of anion and cation. Critical properties calculated by the above mentioned method are shown in Table 2. The first number of a compound is the carbon number of the alkyl group, for example, 4 is butyl. Although these obtained values are close to critical ones, they should be thought as the **calculation parameters** for a generalized equation of state.

3. CO₂ solubility in ionic liquid and glyme

3.1 Thermodynamic properties calculation for the system of CO₂ + glyme

To calculate a mixture property, especially phase equilibria, an interaction parameter is introduced. For a modified generalized BWR EoS [8-12, 3], a binary interaction parameter, m_{ij} , is defined from the cross second virial coefficient [16],

$$T_{cij} = m_{ij} \sqrt{T_{ci} T_{cj}} \quad (7)$$

Changing m_{ij} values of glymes, or ionic liquids, the solubility of CO₂ in the ionic liquids were best fitted.

Calculation of solubility, liquid density and vapor density for CO₂+diglyme at 313.15 K were good in agreement [17]. Solubility of CO₂ +triglyme at 313.15 K were well compared [15] and liquid density and vapor density deviation were 6.3and 1.7% each [13].

Solubility of CO₂+ tetraglyme at 313.15 K were well compared for $m_{ij} = 0.840$ as shown in Fig.2 and liquid density and vapor density average deviation were 10.5 and 1.8% each as shown in Figs. 3 and 4 [13].

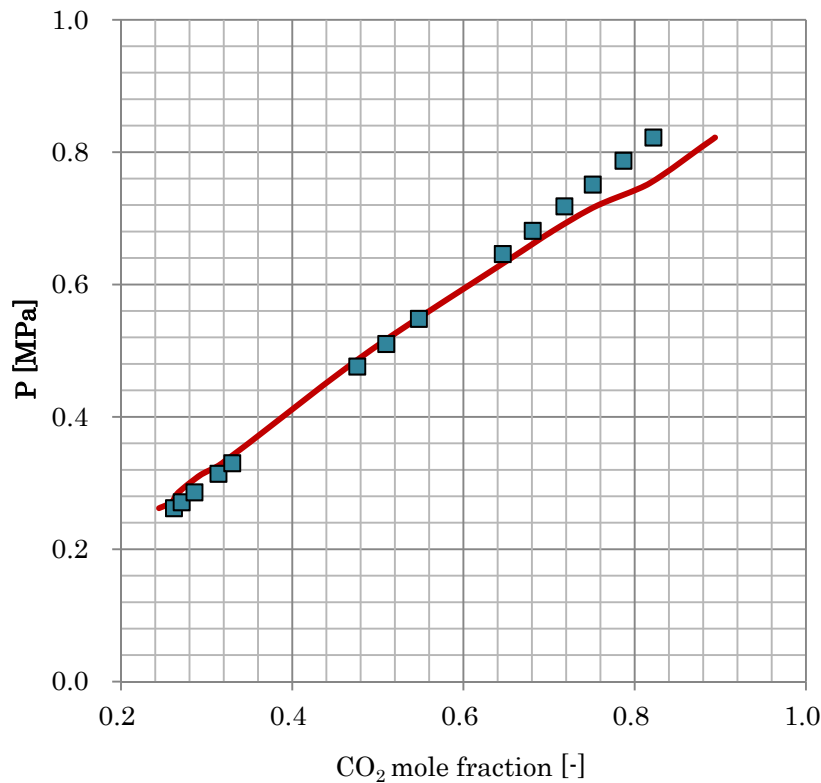


Fig.2 Solubility of CO₂ in tetraglyme at 313.15 K. Squares are experimental data from Kodama et al. [13], solid line: calculation with modified generalized BWR EoS for optimal $m_{ij}=0.840$.

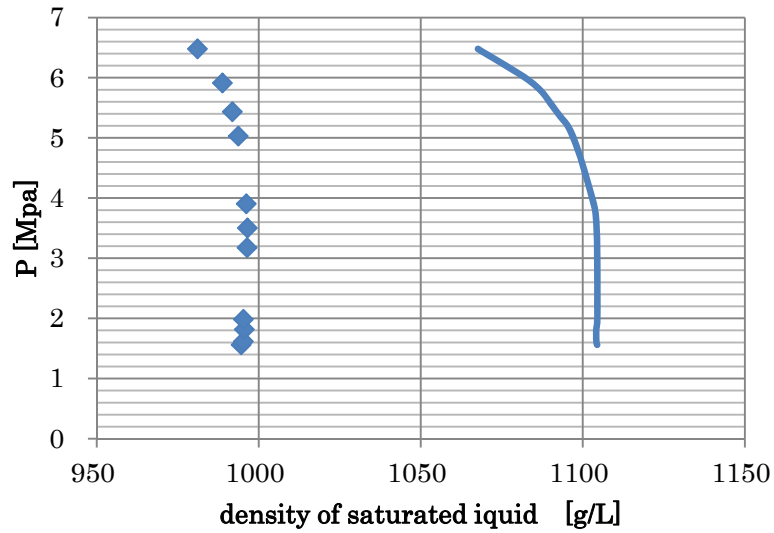


Fig.3 Liquid density calculation for the system of CO₂+tetraglyme at 313.15 K. Diamonds are experimental data from Kodama et al. [13], solid line: calculation with modified generalized BWR EoS (optimal $m_{ij}=0.840$).

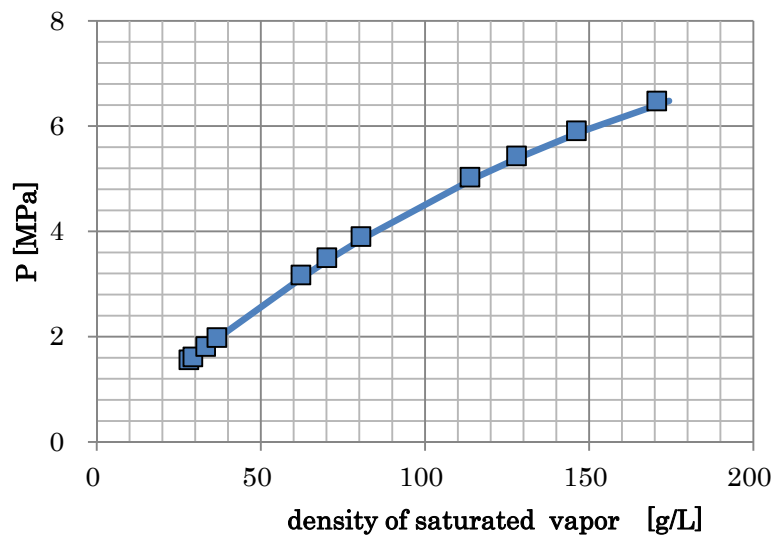


Fig.4 Vapor density calculation for the system of CO₂+tetraglyme at 313.15 K. Squares are experimental data from Kodama et al. [13], solid line: calculation with modified generalized BWR EoS (optimal $m_{ij}=0.840$).

3.2 CO₂ solubility calculation for the ionic liquid containing [TCM]⁻ or [Tf2N]⁻ anion

Three kinds of ionic liquids containing tricyanomethanide anion ([TCM]⁻) were examined.

Fig.6 shows temperature dependence of three kinds of ionic liquids containing tricyanomethanide anion ([TCM]⁻). With temperature increases, optimal m_{ij} increases. Nohka et al. [18] deduced that m_{ij} for the system composed of polar and non-polar mixture has a function of

$$m_{ij} \propto \left[1 + \frac{2}{3} \frac{\tilde{\mu}_j^2}{\tilde{T}_j} + 2\tilde{\alpha}_j \tilde{\mu}_j^2 \right]^{-1/2} \quad (8)$$

where α is polarity, μ is dipole moment and \tilde{T} indicate dimensionless temperature etc.. It shows that polarity works at lower temperature and reaches steady at non-polarity state. For a polar substance, m_{ij} becomes a complex function of temperature and liquid composition [12].

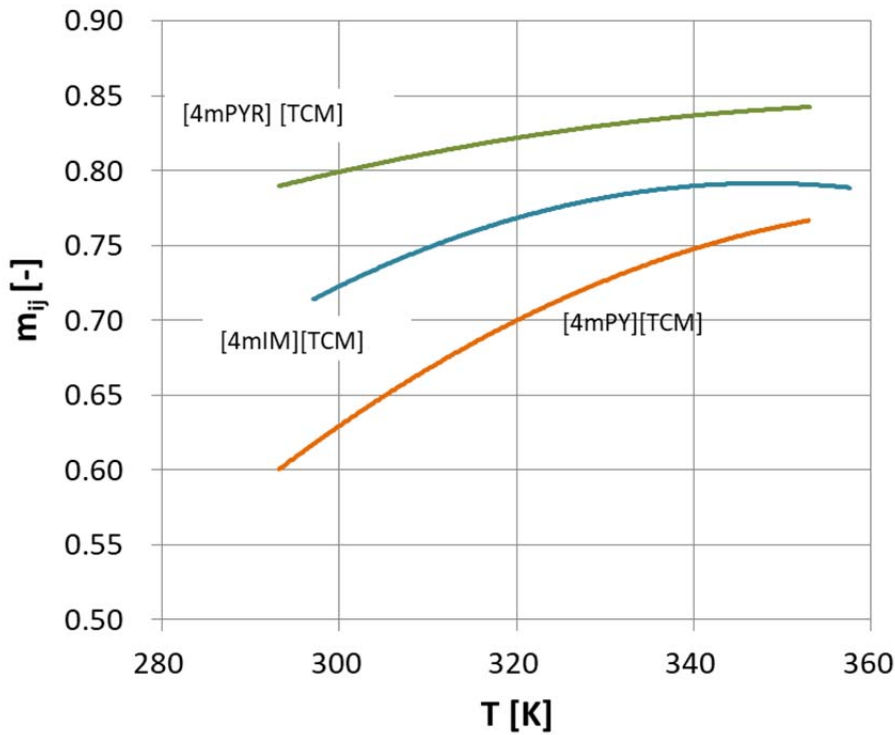


Fig.6 Temperature dependence of optimal m_{ij} for the system of $+[4mPYR]^+ [TCM]^-$, $CO_2 + [4mIM]^+ [TCM]^-$ and, $CO_2 + [4mPY]^+ [TCM]^-$ [19]

The ionic liquids containing [Tf2N]⁻ anion were also examined. The m_{ij} values have similar temperature dependence.

The optimal m_{ij} values for CO₂ solubility in glymes or ionic liquids are summarized in Table 3.

Table 3. Optimal m_{ij} for CO₂ solubility in glymes or ionic liquids

	component*	m_{ij}	Temp. [K]	$V_c/V_{c,CO_2}$	Reference
glyme					
	Diglyme	0.920	313.15	4.53	13
	Triglyme	0.885	313.15	5.91	13
	Tetraglyme	0.835	313.15	7.29	13
ionic liquid					
cation	anion				
4mIM	TCM	0.71~0.79	297.11-357.59	7.00	19
4mPY	TCM	0.60~0.77	293.20-354.00	7.68	19
4mPYR	TCM	0.79~0.84	293.15-353.15	7.37	19
3mPYR	Tf2N	0.78~0.82	303.15-373.15	9.97	24
5mPYR	Tf2N	0.77~0.82	303.15-373.15	10.79	24
6mPYR	Tf2N	0.72~0.79	303.15-373.15	11.76	23
7mPYR	Tf2N	0.70~0.80	303.15-373.15	12.36	24
8mPYR	Tf2N	0.62~0.78	303.15-373.15	12.95	23
9mPYR	Tf2N	0.69~0.80	303.15-373.15	13.55	24
2mIM	Tf2N	0.79~.84	312.10-410.9	9.00	20, 21
6mIM	Tf2N	0.74~0.81	293.15-413.2	11.39	20, 22
3mPY	Tf2N	0.75~0.77	313.15-33.15	9.98	25

4. Prediction of CO₂ solubility in ionic liquids and glymes

CO₂ solubility fitting results in ionic liquids and glymes were listed in the right part of Table 3.

For the system composed of non-polar substances, Hudson-McCoubrey derived the following relation [26]

$$m_{ij} = 64 \left\{ \left(\frac{V_{cj}}{V_{ci}} \right)^{1/6} + \left(\frac{V_{cj}}{V_{ci}} \right)^{-1/6} \right\}^{-6} \quad (9)$$

The above relation doesn't give reasonable m_{ij} values of a system composed of non-polar substances. But m_{ij} may be a function of V_c ratio. In 1977, one of authors (Nishiumi) reported that the optimal m_{ij} values for the modified generalized BWR equation of state were found to belong to several family groups expressed as a function of the ratio of critical volumes [3].

Fig. 7 shows the relation between m_{ij} with V_c ratio for the systems composed of CO₂ for a modified generalized BWR EoS [3,15]. This time, optimal m_{ij} values of the CO₂ + non-polar substances recalculated. Obtained CO₂ containing family group is correlated as a simple correlation as follows,

$$m_{ij} = 0.9693 - 0.01193 \frac{V_{c,i}}{V_{c,CO_2}} - 0.000603 \left(\frac{V_{c,i}}{V_{c,CO_2}} \right)^2 \quad (10)$$

where $V_{c,CO_2}=0.0940$ L/mol. A bold curve in the figure shows Eq.(10) and each non-polar system is drawn as a white triangle.

We can find that examined CO₂ solubility calculation in glymes and ionic liquids excellently passes through Eq. (10). As they are polar substances, their m_{ij} values have rough temperature dependence as shown in Eq.(8).

The results show that Eq.(10) can apply not only to the CO₂-nonpolar substances but also to complicated polar systems such as ionic liquids by using a modified generalized BWR EoS [8-12]. It provides an easy prediction method for CO₂ solubility in an ionic liquid.

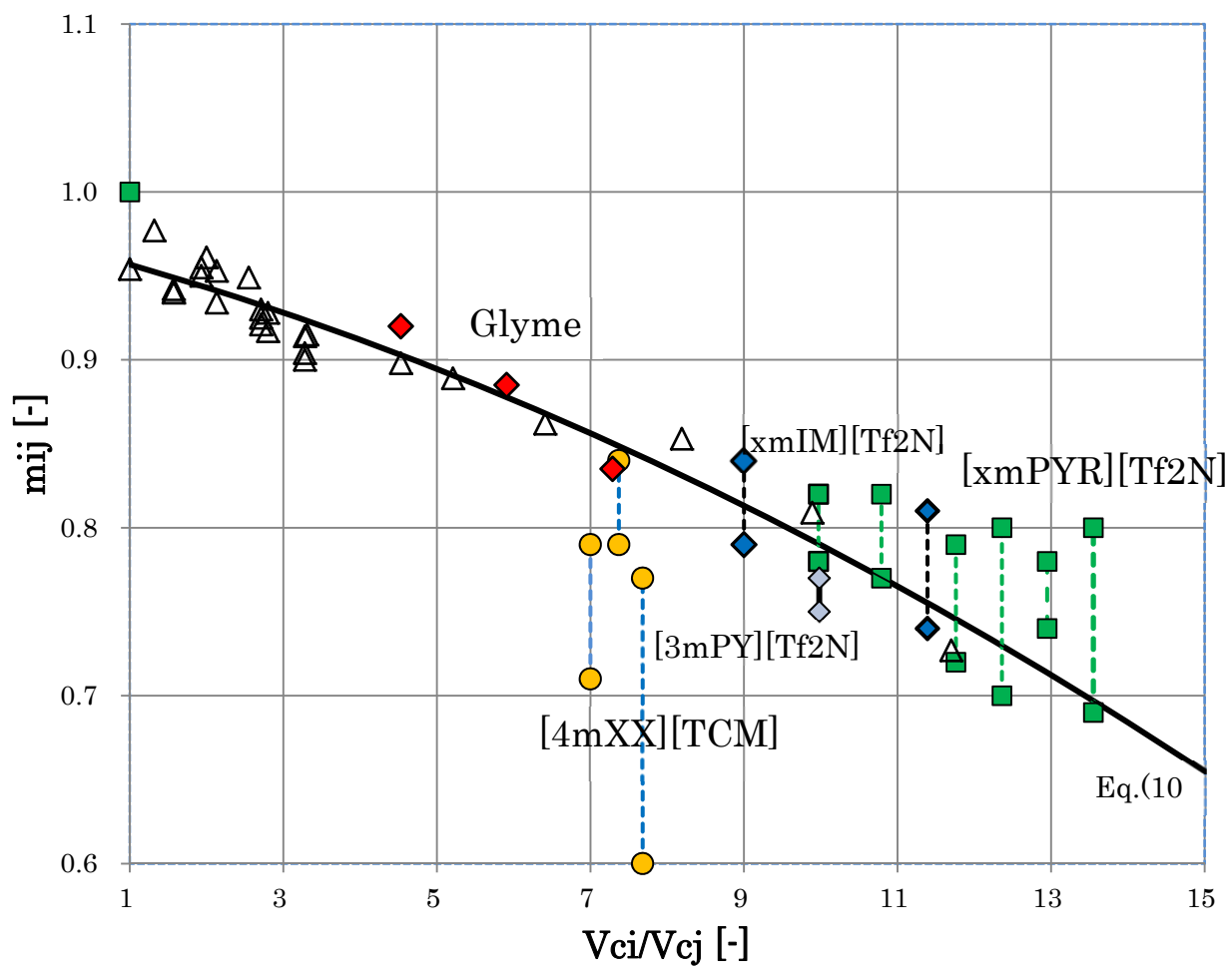


Fig.7 Prediction of CO₂ solubility in glymes and ionic liquids. bold line: Eq.(10). Experimental CO₂+non-polar system: white triangles[3,15], red diamonds:glymes [13], yellow circles:[TCM]compounds [19], blue diamonds: [xmIM][Tf2N] [20,21,22], green squares: [xmPYR][Tf2N] [23,24], grey diamonds [25].

5. Conclusion

Looking for an effective ionic liquid to solve CO₂ in it, you can predict its solubility in ionic liquid as follows,

(1) Using the structural elements of the Joback method in Sec 2.1, you can know the critical temperature T_c , boil point temperature T_b , critical molar volume V_c , and critical pressure P_c , and the molecular weight M.W. of a substance. Moreover, an acentric factor ω can calculate from Eq.(6). Obtained fundamental values of a pure substance should be thought as calculation parameters. You can calculate various thermodynamic properties of a pure substance with a generalized EoS.

(2) A value of m_{ij} necessary for the solubility calculation of CO₂ in glyme or an ionic liquid can roughly predict with Eq.(10) knowing the critical volume ratio $V_{c,i}/V_{c,CO_2}$. Using the modified generalized BWRSN EoS [8-12].

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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