

Prediction of high-pressure viscosities for binary liquid mixtures using the EOS- G^E mixing rule with low-pressure viscosity data

Katsumi Tochigi^{a,*}, Tomohiko Okamura^a, V.K. Rattan^b

^a Department of Materials and Applied Chemistry, Nihon University, 1-8 Surugadai, Kanda, Chiyoda-ku, Tokyo 101-8308, Japan

^b Department of Chemical Engineering Technology, Panjab University, Chandigarh 160014, India

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Abstract

A viscosity model, based on Eyring's absolute rate theory combined with a cubic PRSV equation of state and G^E mixing rule, has been proposed in order to correlate and predict mixture viscosities at atmospheric and high pressure, respectively. In the proposed method, the energy and size parameters in EOS have been obtained using the MHV1 mixing rule combined with the NRTL equation. The NRTL parameters for 22 binary systems have been calculated using viscosity data at atmospheric pressure. The average deviation between the experimental and calculated viscosities is 2.1%. This accuracy is better than the accuracy obtained using the Wong-Sandler mixing rule. The high-pressure viscosities for 10 binary systems have been predicted using NRTL parameters determined and atmospheric pressure viscosity data, and shown to have a deviation of 4.6%.
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1. Introduction

Liquid viscosity is a thermophysical property that is often embedded in equipment and process models, and used by process engineers to design and optimize equipment and chemical processes. A number of predictive methods for determining the viscosities of liquid mixtures have been proposed in the textbook [1]. In the predictive methods, viscosity models [2–4] based on the Eyring's absolute rate theory are useful for a practical point of view, because local composition models are used for evaluating the excess free Gibbs energy. The authors previously proposed a viscosity model based on a combination of the Eyring's absolute rate theory and the ASOG group contribution method for predicting liquid mixture at atmospheric pressures [5]. Recently a predictive method for determining high-pressure viscosity based on low-pressure viscosity data has been proposed using a cubic equation of state combined with an excess free energy mixing rule [3].

This paper deals with the correlation of normal-pressure viscosities for 22 binary systems using the proposed

PRSV + Eyring + MHV1 + NRTL model. Based on this, the high-pressure viscosities for 10 binary systems have been predicted using NRTL parameters determined by atmospheric pressure viscosity data.

2. Calculative equation of viscosities for liquid mixtures

The viscosity of liquid mixture can be shown by the following equation from Eyring's absolute rate theory [6], which makes use of excess Gibbs free energy at the activated state $G^{\ddagger,E}$.

$$\eta = \frac{(\eta V)_{ID}}{V} \exp\left(\frac{G^{\ddagger,E}}{RT}\right) \quad (1)$$

In Eq. (1), $(\eta V)_{ID}$ is the kinematic viscosity of ideal solution, given by Eq. (2):

$$(\eta V)_{ID} = \exp\left[\sum_i x_i \ln(\eta_i^0 V_i^0)\right] \quad (2)$$

From Eqs. (1) and (2), the following equation is given:

$$\ln \eta V = \sum_i x_i \ln(\eta_i^0 V_i^0) + \frac{G^{\ddagger,E}}{RT} \quad (3)$$

* Corresponding author. Tel.: +81 3 3259 0814; fax: +81 3 3293 7572.
E-mail address: tochigi@chem.cst.nihon-u.ac.jp (K. Tochigi).

In Eq. (3), $G^{\neq,E}$ is the excess free energy at activated state and is related with the excess free energy G^E as follows [4,5,7,8]:

$$G^{\neq,E} = kG^E \quad (4)$$

where k depends on the system, temperature and pressure. In the case that only viscosities are considered, the following equation has been widely used by some researchers [5,7]:

$$\ln \eta V = \sum_i x_i \ln(\eta_i^0 V_i^0) - \frac{G^E}{RT} \quad (5)$$

The excess free energy G^E can be evaluated by the thermodynamic relation:

$$\frac{G^E}{RT} = \sum_i x_i (\ln \hat{\phi}_i - \ln \phi_i^0) \quad (6)$$

Here $\hat{\phi}_i$ and ϕ_i^0 are the fugacity coefficients of component i in mixture and pure component, respectively. These coefficients can be evaluated by the following cubic equation of state called PRSV [9].

$$P = \frac{RT}{V-b} - \frac{a}{V(V+b)+b(V-b)} \quad (7)$$

where a and b are the energy and size parameters, respectively. These parameters have been evaluated by the following simplified MHV1 model [10] given by Eqs. (8) and (9).

$$\frac{a}{b} = \sum_i x_i \frac{a_{ii}}{b_i} + \frac{G^E}{(-0.6232)} \quad (8)$$

$$b = \sum_i x_i b_i \quad (9)$$

In this paper, G^E has been evaluated using the following NRTL equation [11].

$$\frac{G^E}{RT} = x_1 x_2 \left(\frac{\tau_{21} G_{21}}{x_1 + x_2 G_{21}} + \frac{\tau_{12} G_{12}}{x_2 + x_1 G_{12}} \right) \quad (10)$$

$$\text{where } \tau_{12} = \frac{\Delta g_{12}}{RT}, \quad \tau_{21} = \frac{\Delta g_{21}}{RT}$$

$$\ln G_{12} = -\alpha_{12} \tau_{12}, \quad \ln G_{21} = -\alpha_{12} \tau_{21}$$

2.1. Correlated results of viscosities at atmospheric pressures

The systems discussed here are 22 binary mixtures which contain hydrocarbons + aromatic hydrocarbons, alcohols + *n*-butylamine, acetonitrile + alcohols, acetonitrile + water, and alcohols + water, as given by Table 1

. Table 1 also shows the classifications by positive, negative and s-type. The classifications mean the signs calculated by $\eta - \sum_i x_i \eta_i$. That is positive (+), negative (−) and S-type (+, −). The acetonitrile + water and acetonitrile + tetraethyleneglycol dimethyl ether systems have S-type shape, although the systems containing acetonitrile have not always S-type shape. The viscosities at normal pressure have been correlated using EOS

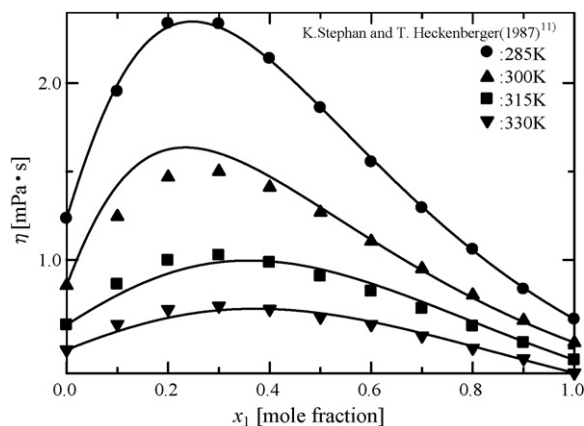


Fig. 1. Correlated results of viscosities by PRSV + MHV1 + NRTL model for acetonitrile (1) + polyether (2) system at 298 K and normal pressure.

and activity coefficient models. The binary parameters ($g_{ij} - g_{ji}$, $\lambda_{ij} - \lambda_{ji}$) in the NRTL equation [9] have been obtained using the following objective function:

$$F_{\text{obj}} = \sum_{k=1}^{\text{NDP}} \left[\frac{\eta_{\text{exp } t} - \eta_{\text{calc}}}{\eta_{\text{exp } t}} \right]_k^2 \quad (11)$$

The volumes of mixture and pure components have been evaluated by Eqs. (7)–(10). The NRTL parameters have been determined for each temperature using viscosity data at atmospheric pressure [12–19]. For α_{12} , the optimum value in 0.2, 0.3 and 0.47 that Renon and Prausnitz [11] recommended has been obtained. Table 1 shows the binary NRTL parameters at atmospheric pressure with the average deviations obtained using the MHV1 model. The absolute average deviation between the experimental and calculated viscosities is 2.09%. For acetonitrile + water system having S-type, the average deviation is 2.61%. This model produces good results for acetonitrile containing systems having S-type. Table 1 shows the comparisons of calculated results using MHV1 and WS [20], respectively. From these results, MHV1-NRTL produces better results than the WS-NRTL equation. The average deviations using PRSV + WS + van Larr that Macias-Salinas et al. [3] has applied for excess free energy at activated state for three aqueous alcohols is 3.05%. Figs. 1 and 2 show the correlated viscosities for the acetonitrile + polyether and methanol + water systems, respectively, obtained using equation MHV1-NRTL. In Fig. 2, the accuracy at 300 K is 3.94%, because the shape of viscosity diagram will be not simple.

2.2. Predicted results of viscosities at high pressures

The high-pressure viscosities for 10 binary systems have been predicted using binary NRTL parameters, determined at atmospheric pressure. Table 2 shows the predicted results using the MHV1-NRTL and WS-NRTL models. From these results, MHV1-NRTL produces better results than the WS-NRTL equation. Figs. 3 and 4 show the predicted results for the benzene + cyclohexane and methanol + water systems. In Fig. 4, the deviation between the experimental and predicted values will

Table 1
Binary parameters in PRSV-Eyring-MHV1-NRTL model

Mixture	T (K)	$g_{12} - g_{22}$ (J/mol)	$g_{21} - g_{11}$ (J/mol)	α_{12}	$[\Delta\eta/\eta]_{\text{av}} \times 100$ (%)		Type ^a	Reference
					MHV1-NRTL	WS-NRTL		
Pentane + decane	298	5374.0	−2243.9	0.3	0.93	0.94	Positive	[16]
Cyclohexane + <i>n</i> -octane	298	−3292.6	5432.0	0.3	0.56	0.34	Negative	[14]
	323	−2878.3	4844.7	0.3	0.35	0.16		
	348	−2035.7	3456.8	0.3	0.37	0.48		
Benzene + cyclohexane	313	1773.8	−2815.0	0.3	0.06	0.64	Negative	[13]
Methanol + <i>n</i> -butylamine	298	9148.3	112.5	0.3	1.03	1.29	Positive	[15]
Ethanol + <i>n</i> -butylamine	298	5510.8	−2199.7	0.3	1.64	0.73	Positive	[15]
1-Propanol + <i>n</i> -butylamine	298	572.3	−752.2	0.3	0.46	0.70	Negative	[15]
1-Butanol + <i>n</i> -butylamine	298	−2706.2	4083.2	0.3	0.51	0.52	Negative	[15]
Acetonitrile + methanol	298	244.6	−1207.7	0.3	0.56	0.76	Negative	[17]
	303	−951.6	−44.5	0.3	0.60	0.56		
	308	−2268.8	1736.9	0.3	1.29	0.53		
	313	−894.6	39.8	0.3	0.63	0.65		
Acetonitrile + ethanol	298	−2220.9	−201.1	0.3	1.83	0.58	Negative	[17]
	303	61.5	−2401.3	0.3	0.42	1.67		
	308	−3280.4	1550.1	0.3	1.13	0.53		
	313	−3454.8	1908.9	0.3	0.93	0.37		
Acetonitrile + 1-propanol	298	−2709.5	−264.6	0.3	0.64	0.57	Negative	[17]
	303	−92.2	−2535.7	0.3	0.72	2.20		
	308	−2385.6	−166.0	0.3	1.14	1.08		
	313	−2507.6	−107.4	0.3	1.32	1.58		
Acetonitrile + 2-propanol	298	−4196.2	179.0	0.3	1.68	2.02	Negative	[17]
	303	−2916.4	−1424.2	0.3	1.70	1.66		
	308	276.4	−3950.4	0.3	1.65	3.61		
	313	−3450.8	−436.9	0.3	1.42	1.42		
Acetonitrile + 1-butanol	298	−1323.2	−2120.1	0.3	1.56	1.57	Negative	[17]
	303	−1105.9	−2297.5	0.3	1.68	1.68		
	308	−1567.1	−1628.3	0.3	1.53	1.27		
	313	−36.7	−2562.6	0.3	0.82	1.50		
Acetonitrile + <i>iso</i> -butanol	298	−3014.3	−196.6	0.3	0.67	0.67	Negative	[17]
	303	−3368.7	436.5	0.3	0.92	0.72		
	308	−3202.9	466.3	0.3	2.98	1.02		
	313	−2664.8	2.4	0.3	0.98	1.40		
Acetonitrile + <i>tert</i> -butanol	298	−5804.6	2336.2	0.3	1.76	0.92	Negative	[17]
	303	−4200.2	2.4	0.3	0.67	1.71		
	308	−5662.2	4002.0	0.3	0.97	0.96		
	313	−5176.5	3588.5	0.3	2.42	1.23		
Acetonitrile + ethylene glycol dimethyl ether	298	743.4	279.0	0.3	0.37	0.42	Positive	[19]
Acetonitrile + diethylene glycol dimethyl ether	298	6945.8	718.6	0.3	0.33	0.40	Positive	[19]
Acetonitrile + triethylene glycol dimethyl ether	298	16575.1	2206.5	0.2	0.50	1.32	Positive	[19]
Acetonitrile + tetraethylene glycol dimethyl ether	298	22257.2	9657.5	0.2	0.45	11.53	S-type	[19]
Acetonitrile + water	298	−1645.7	13197.4	0.3	5.83	3.12	S-type	[18]
	303	−1377.9	16020.8	0.3	2.39	2.02		
	308	−1575.8	14600.9	0.3	2.50	2.00		
	313	−1334.7	16916.1	0.3	1.05	1.04		
	318	−1357.4	13020.3	0.3	1.28	2.79		
	285	987.3	15913.9	0.2	0.68	2.84		
	290	815.0	18420.2	0.2	0.59	1.33		
Methanol + water	295	757.1	15180.2	0.2	2.76	1.71	Positive	[12]
	300	501.3	13276.7	0.2	3.94	1.98		
	305	468.3	13097.7	0.2	3.26	1.94		
	310	426.4	11854.7	0.2	3.28	2.14		
	315	428.7	10948.5	0.2	3.57	2.31		

Table 1 (Continued)

Mixture	T (K)	$g_{12} - g_{22}$ (J/mol)	$g_{21} - g_{11}$ (J/mol)	α_{12}	$[\Delta\eta/\eta]_{av} \times 100$ (%)		Type ^a	Reference
					MHV1-NRTL	WS-NRTL		
Ethanol + water	320	436.1	10825.0	0.2	3.27	2.71	Positive	[12]
	325	450.0	9350.9	0.2	3.08	2.42		
	330	408.3	8936.1	0.2	2.57	2.36		
	300	2596.9	21018.6	0.2	5.06	7.19		
	310	549.2	19834.0	0.2	3.19	7.40		
	320	639.9	21948.0	0.2	4.47	3.01		
	330	841.9	17513.1	0.2	6.66	5.70		
	340	630.2	11535.9	0.2	6.65	6.60		
1-Propanol + water	350	979.1	9739.3	0.2	6.36	7.51	Positive	[12]
	295	−689.1	66436.4	0.2	7.97	11.67		
	300	556.6	66752.0	0.2	6.69	10.72		
	310	4913.1	27876.0	0.2	5.14	8.88		
	320	59383.9	1362.3	0.2	3.84	6.19		
Overall	370	−1327.5	28195.1	0.2	1.80	4.85		
Overall					2.09	2.48		

^a Signs calculated by $\eta - \sum_i x_i \eta_i$.

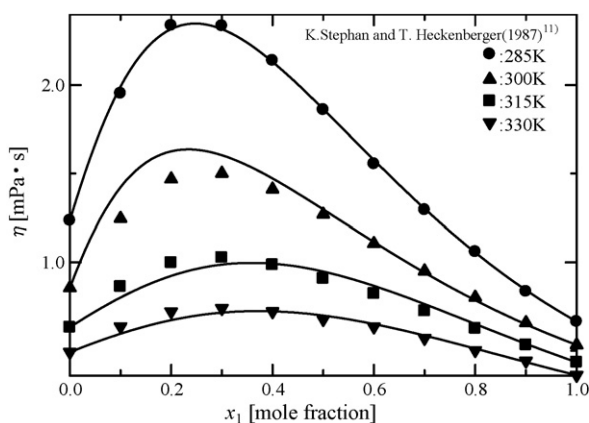


Fig. 2. Correlated results of viscosities by PRSV + MHV1 + NRTL model for methanol (1) + water (2) system at normal pressure.

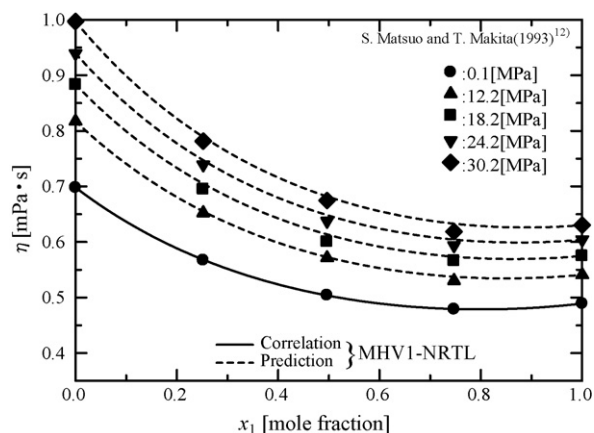


Fig. 3. Predicted results of viscosities by PRSV + MHV1 + NRTL model for benzene (1) + cyclohexane (2) system at 313 K and high pressures.

Table 2

Prediction results of viscosities using PRSV-Eyring- G^E mixing-NRTL model at high pressures

Mixture	T (K)	P (MPa)	NDT	$[\Delta\eta/\eta]_{av} \times 100$ (%)		Reference
				MHV1-NRTL	WS-NRTL	
Pentane + decane	298	5–25	5	1.30	1.23	[16]
Cyclohexane + <i>n</i> -octane	298–348	20–100	7	2.34	5.46	[14]
Benzene + cyclohexane	313	12–30	4	0.79	0.63	[13]
Methanol + <i>n</i> -butylamine	298	4–72	10	2.89	1.44	[15]
Ethanol + <i>n</i> -butylamine	298	4–72	10	3.05	3.81	[15]
1-Propanol + <i>n</i> -butylamine	298	4–72	10	2.60	3.49	[15]
1-Butanol + <i>n</i> -butylamine	298	4–52	9	2.12	2.21	[15]
Methanol + water	285–330	10–65	70	4.34	2.61	[12]
Ethanol + water	300–350	10–45	30	6.03	6.84	[12]
1-Propanol + water	295–370	10–49	25	8.42	13.07	[12]
Overall			180	4.59	4.83	

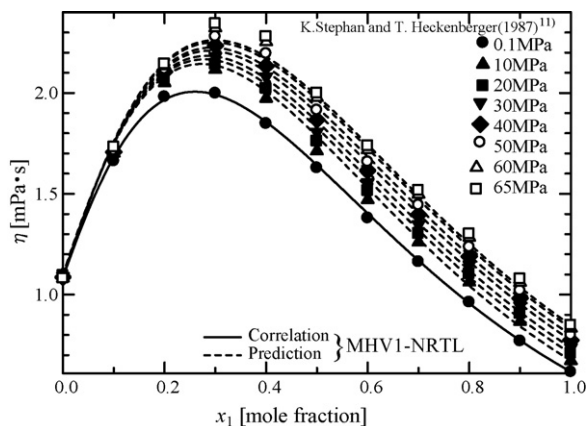


Fig. 4. Predicted results of viscosities by PRSV + MHV1 + NRTL model for methanol (1) + water (2) system at 290 K and high pressures.

be large at high pressure like 65 MPa, as it is pointed out that PRSV will be not generally used at the pressures higher than 20 MPa.

3. Conclusions

A predictive method for determining the viscosities of liquid mixtures has been proposed using the PRSV + MHV1 + NRTL equation. The viscosities for 22 binary systems have been calculated with an average deviation of 2.1%. While the viscosities for 10 binary systems have been predicted with an average deviation of 4.6% using the parameters obtained from atmospheric pressure viscosity data. The accuracy afforded by this method will be reasonable for the non-polar + non-polar, non-polar + polar and polar + polar systems, and this model will be useful for designing chemical processes. In the future, the proposed model may be applied for the viscosity of multiphase like emulsion, and the analogical model may be used for calculating the transport properties like heat conductivity and diffusion coefficient.

List of symbols

a energy parameter in Eq. (7)

b size parameter in Eq. (7)

$g_{12} - g_{22}$, $g_{21} - g_{11}$ NRTL parameters in Eq. (10)

G^E excess Gibbs free energy
 $G^{\neq,E}$ excess Gibbs free energy at activated state
 R gas constant
 T temperature
 V molar volume
 x liquid mole fraction

Greek letters

α_{12} non-randomness parameter in Eq. (10)

η viscosity

φ fugacity coefficients

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