

# Calculation of Viscosities of Liquid Mixtures Using Eyring's Theory in Combination with Cubic Equations of State<sup>\*</sup>

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**Abstract** Cubic equations of state (EOS) have been combined with the absolute rate theory of Eyring to calculate viscosities of liquid mixtures. A modified Huron-Vidal  $g^E$ -mixing rule is employed in the calculation and in comparison with the van Laar and the Redlich-Kister-type mixing rule. The EOS method gives an accurate correlation of liquid viscosities with an overall average deviation less than 1% for 67 binary systems including aqueous solutions. It is also successful in extrapolating viscosity data over a certain temperature range using parameters obtained from the isotherm at a given temperature and in predicting viscosities of ternary solutions from binary parameters for either polar or associated systems.

**Keywords** viscosity, equation of state, mixing rule, absolute rate theory

## 1 INTRODUCTION

The viscosity, particularly that of liquid mixtures, is very important in engineering calculations involved in the process design for petroleum and other chemical industries. Since the successful development of a one-parameter equation for correlating the liquid viscosity of nonpolar mixtures by Grunberg and Nissan<sup>[1]</sup>, many other models have been proposed. Most of them are based on the corresponding state principle, the absolute rate theory of Eyring<sup>[2]</sup>, or the free volume theory. A detailed review about viscosity calculations was given by Poling *et al.*<sup>[3]</sup>. Among the corresponding state models, the generalized corresponding state principle (GCSP) proposed by Teja and Rice<sup>[4]</sup> is important. By using two reference fluids and in combination with a van Laar-type of mixing rule, it can be used to correlate viscosities of nonaqueous polar binary liquid mixtures over a certain temperature range. Unfortunately, it is not adequate for strongly associated systems such as aqueous solutions, where a maximum exists in the viscosity-composition curve<sup>[5]</sup> and its extension to ternary systems is not very successful either<sup>[6]</sup>. For the methods based on the Eyring's theory, the estimation of the activation Gibbs energy of flow plays an important role. McAllister<sup>[7]</sup> calculated this quantity by using an empirical cubic composition-dependent function. The resultant model is very successful in correlating viscosities of liquid mixtures. However, its parameters are strongly temperature-dependent and for ternary systems, additional ternary parameters are necessary. Another application of Eyring's theory is the combination of the viscosity

model directly with activity coefficient equations. Wei and Rowley<sup>[8]</sup> developed a local composition model. They used the nonrandom two liquids (NRTL) equation to estimate the entropy part of the excess activation Gibbs energy of flow. However, the viscosity calculation needs not only the NRTL parameters obtained from vapor-liquid equilibrium (VLE) data but also the experimental excess enthalpies and the liquid densities. Wu<sup>[9]</sup> and Chevalier *et al.*<sup>[10]</sup> estimated the excess activation Gibbs energy of flow by using a group-contribution (GC) concept such as the universal quasi-chemical functional group activity coefficient (UNIFAC) method. The proposed UNIFAC-VISCO model can give a satisfactory prediction for nonpolar systems. Unfortunately, the predictions are not always reliable for polar mixtures, particularly for aqueous solutions. A similar strategy was used by Chao *et al.*<sup>[11,12]</sup> to calculate viscosities and vapor-liquid equilibria simultaneously, but only nonaqueous mixtures were investigated. Another way of estimating the activation Gibbs energy of flow is by using the equations of state. Lee *et al.*<sup>[13]</sup> combined the Eyring's theory with Patel-Teja equation of state (PTEOS) to form an Eyring-Patel-Teja viscosity model. It can correlate the viscosities of binary systems very well even at elevated pressures and is successfully extended to ternary systems, however, the results for aqueous solutions are not very satisfactory possibly because the Redlich-Kister-type (RK) mixing rule was employed<sup>[14]</sup>, which is not very suitable for multicomponent systems<sup>[15]</sup>. A successful model based on the free volume theory was proposed by Liu *et al.*<sup>[5]</sup>. With two

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temperature-independent parameters, the free volume model can describe the viscosities of liquid mixtures satisfactorily over a certain temperature range even for aqueous systems.

As discussed above, a reasonable model for the calculation of the liquid viscosity is able to describe its temperature dependence, can be extended to multi-component systems, and is suitable for strongly associated solutions. In this study, the cubic equations of state in combination with a modified Huron-Vidal  $g^E$ -mixing rule (see Appendix) are incorporated into the Eyring's theory to calculate liquid viscosities of either nonpolar or polar systems including aqueous solutions. The temperature extrapolation and the prediction of viscosities for multicomponent systems are investigated. The van Laar-type (VL) mixing rule<sup>[16]</sup> and the RK mixing rule<sup>[14]</sup> are used in the calculation for comparison.

## 2 VISCOSITY MODEL

According to the absolute rate theory of Eyring, the dynamic viscosity  $\eta$  can be estimated by

$$\eta v = N_A h_0 \exp\left(\frac{\Delta g^\#}{RT}\right) \quad (1)$$

where,  $\Delta g^\#$  is the activation Gibbs energy of flow that is required to remove molecules within the fluid from their energetically most favorable state to the activated state and the quantities  $v$ ,  $N_A$  and  $h_0$  represent the molar volume, the Avogadro and the Planck constant, respectively. Eq.(1) can be used either for pure fluids or for mixtures. For a liquid solution the activation Gibbs energy of flow can be separated into a hypothetical ideal solution part and an excess part.

$$\Delta g^\# = \Delta g^{\#id} + g^{\#E} \quad (2)$$

From the ideal activation Gibbs energy of flow the viscosity of an ideal solution is given

$$(\eta v)^{id} = N_A h_0 \exp\left(\frac{\Delta g^{\#id}}{RT}\right) \quad (3)$$

The combination of Eqs.(2), (3), and (1) follows the viscosity equation of liquid mixtures

$$\eta v = (\eta v)^{id} \exp\left(\frac{g^{\#E}}{RT}\right) \quad (4)$$

where  $(\eta v)^{id}$  can be estimated by a simple combination of the (kinematic) viscosities of the pure fluids  $[(\eta v)_{oi}]$

$$\ln(\eta v)^{id} = \sum_k x_k \ln(\eta v)_{ok} \quad (5)$$

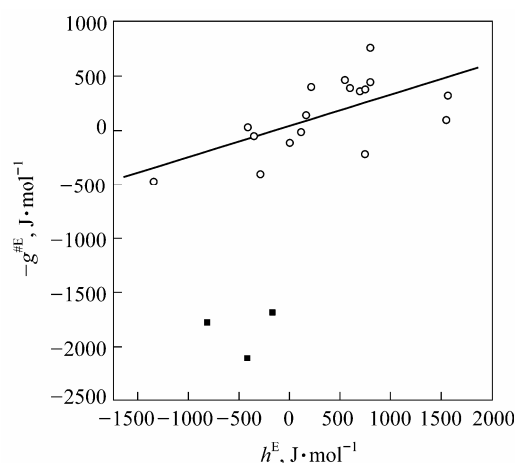
There are several ways to calculate the excess activation Gibbs energy of flow ( $g^{\#E}$ ) in the literature. One such calculation is to relate it to the excess Gibbs free energy ( $g^E$ ). Wei and Rowley<sup>[8]</sup> proposed a simple relation

$$g^{\#E} = -\sigma g^E \quad (6)$$

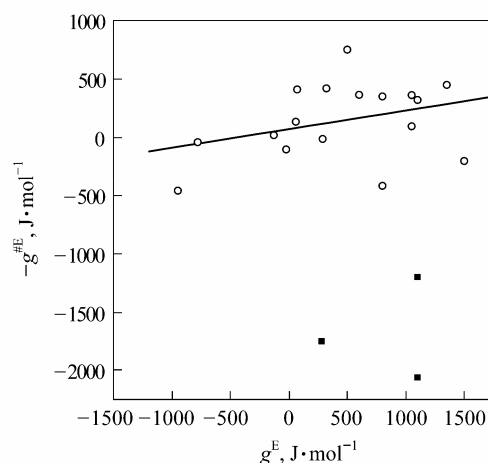
where  $\sigma$  is a proportional factor. Figs.1(a) and 1(b) show the  $g^{\#E}$  values at  $x_i=0.5$  for 20 binary systems

(Table 1) calculated using the experimental viscosity data in comparison with the experimental excess enthalpies ( $h^E$ )<sup>[31]</sup> and the excess Gibbs energies obtained from the experimental VLE data, respectively. It can be seen that a rough linear relationship between the excess activation Gibbs energy of flow and the excess Gibbs free energy or the excess enthalpy exists for nonaqueous systems, which provides to some extent a background for relating the transport properties to the thermodynamic properties (quasi-thermodynamic consideration), and also provides a simple way to incorporate the flexible structure of thermodynamic models into the absolute rate theory of Eyring. Nevertheless, a direct prediction of viscosities using VLE or  $h^E$  data seems to be impossible, particularly for aqueous systems. The viscosity equation for liquid mixtures is obtained by substituting Eq.(6) into Eq.(4)

$$\eta v = (\eta v)^{id} \exp\left(\frac{-\sigma g^E}{RT}\right) \quad (7)$$



(a) With the experimental excess enthalpy



(b) With the excess Gibbs energy obtained from the experimental VLE data

**Figure 1 Comparison of the excess activation Gibbs energy of flow with the experimental excess enthalpy and the excess Gibbs energy obtained from the experimental VLE data**  
 ○ nonaqueous; ■ aqueous; — fitting nonaqueous

Table 1 Correlation of viscosity isotherms of binary systems

System	$\vartheta$ , °C	oC3EOS				PREOS				PT EOS
		$\delta_{rel}(\rho)$	$\delta_{rel}(\eta)_{VL}$	$\delta_{rel}(\eta)_{2p}$	$\delta_{rel}(\eta)_{3p}$	$\delta_{rel}(\rho)$	$\delta_{rel}(\eta)_{VL}$	$\delta_{rel}(\eta)_{2p}$	$\delta_{rel}(\eta)_{3p}$	$\delta_{rel}(\eta)_{RK}$
acetone+cyclohexane <sup>[17]⊙</sup>	25	1.39	0.57	0.65	0.34	5.08	0.62	0.64	0.30	0.75
acetone+ethanol <sup>[17]⊙</sup>	25	2.28	0.45	0.27	0.17	10.35	0.50	0.29	0.17	0.57
acetone+hexane <sup>[17]⊙</sup>	25	0.76	0.71	0.74	0.34	5.78	0.61	0.93	0.30	0.72
acetone+methanol <sup>[17]⊙</sup>	25	1.69	0.20	0.23	0.23	14.14	0.21	0.24	0.23	0.25
acetone+propan-2-ol <sup>[17]</sup>	25	3.28	0.79	6.55	0.19	10.94	0.81	6.83	0.28	1.20
acetone+carbon tetrachloride <sup>[17]</sup>	25	1.47	0.91	0.92	0.91	4.98	1.02	0.92	0.92	0.95
acetone+water <sup>[18]⊙</sup>	25	2.07	1.29	11.96	5.39	11.22	1.30	12.39	5.74	1.87
benzene+cyclohexane <sup>[19]⊙</sup>	25	2.30	0.30	0.28	0.20	2.94	0.31	0.28	0.33	0.38
benzene+decane <sup>[19]</sup>	25	3.13	0.62	0.98	0.46	4.32	0.72	0.87	0.98	0.67
benzene+ethanol <sup>[20]⊙</sup>	25	0.89	0.21	0.21	0.21	2.43	0.18	0.22	0.18	0.40
benzene+hexane <sup>[21]⊙</sup>	25	0.61	0.20	0.18	0.17	1.25	0.21	0.18	0.15	0.09
benzene+toluene <sup>[21]</sup>	25	0.98	0.11	0.13	0.11	1.14	0.11	0.14	0.11	0.08
butan-1-ol+ethyl acetate <sup>[22]</sup>	25	3.36	0.35	2.05	0.31	4.39	0.36	2.33	0.35	0.98
butan-1-ol+ethyl benzene <sup>[22]</sup>	25	3.85	0.57	0.70	0.47	2.15	0.58	2.74	0.49	0.30
butan-1-ol+xylene <sup>[22]</sup>	25	4.00	0.27	0.45	0.21	3.55	0.28	1.54	0.20	0.13
chlorobenzene+benzyl alcohol <sup>[23]</sup>	30	2.98	0.66	0.58	0.57	0.83	0.64	0.58	0.64	0.41
chlorobenzene+1-hexanol <sup>[24]</sup>	30	3.69	0.28	0.30	0.28	1.71	0.28	0.31	0.29	0.29
chloroform+benzene <sup>[24]⊙</sup>	25	0.84	0.35	0.46	0.36	4.75	0.37	0.46	0.35	0.28
chloroform+methanol <sup>[17]⊙</sup>	25	2.31	1.33	3.56	1.82	4.36	1.60	3.86	1.92	0.84
chloroform+toluene <sup>[24]</sup>	25	0.77	0.13	0.21	0.13	3.31	0.13	0.26	0.15	0.13
cyclohexane+propan-2-ol <sup>[17]</sup>	25	1.23	0.53	0.49	0.46	1.60	0.59	0.49	0.57	0.41
dimethylsulfoxide+chloroform <sup>[17]⊙</sup>	25	2.15	3.10	3.28	3.17	10.09	3.11	3.24	3.17	2.87
dimethylsulfoxide+methanol <sup>[17]⊙</sup>	25	3.71	0.46	0.38	0.47	19.58	0.47	0.48	0.47	0.48
ethanol+cyclohexane <sup>[17]</sup>	25	0.24	0.74	0.61	0.55	2.081	0.47	0.60	0.61	1.73
ethanol+dimethylformamide <sup>[17]</sup>	25	2.49	0.16	0.22	0.22	19.08	0.29	1.35	0.39	2.40
ethanol+heptane <sup>[25]</sup>	25	0.26	1.05	1.35	1.13	3.22	1.83	1.37	1.34	1.12
ethanol+octane <sup>[26]</sup>	25	2.22	0.60	1.18	0.55	4.67	0.62	1.05	1.13	0.66
ethanol+pentane <sup>[26]</sup>	25	2.40	2.80	1.86	1.46	2.01	2.25	1.83	1.81	1.31
ethanol+propan-1-ol <sup>[18]</sup>	25	1.31	0.35	0.33	0.12	3.67	0.25	0.30	0.13	0.18
ethanol+propan-2-ol <sup>[17]</sup>	25	0.22	0.24	0.24	0.24	4.66	0.24	0.24	0.24	0.24
ethanol+carbon tetrachloride <sup>[27]</sup>	25	0.84	0.57	1.65	0.47	2.31	0.83	1.78	0.63	1.16
ethanol+water <sup>[18]⊙</sup>	30	2.37	2.21	1.64	1.62	11.71	2.31	1.64	1.62	4.20
ethan-1,2-diol+water <sup>[18]</sup>	25	2.94	0.74	0.52	0.51	11.18	0.79	0.51	0.52	0.98
heptane+benzene <sup>[20]</sup>	25	1.03	0.45	0.44	0.38	0.78	0.45	0.44	0.41	0.46
hexane+benzyl alcohol <sup>[25]</sup>	30	2.58	2.87	2.89	2.87	1.50	2.95	2.90	2.90	3.12
hexane+chlorobenzene <sup>[28]</sup>	30	0.69	0.56	0.71	0.74	0.36	0.51	0.71	0.74	0.76
hexane+chloroform <sup>[17]</sup>	25	1.07	0.33	0.35	0.32	3.62	0.53	0.35	0.31	0.31
hexane+cyclohexane <sup>[17]⊙</sup>	25	0.85	0.30	0.29	0.28	1.62	0.30	0.29	0.29	0.28
hexane+decane <sup>[18]</sup>	25	2.00	0.60	0.59	0.60	3.66	0.60	0.60	0.63	0.52
hexane+ethanol <sup>[17]⊙</sup>	25	0.53	0.82	0.74	0.23	2.75	0.34	0.77	0.21	1.04
hexane+heptane <sup>[18]</sup>	25	0.40	0.14	0.14	0.14	1.30	0.13	0.14	0.14	0.06
hexane+hexan-1-ol <sup>[28]</sup>	30	2.58	1.10	1.12	1.05	1.02	1.09	1.18	1.11	0.96
hexane+nonane <sup>[18]</sup>	25	1.25	0.36	0.40	0.36	2.59	0.36	0.39	0.38	0.29
hexane+octane <sup>[18]</sup>	25	1.86	0.43	0.42	0.42	1.52	0.43	0.43	0.43	0.35
hexane+toluene <sup>[28]</sup>	30	0.22	0.79	0.83	0.87	0.31	0.99	0.82	0.80	0.81
hexan-1-ol+benzyl alcohol <sup>[23]</sup>	30	4.39	0.59	0.45	0.47	0.27	0.53	0.45	0.47	0.37
methanol+ethanol <sup>[17]⊙</sup>	25	0.62	0.22	0.31	0.19	11.16	0.21	0.32	0.17	0.23
methanol+heptane <sup>[26]</sup>	25	1.00	0.56	0.64	0.49	6.88	0.57	0.66	0.51	0.58
methanol+hexane <sup>[26]⊙</sup>	25	2.25	0.77	1.32	0.77	5.51	0.77	1.33	0.78	0.95
methanol+pentane <sup>[26]</sup>	25	3.95	1.08	1.06	0.42	5.27	0.99	1.50	1.58	1.18
methanol+propan-1-ol <sup>[18]</sup>	25	1.17	1.28	1.29	1.28	6.84	1.28	1.28	1.27	1.26
methanol+propan-2-ol <sup>[17]</sup>	25	0.62	0.27	0.27	0.27	9.50	0.27	0.27	0.27	0.27
methanol+toluene <sup>[29]</sup>	25	0.58	0.89	1.69	1.04	5.45	0.91	1.76	1.08	0.77

**Table 1** (Continued)

System	$\vartheta$ , °C	oC3EOS				PREOS				PT EOS
		$\delta_{\text{rel}}(\rho)$	$\delta_{\text{rel}}(\eta)_{\text{VL}}$	$\delta_{\text{rel}}(\eta)_{2\text{p}}$	$\delta_{\text{rel}}(\eta)_{3\text{p}}$	$\delta_{\text{rel}}(\rho)$	$\delta_{\text{rel}}(\eta)_{\text{VL}}$	$\delta_{\text{rel}}(\eta)_{2\text{p}}$	$\delta_{\text{rel}}(\eta)_{3\text{p}}$	$\delta_{\text{rel}}(\eta)_{\text{RK}}$
methanol+water <sup>[18]Ⓣ</sup>	30	1.79	1.13	0.59	0.62	13.50	1.19	0.58	0.64	1.62
methyl acetate+chloroform <sup>[17]</sup>	25	2.62	0.59	1.01	0.60	2.86	0.65	0.99	0.64	0.30
methyl acetate+hexane <sup>[17]</sup>	25	1.72	0.30	0.31	0.22	1.94	0.31	0.31	0.29	0.27
propan-1-ol+heptane <sup>[26]</sup>	25	1.91	0.86	0.64	0.59	1.80	0.82	0.64	0.60	0.43
propan-1-ol+hexane <sup>[26]</sup>	25	1.02	1.80	1.71	1.54	0.69	1.73	1.72	1.52	1.57
propan-1-ol+octane <sup>[26]</sup>	25	3.98	0.95	0.64	0.59	3.27	1.00	0.64	0.65	0.52
propan-1-ol+pentane <sup>[26]</sup>	25	1.23	2.84	2.61	2.52	1.23	2.72	2.62	2.43	1.81
propan-1-ol+water <sup>[26]</sup>	25	1.75	2.69	3.57	0.30	5.58	2.94	5.53	0.58	5.00
carbon tetrachloride+propan-1-ol <sup>[17]</sup>	25	0.84	0.42	0.46	0.41	1.39	0.39	0.46	0.37	0.29
carbon tetrachloride+benzene <sup>[30]Ⓣ</sup>	25	0.63	0.05	0.20	0.13	3.56	0.04	0.20	0.20	0.18
carbon tetrachloride +cyclohexane <sup>[30]Ⓣ</sup>	25	0.84	0.09	0.10	0.12	4.31	0.09	0.26	0.25	0.32
triethylamine+chloroform <sup>[17]</sup>	25	0.84	2.21	2.22	2.04	6.80	2.24	2.36	2.07	2.11
triethylamine+methanol <sup>[17]</sup>	25	1.25	0.31	3.42	0.60	5.92	0.31	3.93	0.78	0.83
toluene+decane <sup>[19]</sup>	25	3.06	0.46	0.51	0.48	4.91	0.49	0.52	0.52	0.47
overall average deviation		1.76	0.78	1.18	0.71	4.85	0.81	1.31	0.78	0.89

Ⓣ System involved in Figs.1(a) and 1(b).

Note:  $\delta_{\text{rel}}(x) = \sum |1 - x_{\text{cal}}/x_{\text{exp}}| \times 100\%$ .

where the excess Gibbs free energy  $g^E$  can be calculated by the following equation

$$g^E = RT \sum_k x_k (\ln \phi_k^* - \ln \phi_{ok}^*) \quad (8)$$

Here,  $\phi_i^*$  and  $\phi_{oi}^*$  represent the fugacity coefficients of the component  $i$  in mixtures and at a pure liquid state, respectively. They can be evaluated using the equations of state. In this study, the optimized cubic 3-parameter equation of state (oC3EOS) proposed in the literature<sup>[32]</sup>, which can describe  $pVT$ -behavior satisfactorily over a wide temperature and pressure range, and the Peng-Robinson equation of state (PR EOS) in combination with a modified Huron-Vidal  $g^E$ -mixing rule<sup>[33]</sup> based on the zero pressure reference state and the van Laar-type mixing rule has been incorporated into Eq.(7) to calculate liquid viscosities. The details on the oC3EOS and the mixing rules used are given in the Appendix. Thus, the viscosity model proposed comprises Eqs.(5), (7) and (8).

### 3 CALCULATION

#### 3.1 Correlation of viscosities for binary systems

Viscosities of 67 binary liquid systems including strongly associated solutions are investigated, most of them being isothermal data at 25°C (with a few at 30°C). The procedure of viscosity calculations is as follows. First, the kinematic viscosity  $(\eta\nu)^{\text{id}}$  of an ideal solution is estimated using Eq.(5). Second, the excess Gibbs free energy ( $g^E$ ) is evaluated using Eq.(8), in which the fugacity coefficients are calculated using EOS methods. The viscosity of liquid mixtures are then obtained by substituting the value of  $(\eta\nu)^{\text{id}}$  and  $g^E$  into Eq.(7), in which the proportional factor  $\sigma$  is taken

as a constant equal to 0.25, which was suggested by Wei and Rowley<sup>[8]</sup>. The molar volume of both pure liquids and liquid mixtures used in Eqs.(5) and (7) are predicted using the equations of state. In the  $g^E$ -mixing rule the NRTL equation is used to estimate the excess Gibbs free energy of mixtures at zero pressure. The parameters in the mixing rules are optimized using the following objective function:

$$F_{\text{obj}} = \frac{1}{N} \sum_1^N \left| \frac{\eta_{\text{exp}} - \eta_{\text{cal}}}{\eta_{\text{exp}}} \right|_n \quad (9)$$

In the calculation the nonrandomness parameter  $\alpha$  in the  $g^E$ -mixing rule is either set as constant value of 0.2 (2p  $g^E$ -mixing rule) or fitted together with the NRTL energy parameters ( $A_{ij}$  and  $A_{ji}$ ) (3p  $g^E$ -mixing rule) using the experimental viscosity data. The results of the oC3EOS using the two variants of  $g^E$ -mixing rule and the van Laar-mixing rule are listed in Table 1 in comparison with those of the PREOS. During the viscosity correlation, the densities of the liquid mixtures are estimated simultaneously using the correlated parameters. The density prediction results of both the EOS with the 3p  $g^E$ -mixing rule are also presented.

As shown in Table 1, by the use of the 3p  $g^E$ -mixing rule, both the oC3EOS and the PREOS can reproduce experimental liquid viscosity values very well not only for nonpolar liquid mixtures but also for polar liquid mixtures and even for strongly associated systems. The overall average relative deviation amounts to 0.7% for the oC3EOS and 0.8% for the PREOS. For the majority of the systems, the use of a constant nonrandom parameter  $\alpha$  (0.2) leads to no obvious loss of accuracy. Only in the case of some

strongly polar systems, the adjustment of  $\alpha$  is necessary. It is remarkable that the van Laar-type mixing rule is as flexible as the  $g^E$ -mixing rule in the correlation, and because of its composition asymmetry, it can represent more accurately the experimental viscosities for the system acetone+water, of which the composition dependence of the viscosity is very strong and asymmetric. However, it should be noted that the van Laar-mixing rule needs a very large binary interaction correction term for aqueous systems. The value at a certain composition range is larger than 1 (Table A1), which is too large from the theoretical point of view and, as shown later, could lead to problems in the extension to multicomponent systems. The oC3EOS predicts saturated liquid densities more accurately than the PREOS. The overall average deviation of the estimated liquid densities is 1.8% for the oC3EOS and 4.9% for the PREOS. However, no obvious advantage of the oC3EOS over the PREOS is shown in the dynamic viscosity correlation. It seems that the accurate description of the liquid molar volume plays no significant role in this case. Possibly this resulted from the fact that the molar volume appears on either sides of Eq.(7) and therefore, its influence becomes relatively small.

For comparison, similar calculations are carried out using the PT EOS together with the RK mixing rule proposed by Adachi and Sugie<sup>[14]</sup>. As shown in Table 1, the asymmetric RK mixing rule gives results very similar to those of the van Laar-mixing rule. Only for aqueous systems, the deviation of dynamic viscosities is slightly larger. The overall deviation of this model amounts to 0.89%, only slightly larger than those of the other two EOS together with the van Laar-mixing rule.

### 3.2 Prediction of viscosities for binary systems

The liquid viscosity is usually strongly temperature dependent. It is of great importance if a model can be used to extrapolate the viscosities over a certain temperature range using the information obtained at a given temperature. The viscosities of 11 binary systems with a total of 38 isotherms have been predicted using the parameters obtained from the correlation of viscosity isotherms at 25°C (for a few systems at 30°C), as described above. The extrapolation is satisfactory, particularly for the nonaqueous systems. Fig.2 shows the results of the system hexane+hexan-1-ol using the oC3EOS in combination with the 3p  $g^E$ -mixing rule (solid lines), the 2p  $g^E$ -mixing rule (dashed lines) and the van Laar-mixing rule (dotted lines). The predicted viscosities agree well with the experimental values for all the three mixing rules. Reasonable predictions are also obtained for the aqueous systems. In Fig.3, the solid lines represent the dynamic viscosity values of the system methanol+water predicted using the 3p  $g^E$ -mixing rule with

parameters obtained from the isotherm at 25°C, whereas the dash-dot lines show the results calculated with parameters from the isotherm at 10°C. It is remarkable that there is no considerable loss of the extrapolation accuracy even if the temperature range is doubled. The average deviations of the 11 systems for both the oC3EOS and PREOS are shown in Table 2 in comparison with those of the PTEOS with the RK mixing rule. For nonaqueous systems, the three EOS give very similar results. For aqueous systems, the difference of extrapolations obviously depends mainly on the flexibility of the mixing rule used.

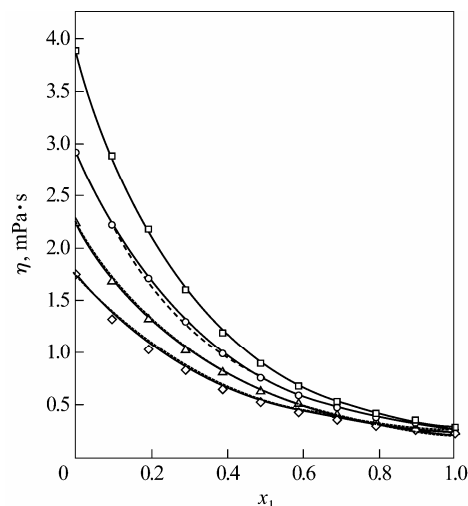


Figure 2 Prediction of viscosities of the system hexane+hexan-1-ol using the oC3EOS with the 3p and 2p variants of  $g^E$ -mixing rule and the van Laar-mixing rule  
 □ 30°C; ○ 40°C; △ 50°C; ◇ 60°C;  
 — oC3EOS 3p  $g^E$ ; --- oC3EOS 2p  $g^E$ ; ..... oC3EOS VL

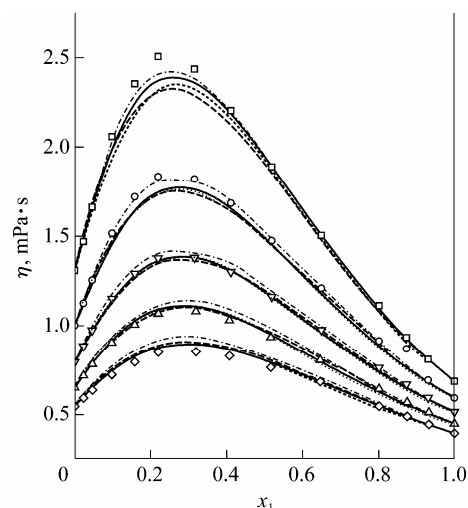


Figure 3 Prediction of viscosities of the system methanol+water using the oC3EOS with the 3p and 2p variants of  $g^E$ -mixing rule and the van Laar-mixing rule  
 □ 10°C; ○ 20°C; ▽ 25°C; △ 40°C; ◇ 50°C;  
 — oC3EOS 3p  $g^E$ ; -·-·- oC3EOS 3p  $g^{E*}$ ;  
 --- oC3EOS 2p  $g^E$ ; ..... oC3EOS VL

### 3.3 Prediction of viscosity for ternary systems

The viscosities of ternary systems are predicted

Table 2 Prediction (extrapolation) of viscosities for binary systems

Systems	$g$ , °C	oC3EOS			PREOS			PT EOS
		$\delta_{rel}(\eta)_{VL}$	$\delta_{rel}(\eta)_{2p}$	$\delta_{rel}(\eta)_{3p}$	$\delta_{rel}(\eta)_{VL}$	$\delta_{rel}(\eta)_{2p}$	$\delta_{rel}(\eta)_{3p}$	$\delta_{rel}(\eta)_{RK}$
hexane + toluene <sup>[28]</sup>	40	2.01	2.03	1.98	2.01	1.99	1.97	1.69
	50	1.13	1.07	1.13	1.14	1.06	1.14	1.39
	60	1.86	1.75	1.78	1.85	1.68	1.80	2.00
hexane + chlorobenzene <sup>[25]</sup>	40	1.94	1.86	1.76	1.64	1.84	1.77	1.86
	50	1.09	0.88	0.92	0.66	0.90	0.91	0.74
	60	0.98	0.90	0.92	0.82	0.92	0.91	0.96
hexane + benzyl alcohol <sup>[25]</sup>	40	2.75	3.15	3.15	2.77	3.02	3.14	3.41
	50	1.76	2.77	2.76	2.19	2.63	2.69	2.85
	60	3.75	4.60	4.61	4.08	4.49	4.53	4.67
hexane + hexan-1-ol <sup>[28]</sup>	40	1.90	2.36	2.33	1.73	2.38	2.34	1.89
	50	1.41	1.18	1.17	1.58	1.19	1.19	1.58
	60	3.77	2.57	2.60	4.11	2.54	2.57	3.62
chlorobenzene+benzyl alcohol <sup>[23]</sup>	40	2.89	3.30	3.30	3.08	3.32	3.35	2.55
	50	2.66	3.12	3.13	2.72	3.14	3.15	2.34
	60	3.09	3.49	3.51	3.17	3.50	3.48	2.71
chlorobenzene+hexan-1-ol <sup>[23]</sup>	40	2.65	2.98	2.98	2.59	2.99	3.00	2.57
	50	1.39	0.74	0.74	1.49	0.72	0.71	1.47
	60	3.02	1.99	1.99	3.14	1.92	1.93	3.07
hexan-1-ol+benzyl alcohol <sup>[23]</sup>	40	1.23	1.65	1.49	1.46	1.65	1.62	1.34
	50	2.26	1.54	1.70	1.87	1.53	1.60	1.97
	60	7.37	6.38	6.55	6.83	6.26	6.43	7.02
methanol + ethanol <sup>[18]</sup>	10	1.90	2.05	1.97	2.01	2.30	1.96	1.73
	20	1.01	0.90	1.00	1.00	1.13	0.99	0.97
	30	0.91	0.64	0.84	0.81	0.90	0.84	0.73
	40	1.23	0.98	1.13	1.08	1.39	1.09	0.78
	50	1.21	1.11	1.10	1.04	1.71	1.00	0.46
acetone + water <sup>[18]</sup>	20	1.62	12.77	6.39	1.64	13.20	6.78	2.42
	30	1.13	11.15	4.86	1.14	11.59	5.17	1.93
	37.8	1.41	10.44	4.46	1.54	10.90	4.83	2.08
	40	1.99	9.524	4.00	2.16	10.02	4.38	2.47
ethanol + water <sup>[18]</sup>	10	5.92	5.50	5.23	6.37	6.04	5.26	7.64
	20	4.17	3.64	3.49	4.44	4.12	3.51	5.71
	40	5.07	4.07	4.02	5.25	3.80	4.37	6.26
	50	6.91	6.17	6.01	7.24	6.04	6.54	8.23
methanol + water <sup>[18]</sup>	10	3.02	2.90	1.54	3.36	3.16	1.65	2.86
	20	3.18	2.80	2.02	3.38	2.95	2.14	3.06
	40	2.35	1.76	1.55	2.39	1.74	1.45	2.45
	50	3.95	3.47	2.67	4.03	3.03	2.62	3.89
overall relative deviation		2.53/2.70 <sup>①</sup>	3.43/2.54	2.70/2.44	2.63/2.74	3.52/2.59	2.76/2.47	2.78/2.84

① Overall relative deviation excluding the system acetone + water.

using the binary parameters obtained from the viscosity isotherm of binary solutions. Eighteen ternary systems including 29 isotherms are investigated with the binary parameters obtained in the calculation carried out in section 3.1. The relative deviations of the predicted values of viscosities from the experimental ones are summarized in Table 3. The prediction using the equations of state together with the  $g^E$ -mixing rule is successful not only for polar systems but also for the aqueous solutions. The overall average deviations

of the oC3EOS with either the 3p or the 2p variants of the  $g^E$ -mixing rule are less than 2%. It is to be noted that the isotherms at temperatures above 30°C for the last four systems are extrapolated using the binary parameters obtained at 30°C. The results of the extrapolation are also satisfactory. Fig.4 illustrates the viscosities of the system chlorobenzene+hexan-1-ol+benzyl alcohol at different temperatures predicted using the oC3EOS. The solid and dashed lines represent results by using the 3p and 2p  $g^E$ -mixing rule, respectively

Table 3 Prediction of viscosities for ternary systems

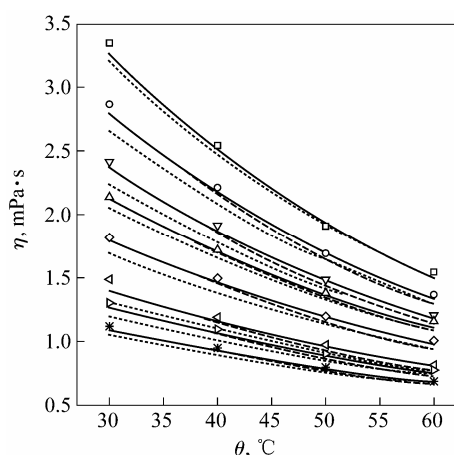
System	$\rho$ , °C	oC3EOS			PREOS			PTEOS
		$\delta_{rel}(\eta)_{VL}$	$\delta_{rel}(\eta)_{2p}$	$\delta_{rel}(\eta)_{3p}$	$\delta_{rel}(\eta)_{VL}$	$\delta_{rel}(\eta)_{2p}$	$\delta_{rel}(\eta)_{3p}$	$\delta_{rel}(\eta)_{RK}$
acetone+ethanol+propan-2-ol <sup>[34]</sup>	25	9.76	4.16	2.47	9.92	4.43	1.35	2.92
acetone+ethanol+methanol <sup>[34]</sup>	25	7.82	3.02	3.58	8.30	3.01	3.96	2.60
acetone+hexane+cyclohexane <sup>[34]</sup>	25	1.72	1.28	1.34	5.35	0.95	3.66	1.39
acetone+hexane+ethanol <sup>[34]</sup>	25	1.85	1.18	1.04	3.69	1.03	1.34	1.42
acetone+carbon tetrachloride+cyclohexane <sup>[34]</sup>	25	1.58	0.53	0.77	3.29	0.60	0.47	0.63
dimethylsulfoxide+chloroform+methanol <sup>[34]</sup>	25	7.83	1.79	1.44	3.15	1.75	1.26	5.71
ethanol+acetone+cyclohexane <sup>[34]</sup>	25	2.13	1.51	1.41	4.53	1.31	2.16	3.04
ethanol+cyclohexane+propan-2-ol <sup>[34]</sup>	25	4.73	1.47	1.82	6.13	2.07	1.90	1.69
hexane+cyclohexane+ethanol <sup>[34]</sup>	25	2.41	1.57	1.28	4.09	1.38	4.35	2.16
methanol+ethanol+propan-1-ol <sup>[18]</sup>	30	2.32	1.23	0.78	2.24	0.85	0.84	0.88
methanol+ethanol+propan-2-ol <sup>[34]</sup>	25	3.95	2.00	1.44	2.67	2.01	2.59	1.78
tetrachloromethane+cyclohexane+propan-2-ol <sup>[34]</sup>	25	5.23	0.82	0.73	5.84	3.22	1.24	1.86
ethanol+propan-1-ol+water <sup>[18]</sup>	30	55.24	2.53	2.52	45.95	4.20	1.65	9.47
methanol+propan-1-ol+water <sup>[18]</sup>	30	46.98	1.69	1.94	38.57	1.48	2.34	6.88
methanol+ethanol+water <sup>[18]</sup>	30	35.30	1.18	1.85	36.51	1.25	1.94	5.24
	40	36.30	2.50	1.16	36.85	2.92	1.31	4.58
	50	37.20	4.92	2.89	37.54	5.72	3.34	4.46
chlorobenzene+hexan-1-ol+benzyl alcohol <sup>[35]</sup>	30	7.11	2.19	2.30	8.00	2.22	2.86	2.89
	40	7.28	3.17	3.29	8.21	3.22	3.83	3.37
	50	4.85	1.36	1.48	5.83	1.43	2.02	1.10
hexane+benzyl alcohol+chlorobenzene <sup>[25]</sup>	60	5.24	2.40	2.51	6.22	2.48	3.03	2.14
	30	3.52	1.83	1.55	5.96	1.87	1.69	3.06
	40	2.25	0.85	0.85	0.72	0.84	0.78	1.86
hexane+benzyl alcohol+hexan-1-ol <sup>[25]</sup>	50	3.86	1.82	1.67	1.32	1.84	1.65	3.29
	60	2.31	1.86	1.88	1.14	1.88	1.75	2.79
	30	1.03	1.43	1.36	3.05	1.60	0.92	1.85
hexane+benzyl alcohol+hexan-1-ol <sup>[25]</sup>	40	2.47	1.55	1.58	4.55	1.51	1.75	2.25
	50	1.07	0.93	0.89	2.66	1.02	0.64	1.67
	60	2.37	2.34	2.39	3.84	2.29	2.39	2.88
overall average deviation		10.92	1.90	1.71	10.93	2.08	2.01	2.97

and the dotted lines represent the results using the van Laar-mixing rule. The 3p  $g^E$ -mixing rule reproduces the experimental data very well over the whole temperature range. The prediction using the 2p  $g^E$ -mixing rule is satisfactory at low temperatures, whereas its deviation from experimental data increases with the increase in temperature. For the asymmetric van Laar-mixing rule, there exist obvious systematic deviations of the calculated values from the experimental ones. Such deviations become even larger for aqueous ternary systems. As shown in Fig.5, by the example system methanol+ethanol+water, the deviations are very large with an average error of more than 35%, which means that the van Laar-mixing rule is not suitable for such calculations, particularly, for associated systems. On the contrast, the prediction results of non-

mal systems obtained by using the RK mixing rule are similar to those by using  $g^E$ -mixing rule, however, for aqueous systems, it gives relatively larger deviations.

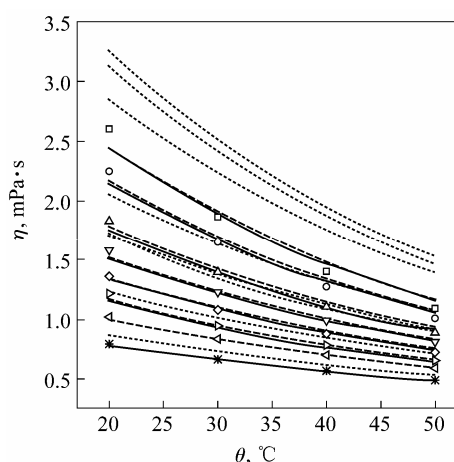
#### 4 SUMMARY

The cubic equations of state have been incorporated into the absolute rate theory of Eyring to calculate the viscosity of liquid mixtures. A modified Huron-Vidal  $g^E$ -mixing rule based on the zero pressure reference state, in which the NRTL equation is used, has been employed in the calculation in comparison with the van Laar and the RK mixing rule. With three adjusted model parameters, the equations of state with the  $g^E$ -mixing rule can give a very satisfactory viscosity correlation for either nonpolar or polar systems and even for aqueous solutions. In



**Figure 4** Prediction of viscosities of the system chlorobenzene+hexan-1-ol+benzyl alcohol from information of binary systems at 25°C using the oC3EOS with the 3p and 2p variants of the  $g^E$ -mixing rule and the van Laar-mixing rule

□  $x_1=0.068, x_2=0.552$ ; ○  $x_1=0.154, x_2=0.413$ ;  
 ▽  $x_1=0.272, x_2=0.492$ ; △  $x_1=0.347, x_2=0.050$ ;  
 ◇  $x_1=0.413, x_2=0.118$ ; ◁  $x_1=0.497, x_2=0.353$ ;  
 ▷  $x_1=0.569, x_2=0.224$ ; \*  $x_1=0.641, x_2=0.296$ ;  
 — oC3EOS 3p  $g^E$ ; - - - oC3EOS 2p  $g^E$ ; ···· oC3EOS VL



**Figure 5** Prediction of viscosities of the system methanol+ethanol+water from information of binary systems at 25°C using the oC3EOS with the 3p and 2p variants of the  $g^E$ -mixing rule and the van Laar-mixing rule

□  $x_1=0.070, x_2=0.241$ ; ○  $x_1=0.209, x_2=0.511$ ;  
 ▽  $x_1=0.153, x_2=0.263$ ; △  $x_1=0.258, x_2=0.297$ ;  
 ◇  $x_1=0.552, x_2=0.190$ ; ◁  $x_1=0.554, x_2=0.054$ ;  
 ▷  $x_1=0.710, x_2=0.061$ ; \*  $x_1=0.850, x_2=0.033$ ;  
 — oC3EOS 3p  $g^E$ ; - - - oC3EOS 2p  $g^E$ ; ···· oC3EOS VL

majority of the cases the nonrandomness parameter  $\alpha$  in the  $g^E$ -mixing rule can be set as a constant of 0.2 without loss of accuracy. This EOS method can be successfully used to predict viscosities of binary systems over a certain temperature range using the parameters obtained from a viscosity isotherm at a given low temperature. It can also be successfully used to predict the liquid viscosities of ternary systems using binary parameters even for aqueous systems. Good

results are obtained in the extrapolation of viscosities of ternary systems using only binary parameters obtained at a given temperature. The asymmetric van Laar and RK mixing rule can be used very successfully to correlate and extrapolate the liquid viscosities of binary systems, although the van Laar-mixing rule is unsuitable for the viscosity prediction of multi-component systems, particularly of aqueous systems. The RK mixing rule can be used to predict the viscosities of ternary solutions reasonably well for nonaqueous systems, however, for aqueous systems, it gives relatively poor results. In addition, there is no considerable difference in the calculation of dynamic viscosities among the three cubic EOS used, although their description of the  $pvT$ -behavior is quite different. The density of liquids and liquid mixtures is not significant in the calculation of dynamic viscosities.

## NOMENCLATURE

$A_{ij}$	energy parameters of the NRTL model in the $g^E$ -mixing rule
$a, b, u$	parameters in the cubic 3-parameter equation of state oC3EOS
$F_{\text{obj}}$	objective function
$g^E$	molar excess Gibbs free energy, $\text{J}\cdot\text{mol}^{-1}$
$\hat{g}^E$	dimensionless excess Gibbs free energy [ $\hat{g}^E = g^E / (RT)$ ]
$\Delta g^{\#}$	molar activation Gibbs energy of flow, $\text{J}\cdot\text{mol}^{-1}$
$g^{\#E}$	molar excess activation Gibbs energy of flow, $\text{J}\cdot\text{mol}^{-1}$
$h$	Planck constant
$h^E$	molar excess enthalpy, $\text{J}\cdot\text{mol}^{-1}$
$k$	reciprocal of the packing fraction
$M$	molar mass
$m_1, m_2, m_3$	parameters in the $\alpha(T_i)$ -function
$N$	number of data points
$N_A$	Avogadro constant
$p$	pressure, kPa
$R$	molar gas constant ( $8.314\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ )
$T$	thermodynamic temperature, K
$v$	molar volume, $\text{dm}^3\cdot\text{mol}^{-1}$
$x_i$	mole fraction of component $i$ in liquid mixtures
$z$	compressibility factor
$z_{c,\text{opt}}$	apparent (optimized) critical compressibility factor
$\alpha_{ij}$	nonrandomness parameter of NRTL model
$\alpha(T_i)$	temperature function of CEOS parameter $a$
$\delta$	average deviation
$\eta$	dynamic viscosity
$\theta$	temperature, °C
$\sigma$	proportional factor
$\varphi_i^*$	fugacity coefficient of component $i$ in a mixture
$\varphi_{oi}^*$	fugacity coefficients of pure component $i$
$\Omega_a$	reduced cohesive energy parameter
$\Omega_b$	reduced volumetric parameter

## Superscripts

E	excess property
id	ideal solution

## Subscripts

c	critical
cal	calculated value



exp	experimental value
<i>i</i>	component <i>i</i>
<i>j</i>	component <i>j</i>
<i>k</i>	component <i>k</i>
<i>l</i>	component <i>l</i>
2p	$g^E$ -mixing rule with constant nonrandomness $\alpha$
3p	$g^E$ -mixing rule with constant nonrandomness $\alpha$
RK	Redlich-Kister-mixing rule
r	reduced value
rel	relative deviation
VL	van laar-mixing rule

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**APPENDIX**

 1 Cubic 3-parameter equation of state oC3EOS<sup>[32]</sup>

$$p = \frac{RT}{v-b} - \frac{a(T)}{v^2 + ub(v-b)} \quad (\text{A1})$$

$$a(T) = a_c \alpha(T_r) = \Omega_a \frac{R^2 T_c^2}{p_c} \alpha(T_r) \quad b = b_c = \Omega_b \frac{RT_c}{p_c} \quad (\text{A2})$$

where the dimensionless cohesive energy and volumetric parameter and the parameter  $u$  are estimated using the apparent (optimized) compressibility factor  $z_{c, \text{opt}}$ :

$$\Omega_b^3 + (1 - 3z_{c, \text{opt}})\Omega_b^2 + 3z_{c, \text{opt}}\Omega_b - z_{c, \text{opt}}^3 = 0 \quad (\text{A3})$$

$$\Omega_a = 1 - 3z_{c, \text{opt}}(1 - z_{c, \text{opt}}) + 3(1 - 2z_{c, \text{opt}})\Omega_b + 2\Omega_b^2 \quad (\text{A4})$$

$$u = (1 + \Omega_b - 3z_{c, \text{opt}})/\Omega_b \quad (\text{A5})$$

A three-parameter  $\alpha(T_r)$ -function is used in this study

$$\alpha(T_r) = \left\{ 1 + m_1 (1 - T_r^{0.75}) + \left[ m_2 (1 - T_r^{0.75}) + m_3 (1 - T_r^{0.75})^2 \right] (0.7 - T_r^{0.75}) \right\} \quad (\text{A6})$$

The  $z_{c, \text{opt}}$  and the parameters in the  $\alpha(T_r)$ -function ( $m_1$ ,  $m_2$  and  $m_3$ ) are fitted using experimental saturated liquid densities and vapor pressures of pure substances. In the calculation, a generic form of cubic equation of state is used

$$p = \frac{RT}{v-b} - \frac{a(T)}{(v+c)(v+d)} \quad (\text{A7})$$

where the parameter  $c$  and  $d$  for the oC3EOS are estimated by

$$c = b \left( \frac{u - \sqrt{u(u+4)}}{2} \right) \quad d = b \left( \frac{u + \sqrt{u(u+4)}}{2} \right) \quad (\text{A8})$$

and for PREOS by

$$c = (1 - \sqrt{2})b \quad d = (1 + \sqrt{2})b \quad (\text{A9})$$

The fugacity coefficient can be calculated by

$$\ln \varphi_i^* = -\ln \left[ \frac{p(v-b)}{RT} \right] + z - 1 + \frac{1}{v-b} \left( n \frac{\partial b}{\partial n_i} \right) - \frac{1}{RT(c-d)} \left[ a + \left( n \frac{\partial a}{\partial n_i} \right) \right] \ln \frac{v+c}{v+d} +$$

$$\frac{a}{RT(c-d)^2} \left[ \left( n \frac{\partial c}{\partial n_i} \right) \left( \ln \frac{v+c}{v+d} - \frac{c-d}{v+c} \right) - \left( n \frac{\partial d}{\partial n_i} \right) \left( \ln \frac{v+c}{v+d} - \frac{c-d}{v+d} \right) \right] \quad (\text{A10})$$

 2 Modified Huron-Vidal  $g^E$ -mixing rule<sup>[33]</sup> based on zero pressure reference state

$$a(T) = \frac{c-d}{\ln \frac{kb+c}{kb+d}} \times \left( \sum_k x_k \frac{a_{kk}(T)}{c_{kk} - d_{kk}} \ln \frac{kb_{kk} + c_{kk}}{kb_{kk} + d_{kk}} - RT \sum_k x_k \ln \frac{b}{b_{kk}} - RT \hat{g}_0^E \right) \quad (\text{A11})$$

where the packing-fraction ( $1/k$ ) is set as (1/1.1) and the excess Gibbs free energy at zero pressure is estimated using the NRTL equation:

$$\hat{g}_0^E = \frac{g_0^E}{RT} = \sum_k x_k \left( \frac{\sum_l x_l G_{lk} \tau_{lk}}{\sum_l x_l G_{lk}} \right) \quad (\text{A12})$$

$$\tau_{ij} = \frac{A_{ij}}{T} \quad G_{ij} = \exp(-\alpha_{ij} \tau_{ij}) \quad (\alpha_{ij} = \alpha_{ji}) \quad (\text{A13})$$

For parameter  $b$  and  $u$ , a linear combination is used.

3 van Laar-type mixing rule

$$a = \sum_k \sum_l x_k x_l (a_{kk} a_{ll})^{1/2} \left( 1 - \frac{k_{kl} k_{lk}}{x_k k_{kl} + x_l k_{lk}} \right) \quad (\text{A14})$$

4 Patel-Teja equation of state

$$p = \frac{RT}{v-b} - \frac{a(T)}{v(v+b) + c(v-b)} \quad (\text{A15})$$

5 Redlich-Kister-type mixing rule

$$a = \sum_k \sum_l x_k x_l (a_{kk} a_{ll})^{1/2} [1 - k_{kl} - k_{lk}(x_k - x_l)] \quad (\text{A16})$$

**Table A1 Parameters of binary systems used for the prediction of viscosities of ternary aqueous systems using the oC3EOS**

System	Van Laar-type mixing rule		2p $g^E$ -mixing rule <sup>①</sup>		3p $g^E$ -mixing rule			RK mixing rule <sup>②</sup>	
	$k_{kl}$	$k_{lk}$	$A_{12}/K$	$A_{21}/K$	$\alpha_{12}$	$A_{12}/K$	$A_{21}/K$	$k_{kl}$	$k_{lk}$
ethanol+propan-1-ol	-0.028	-0.027	-414.57	385.01	-2.088	-346.10	-140.53	-0.083	-0.080
methanol+ethanol	-0.065	-0.045	-118.82	-73.39	-0.143	151.09	-393.84	-0.025	-0.041
methanol+propan-1-ol	-0.139	-0.128	184.15	-585.89	0.262	-1.20	-442.36	-0.083	-0.080
ethanol+water	-1.384	-0.661	-2675.04	1167.64	0.188	-2773.53	1234.21	-1.245	-0.541
methanol+water	-0.823	-0.523	-1953.22	-168.19	0.127	-2952.48	3035.73	-0.824	-0.546
propan-1-ol+water	-1.555	-0.773	-2810.51	1478.51	0.255	-2511.57	952.569	-1.252	-0.435

 ①  $\alpha_{12}$  set to be 0.2.

② Parameters for PT EOS.