CORRELATION AND PREDICTION OF THE VISCOSITY OF LIQUID MIXTURES

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Introduction

The viscosities of liquid mixtures are required for many practical problems concerning heat transport, mass transport and fluid flow. However, there seems to be no reliable theoretical method to estimate these viscosities. In addition, many viscosity-composition curves are not simple functions of composition. Therefore, the viscosities of most systems cannot be predicted from theory but must be determined experimentally.

This paper shows that the viscosities of binary liquid mixtures can be correlated by using a local mole fraction equation while those of ternary liquid mixtures can be predicted from binary parameters alone.

1. Analysis

On the basis of Eyring's theory of viscosities of pure liquids, Katti and Chaudhri⁶⁾, Heric and Brewer³⁾, and many other investigators have correlated the viscosities of binary liquid mixtures. They defined the excess molar Gibbs free energy of activation of flow (Δ^*G^E) as follows:

$$\frac{\Delta^*G^E}{RT} = \ln \nu M - x_1 \ln \nu_1 M_1 - x_2 \ln \nu_2 M_2 \quad (1)$$

where ν is the kinematic viscosity and M is the molecular weight.

Katti and Chaudhri⁶⁾ used the regular solution type equation, that is, $\Delta^*G^E/RT = x_1 x_2 W_{visc}$. Heric and Brewer³⁾ used the Redlich-Kister type equation for Δ^*G^E :

$$\frac{\Delta^*G^E}{RT} = x_1 x_2 \{A + B(x_1 - x_2) + C(x_1 - x_2)^2 + D(x_1 - x_2)^3\} \quad (2)$$

For the convenience of generalization to multicomponent mixtures, we use the local composition equation proposed by the authors⁸⁾ for vapor-liquid equilibria:

$$\frac{\Delta^*G^E}{RT} = \frac{x_1 x_2 w_{12}}{x_2 + x_1 \exp(-w_{12}/RT)} + \frac{x_1 x_2 w_{21}}{x_1 + x_2 \exp(-w_{21}/RT)} \quad (3)$$

where w_{ij} is the adjustable parameter determined from the binary experimental data. Equation (3) has a feature that the generalization of the equation to multicomponent systems requires no multicomponent parameters except for binary parameters. For multicomponent systems Eq. (3) is generalized to

$$\frac{\Delta^*G^E}{RT} = \sum_{j=1}^N x_j \sum_{i=1}^N \frac{x_i w_{ji}}{\sum_{k=1}^N x_k \exp(-w_{ki})} \quad (4)$$

2. Results and Discussion

Table 1 shows the calculated results for the viscosities of binary liquid mixtures. Table 1 also gives the other calculated values for comparison. For systems which do not exhibit large asymmetric deviations from ideality ($\Delta^*G^E=0$), the agreement between experimental values and calculated results according to Eq. (3) is as good as that given by the four-parameter expansion of the Redlich-Kister type.

On the other hand, for systems which greatly deviate from ideality and the viscosities of which exhibit a maximum when plotted against x , the representation of viscosity according to Eq. (3) is not so good as for the previously mentioned systems. In particular, for the acetone-water system the representation is very poor. Toluene-methanol system has a maximum and minimum on the viscosity-composition diagram. This system also cannot be represented precisely by Eq. (3).

Figure 1 shows the results for the ethanol-water system determined by Kikuchi⁷⁾. This system deviates remarkably from ideality and has a maximum. The values of the error by using Eq. (3) are 0.85 (40°C)–3.85 (15°C). These are large. However, in view of the large extent of deviation from ideality it seems that the representation of the experimental data by using Eq. (3) are satisfactory. Figure 2 shows the variation of the parameters with temperature for the ethanol-water system. The linearity of the parameters with

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Table 1 Fitting results for the viscosities of binary liquid mixtures

System	Temp. [°C]	Eq. (3)	Error (%) [*] Other results	$\Delta^*G^E=0$ Lit. (ideal)	
<i>n</i> -hexadecane- <i>n</i> -hexane	25	0.25	0.22	25.1	3
<i>n</i> -hexadecane-2-bromobutane	25	0.36	0.23	23.0	3
<i>n</i> -hexadecane-carbon tetrachloride	25	0.11	0.11	23.8	3
<i>n</i> -hexadecane-benzene	25	0.34	0.09	20.8	3
2-bromobutane- <i>n</i> -hexane	25	0.09	0.07	3.4	3
carbon tetrachloride- <i>n</i> -hexane	25	0.10	0.13	10.3	3
benzene- <i>n</i> -hexane	25	0.12	0.18	13.2	3
carbon tetrachloride-benzene	25	0.13	0.09	0.8	3
methanol-water	9.9	1.41	—	48.6	6
propanol-water	19.75	0.47	—	61.5	6
ethanol-water	50.02	0.85	—	44.5	6
ethanol-water	40.03	1.34	—	48.0	6
ethanol-water	30.01	2.03	—	51.8	6
ethanol-water	20.03	3.09	—	55.9	6
ethanol-water	15.01	3.85	—	58.1	6
acetone-water	25	12.65	—	39.6	1
chloroform-acetone	25	1.37	—	11.8	1
dimethyl sulphoxide-water	25	6.04	—	61.4	1
dimethyl sulphoxide-acetic acid	25	3.06	—	38.4	1
benzene-cyclohexane	25	1.04	—	14.5	1
dimethyl sulphoxide-acetonitrile	25	0.46	—	2.0	1
<i>o</i> -chlorophenol-dioxane	25	3.20	—	42.7	1
toluene-methanol	20	1.91	—	10.8	2
<i>n</i> -heptane-isooctane	25	0.08	0.08	5.4	9
isooctane-toluene	25	0.32	0.29	4.2	9
toluene- <i>n</i> -heptane	25	0.86	0.60	3.5	9
acetone-methanol	30	0.47	0.60	6.5	5
methanol-ethylene glycol	30	1.22	1.51	11.5	5
ethylene glycol-acetone	30	5.74	1.45	31.3	5

$$* \text{ Error} = \left[\sum_{i=1}^K \left\{ \frac{100(\nu_{\text{exp}} - \nu_{\text{cal}})}{\nu_{\text{exp}}} \right\}^2 / K \right]^{1/2}$$

temperature is fairly good. Therefore, Eq. (3) can be used for interpolating or predicting the data of viscosities for even strongly deviating systems.

Table 2 shows the predicted results for ternary systems using binary parameters only. Table 2 indicates that Eq. (4) gives a fairly good prediction of multicomponent viscosity from binary viscosity data alone.

Nomenclature

A, B, C, D	= constants	[—]
Δ^*G	= molar Gibbs free energy of activation of flow	[cal/g-mole]
K	= number of data	[—]
M	= molecular weight	[g/g-mole]
N	= number of components	[—]
R	= gas constant	[cal/g-mole·K]
W_{visc}	= interaction energy for the activation of flow	[cal/g-mole]
w_{ij}	= adjustable parameter	[—]

Fig. 1 Comparison of experimentally determined viscosity for the ethanol-water system with values calculated from Eq. (3)

Fig. 2 Temperature dependence of parameters for ethanol (1)-water (2) system

Table 2 Errors of the experimental and the predicted viscosities of ternary liquid mixtures at 25°C

System	Eq. (4)	Error (%) Other results [*]	$\Delta^*G^E=0$ Lit.	
<i>n</i> -hexadecane- <i>n</i> -hexane-2-bromobutane	0.36	0.34	20.5	4
<i>n</i> -hexadecane-benzene- <i>n</i> -hexane	4.40	0.38	16.6	4
<i>n</i> -hexadecane-carbon tetrachloride-benzene	1.21	0.34	19.9	4
<i>n</i> -hexadecane-carbon tetrachloride- <i>n</i> -hexane	2.34	0.50	18.7	4
carbon tetrachloride- <i>n</i> -hexane-benzene	0.31	0.31	16.6	4
<i>n</i> -heptane-isooctane-toluene	3.25	1.02	20.7	9
acetone-methanol-ethylene glycol ^{**}	1.90	0.95	4.6	5

^{*} Fitting results containing one ternary parameter.

^{**} 30°C

x	= liquid mole fraction	[—]
ν	= kinematic viscosity	[cm ² /sec]

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VAPOR-LIQUID EQUILIBRIUM DATA FOR THE SYSTEMS ALLYL ALCOHOL-ETHYLBENZENE AND ALLYL ALCOHOL-*p*-XYLENE

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Introduction

With a view to utilizing alcohols as entraining agents for the separation of close-boiling hydrocarbons, isobaric vapor-liquid equilibrium data for the systems allyl alcohol-ethylbenzene and allyl alcohol-*p*-xylene were obtained at 760 ± 2 mmHg pressure. The system allyl alcohol-ethylbenzene, having a boiling range of 39.3°C , forms a constant-boiling mixture at 96.9°C , which is the normal boiling point of allyl alcohol. The vapor and liquid composition curves merge with each other at concentrations of allyl alcohol above 90 mole %. The system allyl alcohol-*p*-xylene, having a boiling range of 41.5°C , forms a constant-boiling mixture at 96.9°C and at concentrations above 93 mole %.

1. Experimental Procedure

Preliminary drying of allyl alcohol obtained from Riedel was done by refluxing for four hours with chemically pure potassium carbonate and was finally purified by distillation in a well-insulated glass column. The method of purification of ethylbenzene and *p*-xylene along with the details of the experimental set-up for obtaining vapor-liquid equilibrium data are described elsewhere²⁾. The physical properties of the pure compounds are listed in Table 1.

2. Results and Discussion

The activity coefficients were calculated using Eqs. (1) and (2):

$$\gamma_1 = \frac{\pi y_1}{P_1^0 x_1} \exp \left[\frac{(\pi - P_1^0)(B_{11} - V_1)}{RT} + \frac{\pi \delta_{12} y_2^2}{RT} \right] \quad (1)$$

$$\gamma_2 = \frac{\pi y_2}{P_2^0 x_2} \exp \left[\frac{(\pi - P_2^0)(B_{22} - V_2)}{RT} + \frac{\pi \delta_{12} y_1^2}{RT} \right] \quad (2)$$

where

$$\delta_{12} = 2B_{12} - B_{11} - B_{22} \quad (3)$$

Table 2 gives the vapor-liquid equilibrium data for these systems. The correlations used for the estimation of pure component properties of ethylbenzene and *p*-xylene have been described earlier²⁾. Based on the recommendations given elsewhere^{1,8)}, the vapor pressures, second virial coefficients and liquid molar volumes of allyl alcohol were estimated by the correlations of Thek-Stiel¹³⁾, O'Connell-Prausnitz¹¹⁾ and modified Goldhammer⁵⁾, respectively. The cross virial coefficients B_{12} were evaluated by employing the mixing rules described by O'Connell and Prausnitz¹¹⁾. The data for both these systems were found to be thermodynamically consistent by application of the tests of Herington⁶⁾, Norrish-Twigg¹⁰⁾ and Black³⁾. The function (D-J) in the Herington test for the systems allyl alcohol-ethylbenzene and allyl alcohol-*p*-xylene was found to be -12.92 and -11.91 , respectively. The activity coefficient-composition plot as shown in Figs. 1 and 2 for these systems indicate maxima-minima below compositions of about 10

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