$m^{-3})^{1/2}$; $\delta_2(SF_6) = 9916\ (J \cdot m^{-3})^{1/2}$. Finally, Φ_1 is the molar volume fraction of solvent, which for very dilute solutions approaches unity (*17*).

The solubilities obtained from eq 8 at 298.15 K are given in Table IV. We give two series of evaluated values: (a) solubilities evaluated with the partial molal volumes, from eq 9, and (b) solubilities evaluated with the Prausnitz partial molal volumes. We also give a series of experimental solubilities. We can see that for H_2, N_2, and O_2 the solubilities are quite different, while they are similar for the rest of gases; the same behavior is found in the study of solubilities of nonpolar gases in chlorocyclohexane (*1*).

If we compare the results for the solubilities of gases in bromocyclohexane (Table I) with the solubilities of the same gases in chlorocyclohexane given in a previous work (*1*), we observe that the solubilities of all the gases are greater with chlorinated solvents than brominated solvents. The difference fluctuates between 12% for C_2H_4 and C_2H_6 and >40% for the fluorinated gases. Likewise, we can see that the solubilities of these gases in the two liquids are considerably lower than in cyclohexane (*22*).

The solubilities of nonpolar gases in these liquids are in inverse order to the vaporization enthalpies of liquids. This agrees with the predictions of eq 8 and with the biggest intermolecular interactions in the sequence cyclohexane > chlorocyclohexane > bromocyclohexane.

Registry No. H_2, 1333-74-0; D_2, 7782-39-0; N_2, 7727-37-9; O_2, 7782-44-7; CH_4, 74-82-8; C_2H_4, 74-85-1; C_2H_6, 74-84-0; CF_4, 75-73-0; SF_6, 2551-62-4; CO_2, 124-38-9; bromocyclohexane, 108-85-0.

Literature Cited

(1) López, M. C.; Gallardo, M. A.; Urieta, J. S.; Gutiérrez Losa, C. *J. Chem. Eng. Data* **1987**, *32*, 472.
(2) Hildebrand, J. H.; Wood, S. E. *J. Chem. Phys.* **1933**, *12*, 1937.
(3) Prausnitz, J. M.; Shair, F. H. *AIChE J.* **1961**, *7*, 602.
(4) Prausnitz, J. M. *J. Phys. Chem.* **1962**, *66*, 640.
(5) Pierotti, R. A. *J. Chem. Phys.* **1963**, *67*, 1840.
(6) Verlet, L. *Phys. Rev.* **1968**, 201.
(7) Mansoori, G. A.; Canfield, F. B. *J. Chem. Phys.* **1969**, *54*, 4958.
(8) Weeks, J. P.; Chandler, P.; Andersen, M. C. *J. Chem. Phys.* **1971**, *54*, 5237.
(9) De Ligny, C. L.; van der Ween, N. G. *Ind. Eng. Chem. Fundam.* **1976**, *15*, 336.
(10) Nocon, G.; Wedlich, U.; Gmehling, J.; Onken, U. *Can. J. Chem.* **1981**, *59*, 1.
(11) Carnicer, J.; Gibanel, F.; Urieta, J. S.; Gutiérrez Losa, C. *Rev. Acad. Cienc. Zaragoza* **1981**, *34*, 115.
(12) Gallardo, M. A.; Urieta, J. S.; Gutiérrez Losa, C. *J. Chim. Phys.* **1983**, *80*, 718.
(13) Ben Naim, A.; Baer, S. *Trans. Faraday Soc.* **1963**, *59*, 2735.
(14) *Handbook of Chemistry and Physics*, 58th ed.; Weast, R. C., Ed.; Chemical Rubber Co.: Boca Raton, FL, 1977–1978; p C-261.
(15) Dack, R. J. *Techniques of Chemistry* (*Solutions and Solubilities*), *8*; Weissberger, Ed.; 1975; pp 412–413.
(16) Hildebrand, J. H.; Scott, R. L. *Solubility of Nonelectrolytes*; Dover: New York, 1964; pp 239–244, 129.
(17) Shinoda, K. *Principles of Solution and Solubility*; Marcel Dekker: New York and Basel, 1978; p 74.
(18) Wing, Y.; Walkley, J. *J. Phys. Chem.* **1969**, *73*, 2274.
(19) Smith, E. B.; Walkley, J. *J. Phys. Chem.* **1962**, *66*, 579.
(20) Hildebrand, J. H.; Lamoreaux, R. H. *Ind. Eng. Chem.* **1974**, *13*, 110.
(21) Melendo, J. M.; Gallardo, M. A.; Urieta, J. S.; Gutiérrez Losa, C. *Acta Cient. Compostelana* **1985**, *23*, 269.
(22) Wilhelm, E.; Battino, R. *Chem. Rev.* **1973**, *73*, 1.

Received for review May 20, 1988. Accepted November 16, 1988. We are grateful for the financial assistance of the Comisión Asesora de Investigación Científica y Técnica (Madrid) (Proyecto 1788/82).

Dynamic Viscosity of Mixtures of Benzene, Ethanol, and *n*-Heptane at 298.15 K

Stefanos Kouris and Constantinos Panayiotou*

Department of Chemical Engineering, University of Thessaloniki, 54006 Thessaloniki, Greece

Experimental dynamic viscosities and densities are reported for the binary and ternary mixtures of benzene, ethanol, and *n*-heptane at 25 °C. The data are correlated with the generalized corresponding states method of Teja and Rice by treating the ternary system as pseudobinary and by using only binary information. A van Laar type mixing rule is used for the pseudocritical temperature of the binary mixtures. Experimental and calculated viscosities for the ternary system are in satisfactory agreement.

Introduction

The viscosities of multicomponent liquid mixtures are required in many chemical engineering calculations involving fluid flow, heat transfer, and mass transfer. It is impractical to measure viscosities at all external conditions of interest, and thus, methods for the estimation of viscosities of multicomponent mixtures are not only of theoretical but also of great practical interest. Such a method is the generalized corresponding states (GCS) method of Teja and Rice, (*1*) which has been successfully applied to the viscosity of binary liquid mixtures. The method can in principle be extended to multicomponent mixtures by using only binary data. Teja et al. (*2*) have used the GCS method, even, for the estimation of the viscosity of undefined liquid mixtures. Testing of this method and similar methods requires consistent experimental data for the viscosities of pure components, of their binaries, and of their multicomponent mixtures. In this work we are reporting such data for a highly nonideal system containing one associated component, ethanol, one inert solvent, *n*-heptane, and one active aromatic component, benzene. In a previous work (*3*) we reported similar data for the system containing acetone, isooctane, and toluene. The two sets of data are used for testing the "predictive" character of the GCS method of Teja and Rice (*1*).

Table I. Properties of Pure Liquids at 25 °C

	ρ, g/cm^3		η, cP	
liquid	exptl	lit.	exptl	lit.
benzene	0.87347	0.8737[a]	0.6048	0.6028,[e] 0.606[f]
ethanol	0.78509	0.7852[b]	1.0832	1.0812[b]
n-heptane	0.67962	0.6810,[c] 0.680[d]	0.3870	0.386,[e] 0.3967[g]

[a] Reference *8*. [b] Reference *9*. [c] Reference *4*. [d] Reference *10*. [e] Reference *11*. [f] Reference *12*. [g] Reference *13*.

Experimental Section

Materials. All pure liquids used in this work were pro analysi grades from MERCK. Their purity was determined by GL

0021-9568/89/1734-0200$01.50/0

Table II. Coefficients of Eq 2 and Standard Deviation of Fit

system	N^a	v_0	v_1	v_2	v_3	v_4	v_5	σ
n-heptane (1)–benzene (2)	13	2.4069	−0.1973	1.2030	1.1971	−1.5604		0.0102
n-heptane (1)–ethanol (2)	12	1.8611	−0.3166	0.2930	−0.3851	0.8565		0.0063
ethanol (1)–benzene (2)	13	0.1199	0.4795	0.2116	0.0772	0.0772	0.3537	0.0029

[a] Number of data points.

Table III. Experimental Densities, d, and Dynamic Viscosities, η, of Binary Mixtures at 25 °C

x_1	d, g cm^{-3}	η, cP	x_1	d, g cm^{-3}	η, cP
n-Heptane (1)–Benzene (2)					
0.0950	0.8412	0.532	0.5995	0.7321	0.403
0.1973	0.8141	0.485	0.6762	0.7201	0.397
0.2999	0.7892	0.455	0.7309	0.7199	0.395
0.3741	0.7790	0.439	0.7987	0.7032	0.391
0.3984	0.7683	0.431	0.8933	0.6917	0.389
0.4961	0.7495	0.414			
Ethanol (1)–*n*-Heptane (2)					
0.1075	0.6831	0.394	0.5079	0.7071	0.521
0.1999	0.6872	0.408	0.6092	0.7159	0.584
0.3001	0.6922	0.433	0.7009	0.7273	0.653
0.3932	0.6984	0.465	0.8165	0.7440	0.766
0.5009	0.7067	0.517	0.9000	0.7601	0.883
Benzene (1)–Ethanol (2)					
0.1059	0.7990	0.959	0.5993	0.8459	0.638
0.1897	0.8086	0.880	0.6973	0.8531	0.610
0.2966	0.8198	0.794	0.7987	0.8600	0.590
0.3983	0.8295	0.731	0.8995	0.8666	0.582
0.4887	0.8372	0.681			

Table IV. Experimental Densities, d, and Dynamic Viscosities, η, of the Ternary Mixture Ethanol (1)–Benzene (2)–*n*-Heptane (3) at 25 °C

x_1	d, g cm^{-3}	η, cP	x_1	d, g cm^{-3}	η, cP
$x_2/x_3 = 0.25$					
0.0000	0.7030	0.391	0.4891	0.7256	0.520
0.2507	0.7125	0.423	0.5984	0.7336	0.588
0.3999	0.7201	0.477	0.7988	0.7533	0.763
$x_2/x_3 = 0.666$					
0.0000	0.7320	0.404	0.5072	0.7473	0.545
0.2078	0.7359	0.426	0.5964	0.7521	0.602
0.4003	0.7427	0.490	0.7979	0.7652	0.779
$x_2/x_3 = 1.50$					
0.0000	0.7680	0.430	0.5953	0.7746	0.627
0.2040	0.7689	0.451	0.6966	0.7767	0.706
0.4044	0.7713	0.519	0.8476	0.7804	0.858
$x_2/x_3 = 3.99$					
0.0000	0.8134	0.484	0.3965	0.8048	0.559
0.2153	0.8085	0.501	0.5988	0.8000	0.668
0.3069	0.8067	0.525	0.7988	0.7939	0.832

chromatography and was better than 99.7% for benzene, better than 99.5% for ethanol, and better than 99.0% for *n*-heptane. Pure component properties are shown in Table I. The mixtures were prepared by weight with precision ±0.0001 g.

***Density*.** The densities have been measured in a vibrating-tube densitometer, Anton Paar Model DMA 60/602. Bidistilled water and air were used as calibrating substances. The temperature in the measuring cell was regulated to 25.00 ± 0.01 °C through a Haake ultrathermostat and measured by a precision digital thermometer, Anton Paar Model DT-100. The estimated error in the density is $\pm 5 \times 10^{-6}$ g/cm^3.

Excess volumes V^E have been determined from the experimental data on densities according to the equation

$$V^E = \sum_i x_i M_i \left(\frac{1}{d} - \frac{1}{d_i}\right) \qquad (1)$$

where M_i, x_i, and d_i are the molar mass, mole fraction, and density of component i; d is the density of the mixture. The data for the binary mixtures are well represented by a Redlich–Kister–Scatchard type equation

$$V^E = x_1 x_2 \sum_{j=0} v_j (1 - 2x_1)^j \qquad (2)$$

Coefficients in eq 2 are presented in Table II along with the standard deviation σ of the fit.

***Viscosity*.** The kinematic viscosities ν of pure liquids and their mixtures have been measured with two Ostwald viscometers which were thoroughly cleansed, dried, and calibrated in each case. The precision in efflux times was 0.1 s. Viscosity measurements were conducted in a precision thermostat Model TAMSON TMV70 microprocessor controlled with a temperature stability better than ±0.01 °C. The estimated error in the dynamic viscosity η ($\eta = \nu d$) is ±0.0015 cP.

Experimental dynamic viscosities for the binary mixtures are reported in Table III along with their densities. In the case of the ternary mixture, four series of experiments have been conducted, each series being characterized by a constant ratio of the mole fractions of benzene (2) and *n*-heptane (3). Precautions were taken in order to minimize evaporation losses during storage and preparation of solutions. Experimental data for the ternary mixture are reported in Table IV.

Logarithmic excess viscosities, $(\ln \eta)^E$, are defined by

$$(\ln \eta)^E = \ln \eta - \ln \eta_{id} \qquad (3)$$

where $\ln \eta_{id}$ for the ideal binary mixture is given by the Arrhenius equation

$$\ln \eta_{id} = x_1 \ln \eta_1 + x_2 \ln \eta_2 \qquad (4)$$

Experimental $(\ln \eta)^E$ are well represented by an equation analogous to eq 2, namely

$$(\ln \eta)^E = x_1 x_2 \sum_{j=0} H_j (1 - 2x_1)^j \qquad (5)$$

Coefficients of eq 5 are reported in Table V along with the standard deviation, σ, of the fit.

It is worth observing that for all three binaries $(\ln \eta)^E$ is negative and V^E is positive except for the benzene-rich region in the system ethanol–benzene. This finding, $(\ln \eta)^E V^E < 0$, is in conformity with the behavior of many binary systems (*4*, *5*).

GCS Method for Viscosity

Teja and Rice (*1*) have proposed the following generalized corresponding states equation for the dynamic viscosity of a

Table V. Coefficients of Eq 5 and Standard Deviation of Fit

system	N	H_0	H_1	H_2	H_3	$\sigma \times 100$
n-heptane (1)–benzene (2)	13	−0.6192	−0.1684	0.0	−0.4034	0.168
n-heptane (1)–ethanol (2)	12	−0.9036	0.0351	−0.2939	−0.2316	0.100
ethanol (1)–benzene (2)	11	−0.7160	−0.1510	0.0	−0.1731	0.087

Table VI. Binary GCS Parameters and Average Absolute Deviation of Fit

system	K_{12}	K_{21}	AAD × 100
acetone (1)–isooctane (2)	−0.0133		0.739
acetone (1)–toluene (2)	−0.0100		0.298
isooctane (1)–toluene (2)	0.0366		0.177
benzene (1)–*n*-heptane (2)	0.0517		0.684
benzene (2)–ethanol (2)	0.0818		3.153
	0.0544	0.2148	0.159
ethanol (1)–*n*-heptane (2)	0.0738		3.872
	0.3413	0.0431	0.687

fluid with critical parameters T_c, P_c, and V_c and molecular weight M:

$$\ln(\eta\xi) = \ln(\eta\xi)^{r1} + \frac{\omega - \omega^{r1}}{\omega^{r2} - \omega^{r1}}[\ln(\eta\xi)^{r2} - \ln(\eta\xi)^{r1}] \qquad (6)$$

where ω is the acentric factor and

$$\xi = V_c^{2/3} T_c^{-1/2} M^{-1/2} \qquad (7)$$

Superscripts r1 and r2 refer to two (nonspherical) reference fluids at the reduced temperature and pressure of the fluid which are chosen so that they are similar to the pure component of interest or, in the case of mixtures, to the key components of interest. Extension of eq 6 to mixtures requires adoption of appropriate mixing and combining rules for T_c, V_c, ω, and M. Teja and Rice (*1*) proposed the following combining rules for the above properties of the mixture (subscript m)

$$V_{cm} = \sum_i \sum_j x_i x_j V_{cij} \qquad (8)$$

$$T_{cm} V_{cm} = \sum_i \sum_j x_i x_j T_{cij} V_{cij} \qquad (9)$$

$$\omega_m = \sum_i x_i \omega_i \qquad (10)$$

$$M_m = \sum_i x_i M_i \qquad (11)$$

x_i is the mole fraction of component i in the mixture. The following mixing rules for V_{cij} and T_{cij} ($i \neq j$) have been proposed by Teja and Rice (*1*)

$$V_{cij} = ((V_{cii}^{1/3} + V_{cjj}^{1/3})/2)^3 \qquad (12)$$

$$T_{cij} V_{cij} = \psi_{ij} (T_{cii} V_{cii} T_{cjj} V_{cjj}) \qquad (13)$$

where ψ_{ij} is a binary interaction coefficient that must be calculated from experimental data.

The choice of references substances is arbitrary. In the case of binary mixtures Teja and Rice chose the two pure components as their reference substances while for the reference equation for correlating their viscosities with reduced temperature T_R, they adopted the Andrade equation

$$\ln(\eta\xi) = A + B/T_R \qquad (14)$$

A and B being constants easily obtained from experimental data by least-squares methods.

Table VII. Prediction of Ternary Viscosities by the GCS Method; Average Absolute Deviation of Fit for the System Ethanol (1)–Benzene (2)–*n*-Heptane (3)

	AAD × 100	
x_2/x_3	one param	two param
0.250	3.272	1.683
0.666	3.000	2.057
1.500	3.569	1.895
3.990	4.059	2.085

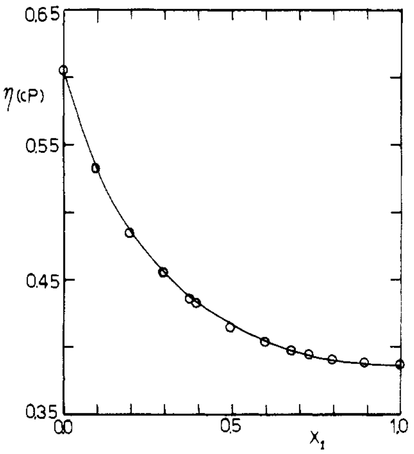

Figure 1. Dynamic viscosities of the benzene (1)–*n*-heptane (2) mixture. (O) Experimental; (—) calculated by the one-parameter GCS method.

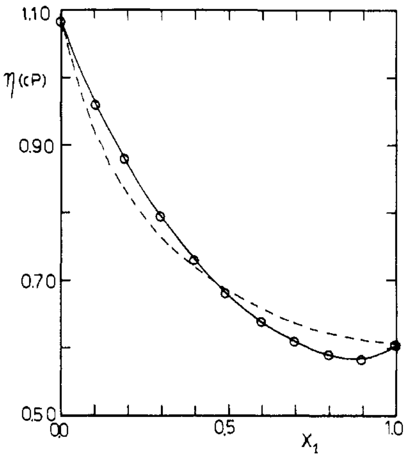

Figure 2. Dynamic viscosities of the benzene (1)–ethanol (2) mixture. (O) Experimental; (---) calculated by the one-parameter GCS method; (—) calculated by the two-parameter GCS method.

Extension of the GCS method to mixtures with more than two components requires, besides others, a judicious choice of the reference substances. Our data for the ternary system (constant ratio x_2/x_3) suggest that an obvious choice of reference substances is pure component 1 and binary mixture of components 2 and 3 with composition satisfying the constant ratio x_2/x_3 of the ternary. This choice does not require any additional information beyond the binary parameters of our systems. Equations 6–14 were initially used for estimating the properties of the binary mixture (2 and 3), and subsequently the same equations were used in order to estimate the properties of the pseudobinary system (1) + (2 and 3). Data for the variation of viscosity of pure compounds with temperature needed in eq 14 were obtained from the compilation of Daubert and Danner (*6*). Values of the binary parameters ψ_{ij} along with the average absolute deviation of calculated and experimental viscosities for the binary systems are reported in Table VI. In this table we have included for comparison the corresponding parameters for the mixtures of acetone, isooctane, and toluene for which data have been reported previously (*3*). As observed, the discrepancy between experimental and calculated viscosities is satisfactory except for the mixtures of ethanol.

The binary parameters ψ_{ij} obtained from the above procedure have, subsequently, been used for the calculation of the viscosities of the ternary systems. Experimental and predicted viscosities for the ternary system acetone–isooctane–toluene are in very good agreement with an average absolute deviation 0.57%. The corresponding deviation for the ternary system benzene–ethanol–*n*-heptane is, however, significantly higher as shown in Table VII. A main cause of the observed discrepancy in ternary viscosities is due to the rather large discrepancy

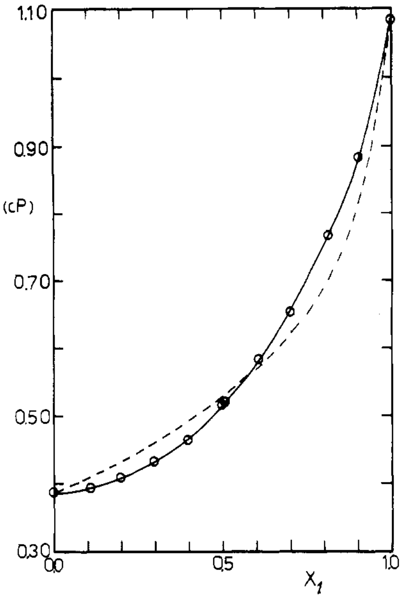

Figure 3. Dynamic viscosities of the ethanol (1)–*n*-heptane (2) mixture. (O) Experimental; (- - -) calculated by one-parameter GCS method; (—) calculated by the two-parameter GCS method.

between experimental and calculated viscosities of the corresponding binaries.

Seeking an improvement of the performance of the GCS method for the highly nonideal systems (such as the mixtures of ethanol), we considered ψ_{ij} composition dependent according to a van Laar type mixing rule or

$$\psi_{ij} = 1 - \frac{K_{ij}K_{ji}}{x_i'K_{ij} + x_j'K_{ji}} \qquad (15)$$

where

$$x_i' = \frac{x_i}{x_i + x_j} \qquad (16)$$

In general $K_{ij} \neq K_{ji}$. When $K_{ij} = K_{ji}$, ψ_{ij} is, as originally (*1*), independent of composition. The van Laar mixing rule, eq 15, has been chosen from among a number of other types of mixing rules as giving the most satisfactory results. Values of the binary parameters for the ethanol mixtures are reported in Table VI along with the corresponding new average absolute deviations. As observed in Table VI and shown in Figures 1–3, the improvement is significant for the binaries. When these parameters are used in the ternary system benzene–ethanol–*n*-heptane, there is a considerable improvement as shown in Table VII although still the performance of the method for this system is less satisfactory than for the system acetone–isooctane–toluene.

In conclusion, the GCS method of Teja and Rice is a useful tool for estimating the viscosities of multicomponent liquid mixtures. In mixtures containing associated components, however, the method may significantly be improved by using more general mixing rules for the pseudobinary critical parameters such as the van Laar type mixing rule of this work. The introduction of the second binary adjustable parameter is certainly an empirical one. Association effects can be taken into account in a more fundamental way (*7*). Incorporation of thermodynamic association models in models for the viscosity of liquid mixtures is in progress in our laboratory.

Acknowledgment

We are grateful to T. Evangelou and to N. Mamagakis for their collaboration.

Registry No. Benzene, 71-43-2; *n*-heptane, 142-82-5; ethanol, 64-17-5.

Literature Cited

(1) Teja, A. S.; Rice, p. *Ind. Eng. Chem. Fundam.* **1981**, *20*, 77.
(2) Teja, A. S.; Thurner, P. A.; Pasumatri, B. *Ind. Eng. Chem. Process Des. Dev.* **1985**, *24*, 344.
(3) Mamagakis, N.; Panayiotou, C. *Z. Phys. Chem.*, in press.
(4) Skubla, P. *Collect. Czech. Chem. Commun.* **1981**, *46*, 303.
(5) Nath, J.; Dubey, S. N. *J. Phys. Chem.* **1981**, *85*, 886.
(6) Daubert, T. E.; Danner, R. P., Eds. *Data Compilation Tables of Properties of Pure Compounds*; AIChE Symposium Series; American Institute of Chemical Engineers: New York, 1985; Vol. 75, No. 203.
(7) Panayiotou, C. *J. Phys. Chem.* **1988**, *92*, 2960.
(8) Bauer, H.; Meerlender, G. *Rheol. Acta* **1984**, *23*, 514.
(9) Wei, I. C. Ph.D. Thesis, Rice University, Houston, TX, 1984.
(10) Lewis, G. L.; Smyth, C. P. *J. Am. Chem. Soc.* **1940**, *62*, 1529.
(11) Prolongo, J.; Horta, A. *J. Phys. Chem.* **1984**, *88*, 2163.
(12) Fischer, J.; Weiss, A. *Ber. Bunsen-Ges. Phys. Chem.* **1986**, *90*, 896.
(13) Musscle, M. J.; Verhoeye, L. *J. Chem. Eng. Data* **1975**, *20*, 46.

Received for review June 15, 1988. Accepted November 22, 1988.

Vapor–Liquid Equilibrium Determination with a Flow-Type Ebulliometer for Six Binary Systems Made of Alcohol and Amine

Masahiro Kato* and Hiroyuki Tanaka

Department of Industrial Chemistry, Faculty of Engineering, Nihon University, Koriyama, Fukushima 963, Japan

Boiling points for the six binary systems made of alcohol (methanol, ethanol, and 2-propanol) and amine (ethylenediamine and dipropylamine) were measured with a flow-type ebulliometer at atmospheric pressure, and their vapor–liquid equilibrium relations were determined by using the Wilson equation.

Introduction

Vapor–liquid equilibria are required for engineering use such as in the design and operation of distillation equipment. Vapor–liquid equilibrium relations can be determined from boiling point curves which are easily obtained rather than the conventional equilibrium measurements. Many researchers proposed some ebulliometers. However, in the general batch-type ebulliometers, it is necessary to correct the difference between the liquid composition at steady state and the feed composition.

The authors (*1*, *2*) previously proposed the apparatus for measuring isobaric dew and bubble points. In the present study, a flow-type ebulliometer was newly constructed. Boiling points were measured with the flow-type ebulliometer for the six binary systems made of alcohol (methanol, ethanol, and 2-propanol) and amine (ethylenediamine and dipropylamine), and

0021-9568/89/1734-0203$01.50/0 © 1989 American Chemical Society