

The acentric factors of both components were estimated by the methods of Reid et al. (8).

Conclusion

1. The apparatus used in this investigation is capable of measuring reliable vapor-liquid equilibrium data for process design purposes.

2. Both the Soave-Redlich-Kwong equation of state and the DDLC-EOS model yield satisfactory results in comparison with the experimental data.

Glossary

a	attractive parameter, $\text{J}\cdot\text{m}^3\cdot\text{mol}^{-2}$
b	repulsive parameter, $\text{m}^3\cdot\text{mol}^{-1}$
C_{ij}	binary interaction parameter
E_{ij}	nonconformal parameter
m	number of datum points
P	pressure, MPa
R	gas constant, $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$
T	absolute temperature, K
v	molar volume, $\text{m}^3\cdot\text{mol}^{-1}$
x	mole fraction of liquid phase
y	mole fraction of vapor phase

Superscripts

° conformal reference state

Subscripts

i, j, k component
cal calculated
exp experimental

Registry No. HFC 134a, 811-97-2; HCFC 141b, 1717-00-6.

Literature Cited

- (1) Soave, G. *Chem. Eng. Sci.* **1972**, *27*, 719.
- (2) Zheng, X. Y.; Wu, G. W.; Zhang, N. W. *J. Chem. Eng. Jpn.* **1988**, *21*, 147.
- (3) Kubota, H.; Inatome, H.; Tanaka, Y.; Makita, T. *J. Chem. Eng. Jpn.* **1983**, *16*, 99.
- (4) Wu, G. W.; Zhang, N. W.; Zheng, X. Y.; Kubota, H.; Makita, T. *J. Chem. Eng. Jpn.* **1988**, *21*, 25.
- (5) Yamashita, T.; Kubota, H.; Tanaka, Y.; Makita, T.; Kashiwagi, H. The 10th Japan Symposium on Thermophysical Properties, Sapporo, Japan, 1989; p 75.
- (6) Sato, H.; Uematsu, M.; Watanabe, K.; Okada, M. *Fluid Phase Equilib.* **1987**, *38*, 167.
- (7) Neider, J. A.; Mead, R. *Comput. J.* **1965**, *8*, 308.
- (8) Reid, R. C.; Prausnitz, J. M.; Sherwood, T. K. *The Properties of Gases and Liquids*, 3rd ed.; McGraw-Hill: New York, 1977.

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Excess Volumes of Isobutanol with Toluene or *o*-Xylene at 303.15 and 308.15 K

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Excess molar volumes for the binary mixtures of isobutanol with toluene and *o*-xylene have been measured at 303.15 and 308.15 K with use of a continuous dilution dilatometer. The excess volumes are positive for both the systems at these temperatures.

Introduction

Brown and Smith (1) have studied the excess volumes of mixing for isobutanol (2-methyl-1-propanol) with benzene in the temperature range of 298.15–318.15 K. Swamy et al. (2) and Raman et al. (3) have reported excess volumes of isobutanol with toluene at 303.15 K. Here we report the excess volumes of isobutanol with toluene and *o*-xylene at 303.15 and 308.15 K. The excess volumes are positive over the entire composition range and increase with temperature.

Experimental Section

A continuous dilution dilatometer of the type used by Kumaran and McGlashan (4) was fabricated to carry out the present study. The dilatometer was immersed in a water bath. Temperature of the bath was controlled by a proportional controller and measured to ± 0.01 K with a K-3 universal potentiometer (Leeds and Nothrup Inc.) A precision cathetometer (Gartener Scientific Co., Chicago, IL) readable to 0.01 mm was used to measure the mercury levels in the dilatometer. The

Table I. Normal Boiling Points T_b and Densities ρ of Pure Components

component	T_b/K		$\rho/(\text{kg m}^{-3})$		
	this work	lit.	T/K	this work	lit.
isobutanol	380.30	380.81 (7)	303.15	795.93	793.8 (7)
			308.15	791.84	789.8 (7)
toluene	383.65	383.78 (8)	303.15	857.79	857.6 (8)
			308.15	852.93	852.9 (8)
<i>o</i> -xylene	417.25	417.58 (8)	303.15	866.08	871.7 (8)
			308.15	861.93	867.5 (8)

estimated uncertainty in the volume measurement was ± 0.004 $\text{cm}^3\cdot\text{mol}^{-1}$. The experimental procedure is similar to the one followed by Kumaran and McGlashan (4) and Pickerell and Plank (5). The details of the experiment are described elsewhere (6).

Purification of Materials

Analytical grade chemicals were purified in a 22-plate distillation column. The middle cut from the distillation product was taken for the experiments. Triple-distilled mercury was used in the experiments. Measured values for normal boiling point and densities of the purified components are presented in Table I, along with literature values (7, 8). The details of the distillation of the chemicals and measurement of physical properties were described earlier (9).

Results and Discussion

The experimental excess molar volumes V^E of isobutanol with toluene and *o*-xylene are presented in Table II. The

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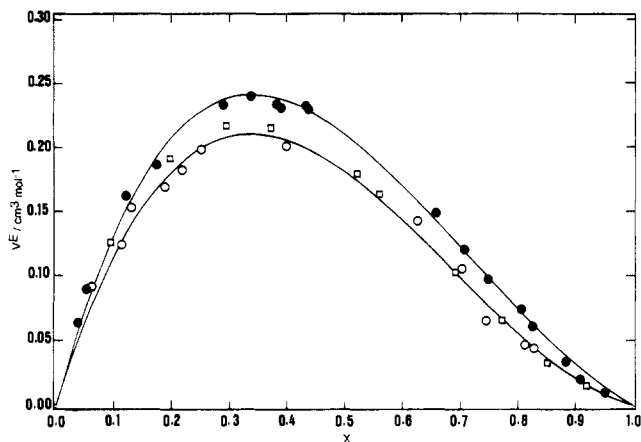


Figure 1. Excess molar volumes V^E of isobutanol + toluene as a function of the mole fraction x of isobutanol. Points, experimental values: \circ , 303.15 K (this work); \square , 303.15 K (3); \bullet , 308.15 K (this work). Curves, fitted values, eq 1.

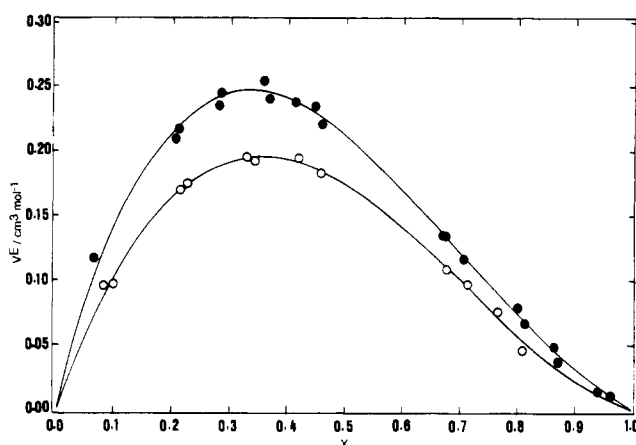


Figure 2. Excess molar volumes V^E of isobutanol + *o*-xylene as a function of the mole fraction x of isobutanol. Points, experimental values: \circ , 303.15 K (this work); \bullet , 308.15 K (this work). Curves, fitted values, eq 1.

results are also shown in Figures 1 and 2. The excess volumes are fitted to the equation

$$V^E/(\text{cm}^3 \text{mol}^{-1}) = x(1-x)[a_0 + a_1(2x-1) + a_2(2x-1)^2] \quad (1)$$

where a_0 , a_1 , and a_2 are adjustable parameters and x is the mole fraction of isobutanol. The values of a_0 , a_1 , and a_2 are obtained by least-squares analysis. The standard deviations are calculated by using the equation

$$\sigma(V^E) = \left[\frac{\sum (V_{\text{expt}}^E - V_{\text{calcd}}^E)^2}{n-p} \right]^{1/2} \quad (2)$$

where n is the number of measurements and p is the number of parameters. The values of the parameters, along with the standard deviations $\sigma(V^E)$, are given in Table II.

At 303.15 and 308.15 K both systems show positive excess volumes with a maximum in isobutanol lean mixtures and increase with temperature. A similar trend is observed by Brown and Smith (1) for isobutanol + benzene mixtures. Literature values reported by Swamy et al. (2, 3) are also included in Figure 2. The literature V^E values of isobutanol + toluene (2, 3) agree with an average absolute and maximum deviations of 0.0063 and 0.0164 $\text{cm}^3 \text{mol}^{-1}$, respectively, with the values calculated from eq 1.

Table II. Excess Molar Volumes V^E of Isobutanol + Toluene or + *o*-Xylene at 303.15 and 308.15 K as a Function of the Mole Fraction x of Isobutanol, Coefficients a_i (Equation 1), and Standard Deviations $\sigma(V^E)$ (Equation 2)

at 303.15 K		at 308.15 K	
x	V^E	x	V^E
Isobutanol + Toluene			
0.0598	0.0923	0.0392	0.0642
0.1153	0.1237	0.0534	0.0899
0.1300	0.1539	0.1224	0.1627
0.1899	0.1686	0.1771	0.1868
0.2204	0.1823	0.2917	0.2336
0.2533	0.1993	0.3392	0.2402
0.3254	0.2117	0.3842	0.2344
0.4000	0.2009	0.3917	0.2312
0.6281	0.1437	0.4342	0.2334
0.7059	0.1063	0.4396	0.2306
0.7454	0.0648	0.6597	0.1498
0.8140	0.0468	0.7094	0.1209
0.8304	0.0441	0.7509	0.0980
		0.8092	0.0751
		0.8849	0.0338
		0.9104	0.0198
		0.9531	0.0089

$$a_0 = 0.72494$$

$$a_1 = -0.65324$$

$$a_2 = 0.05083$$

$$\sigma(V^E)/(\text{cm}^3 \text{mol}^{-1}) = 0.0107$$

$$\sigma(V^E)/(\text{cm}^3 \text{mol}^{-1}) = 0.0064$$

Isobutanol + *o*-Xylene

$$0.0845 \quad 0.0958 \quad 0.0666 \quad 0.1181$$

$$0.1026 \quad 0.0971 \quad 0.2116 \quad 0.2085$$

$$0.2176 \quad 0.1699 \quad 0.2162 \quad 0.2170$$

$$0.2303 \quad 0.1751 \quad 0.2851 \quad 0.2347$$

$$0.3324 \quad 0.1958 \quad 0.2891 \quad 0.2453$$

$$0.3468 \quad 0.1921 \quad 0.3639 \quad 0.2552$$

$$0.4228 \quad 0.1949 \quad 0.3713 \quad 0.2401$$

$$0.4607 \quad 0.1828 \quad 0.4166 \quad 0.2381$$

$$0.6784 \quad 0.1082 \quad 0.4515 \quad 0.2351$$

$$0.7164 \quad 0.0970 \quad 0.4638 \quad 0.2206$$

$$0.7701 \quad 0.0758 \quad 0.6744 \quad 0.1349$$

$$0.8125 \quad 0.0499 \quad 0.6763 \quad 0.1347$$

$$0.7083 \quad 0.1163$$

$$0.8049 \quad 0.0789$$

$$0.8148 \quad 0.0663$$

$$0.8674 \quad 0.0488$$

$$0.8734 \quad 0.0359$$

$$0.9420 \quad 0.0132$$

$$0.9649 \quad 0.0102$$

$$a_0 = 0.70008$$

$$a_1 = -0.53808$$

$$a_2 = -0.01389$$

$$\sigma(V^E)/(\text{cm}^3 \text{mol}^{-1}) = 0.0044$$

$$\sigma(V^E)/(\text{cm}^3 \text{mol}^{-1}) = 0.0075$$

$$a_0 = 0.85196$$

$$a_1 = -0.72162$$

$$a_2 = 0.12987$$

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Literature Cited

- (1) Brown, I.; Smith, F. *Aust. J. Chem.* **1962**, *15*, 1.
- (2) Narayana Swamy, G.; Dharmaraju, G.; Raman, G. K. *Can. J. Chem.* **1980**, *58*, 229.
- (3) Raman, G. K.; Narayana Swamy, G.; Dharmaraju, G. *Int. DATA Ser., Sel. Data Mixtures, Ser. A* **1988**, 155.
- (4) Kumaran, M. K.; McGlashan, M. L. *J. Chem. Thermodyn.* **1977**, *9*, 259.
- (5) Pickerell, D. S.; Plank, C. A. *J. Chem. Eng. Data* **1989**, *34*, 278.
- (6) Mallu, B. V. M.S. Thesis, Indian Institute of Technology, Kanpur, India, 1982.
- (7) Thermodynamic Tables—Non-Hydrocarbons. Thermodynamics Research Center, The Texas A&M University System: College Station, TX, 1967, p. a-5030; 1966, p. d-5030 (loose-leaf data sheets).
- (8) Thermodynamic Tables—Hydrocarbons. Thermodynamics Research Center, The Texas A&M University System: College Station, TX, 1985, p. a-3290; 1977, p. d-3291 (loose-leaf data sheets).
- (9) Chalapati Rao, Y. V.; Basu, R. *J. Chem. Eng. Data* **1985**, *30*, 361.