J. Chem. Eng. Data **1996,** *41,* 1355−1357

Ternary Vapor−Liquid Equilibria of 2-Propanol + Cyclohexane + Toluene at 318.15 K

Isamu Nagata* and Kazuhiro Tamura

Department of Chemistry and Chemical Engineering, Division of Physical Sciences, Kanazawa University, 40-20, Kodatsuno 2-chome, Kanazawa, Ishikawa 920, Japan

Andrzej Książczak

Department of Chemistry, Warsaw University of Technology, Noakowskiego 3, 00-664 Warsaw, Poland

Isothermal vapor−liquid equilibria of 2-propanol + cyclohexane + toluene were measured using a modified Boublik still at 318.15 K. The experimental results are compared with those calculated using the UNIQUAC associated-solution model with only binary parameters.

Introduction

As part of a series of thermodynamic studies for ternary alcohol solutions, this work reports the experimental vapor−liquid equilibria (VLE) for 2-propanol + cyclohexane + toluene at 318.15 K. The measured results are compared with those calculated from the UNIQUAC associated-solution model with binary parameters, obtained from VLE results for three systems: 2-propanol + cyclohexane at 323.15 K (Nagata et al., 1973); 2-propanol + toluene at 313.15 K (Ashcroft et al., 1979); cyclohexane + toluene at 313.15 K (Konakbaeva et al., 1974).

Experimental Section

Materials. Special grade 2-propanol was refluxed over calcium oxide and then fractionally distilled. Analytical-grade cyclohexane and toluene were directly used. A glc analysis showed that the purities of these chemicals were better than 99.9 mol %. The densities, measured with an Anton-Paar densimeter at 298.15 K, the boiling points, and the vapor pressures at 318.15 K agreed well with literature values of Riddick and Bunger (1970) and TRC (1996), as shown in Table 1. Table 2 lists the coefficients of the Antoine equation (Riddick and Bunger, 1970; Riddick et al., 1986; TRC, 1996).

Procedure. VLE measurements at 318.15 K were performed using a modified Boublik vapor-recirculating still as described previously (Nagata, 1985a). The compositions of ternary equilibrated liquid- and vapor-phase samples were withdrawn using preheated Hamilton syringes and analyzed with a thermal conductivity glc (Shimadzu glc, GC-8A) equipped with an electronic integrator (Shimadzu Chromatopac, C-R6A). Good separation of the three components was obtained on a 3 m (i.d. $^1/_8$ in.) long stainless steel column packed with PEG-1000 20−80M (15% by volume poly(ethylene glycol) on Shimalite F) and a thermal-conductivity detector. The glc was calibrated with gravimetrically prepared mixtures. Three analyses were made to obtain a mean value for each sample solution. The experimental errors of the measured variables were mole fraction, ±0.002; pressure, ±0.013 kPa; and temperature, ±0.05 K.

Table 1. Densities *d*, Normal Boiling Points T_b, and Vapor Pressures *P* of the Components

	d(298.15 K)/g·cm^{-3}		T_b (101.325 kPa)/K		P(318.15 K)/kPa	
component	exptl	lit.	exptl	lit.	exptl	lit.
2-propanol	0.781 29	0.781 26[a]	355.3	355.41[a]	18.532	18.543[a]
		0.781 26[b]		355.392[b]		18.177[b]
		0.781 26[c]		355.42[c]		18.542[c]
cyclohexane	0.773 90	0.773 89[a]	353.8	353.875[a]	29.991	29.974[a]
		0.773 89[b]		353.880[b]		29.991[b]
		0.773 87[c]		353.929[c]		29.999[c]
toluene	0.862 30	0.862 31[a]	383.7	383.875[a]	9.893	9.882[a]
		0.862 19[b]		383.780[b]		9.891[b]
		0.862 20[c]		383.762[c]		9.890[c]

[a] Riddick and Bunger, 1970. [b] Riddick et al., 1986. [c] TRC, 1996.

Table 2. Antoine Coefficients *A*, *B*, and *C*

component	*A*	*B*	*C*
2-propanol	7.242 79[a]	1580.92	−53.54
	6.866 18[b]	1360.131	−75.558
	7.242 68[c]	1580.92	−53.54
cyclohexane	5.969 88[a]	1203.53	−50.29
	5.964 07[b]	1200.31	−50.646
	5.930 02[c]	1182.774	−52.532
toluene	6.079 54[a]	1344.80	−53.67
	6.085 40[b]	1348.77	−53.174
	6.050 43[c]	1327.625	−55.525

$$\log P_i^0/\text{kPa}) = A - B/[(T/K) + C]$$

[a] Riddick and Bunger, 1970. [b] Riddick et al., 1986. [c] TRC, 1996.

Table 3. Vapor Pressures P_i^0, Liquid Molar Volumes V_i^0, Structural Parameters r_i and q_i, and Second Virial Coefficients B_{ij} at 318.15 K

	2-propanol	cyclohexane	toluene
P_i^0/kPa	18.532	29.991	9.893
V_i^0/cm^3·mol^{-1}	80.06	111.46	109.06
r_i	2.23	3.18	3.10
q_i	1.98	2.55	2.48
$-B_{ii}$/cm^3·mol^{-1}	2129	1449	2136

	2-propanol + cyclohexane	2-propanol + toluene	cyclohexane + toluene
$-B_{ij}$/cm^3·mol^{-1}	909	1035	1716

---

* Fax: 81-762-34-4829. e-mail: tamura@heikou1.ch.t.kanazawa-u.ac.jp.

S0021-9568(96)00191-4 CCC: $12.00

Table 4. Isothermal Vapor−Liquid Equilibrium Data, Liquid-Phase Mole Fractions x_i and Vapor-Phase Mole Fractions y_i, Vapor Pressures *P*, Activity Coefficients γ_i, and Fugacity Coefficients ϕ_i for 2-Propanol (1) + Cyclohexane (2) + Toluene (3) at 318.15 K

point	x_1	x_2	x_3	y_1	y_2	y_3	*P*/kPa	γ_1	γ_2	γ_3	ϕ_1	ϕ_2	ϕ_3
1	0.141	0.725	0.134	0.266	0.677	0.057	36.104	3.668	1.122	1.526	0.984	0.982	0.976
2	0.152	0.563	0.285	0.288	0.591	0.121	33.051	3.375	1.156	1.397	0.985	0.984	0.978
3	0.235	0.507	0.258	0.319	0.570	0.111	33.717	2.464	1.264	1.444	0.984	0.984	0.978
4	0.237	0.489	0.274	0.320	0.556	0.124	33.331	2.423	1.264	1.502	0.984	0.984	0.978
5	0.201	0.393	0.406	0.332	0.495	0.173	30.424	2.709	1.280	1.294	0.985	0.986	0.980
6	0.324	0.369	0.307	0.358	0.505	0.137	31.997	1.903	1.462	1.424	0.984	0.985	0.980
7	0.317	0.278	0.405	0.381	0.430	0.189	29.771	1.927	1.539	1.388	0.984	0.984	0.978
8	0.388	0.187	0.425	0.440	0.330	0.230	27.544	1.682	1.628	1.493	0.984	0.988	0.983
9	0.360	0.052	0.588	0.516	0.126	0.358	22.385	1.732	1.823	1.371	0.986	0.992	0.987
10	0.522	0.042	0.436	0.574	0.101	0.325	23.025	1.365	1.862	1.728	0.985	0.992	0.988
11	0.600	0.078	0.322	0.555	0.200	0.245	25.491	1.269	2.195	1.949	0.983	0.991	0.987
12	0.597	0.074	0.329	0.546	0.210	0.244	25.411	1.251	2.422	1.894	0.984	0.991	0.987
13	0.727	0.071	0.202	0.581	0.231	0.188	25.865	1.112	2.828	2.421	0.983	0.991	0.987
14	0.676	0.114	0.210	0.528	0.305	0.167	27.691	1.163	2.485	2.210	0.982	0.990	0.985
15	0.429	0.457	0.114	0.362	0.582	0.056	36.570	1.656	1.551	1.787	0.981	0.983	0.977
16	0.739	0.159	0.102	0.495	0.417	0.088	30.891	1.110	2.713	2.668	0.981	0.988	0.983
17	0.676	0.158	0.166	0.481	0.395	0.124	30.171	1.153	2.525	2.256	0.982	0.988	0.983
18	0.610	0.237	0.153	0.436	0.467	0.097	32.597	1.251	2.146	2.064	0.981	0.986	0.981
19	0.552	0.344	0.104	0.387	0.553	0.060	35.370	1.331	1.896	2.033	0.981	0.984	0.978
20	0.615	0.223	0.162	0.443	0.450	0.107	32.024	1.239	2.160	2.114	0.981	0.987	0.981
21	0.477	0.408	0.115	0.367	0.574	0.059	35.944	1.486	1.687	1.838	0.981	0.984	0.978
22	0.420	0.469	0.111	0.350	0.596	0.054	36.570	1.636	1.548	1.770	0.981	0.983	0.977
23	0.319	0.560	0.121	0.316	0.627	0.057	36.784	1.958	1.371	1.722	0.982	0.982	0.976

Table 5. Parameters and Root-Mean-Squared Deviations between Calculated and Experimental Pressures, Temperatures, and Liquid-Phase and Vapor-Phase Mole Fractions Obtained Using the UNIQUAC Association Model for Binary Systems

binary mixture (A + B)	*T*/K	$K^0_{AB}(T)^a$	$-h_{AB}$/kJ·mol^{-1}	a_{AB}/K	a_{BA}/K	δP/kPa	δT/K	$10^3\delta x$	$10^3\delta y$
2-propanol + cyclohexane	323.15			155.98	−84.76	0.1467	0.04	0.4	3.8
2-propanol + toluene	313.15	2.5	8.3	10.33	122.52	0.2386	0.00	0.8	
cyclohexane + toluene	313.15			−47.56	138.97	0.1907	0.00	0.3	

[a] $T = 323.15$ K.

Results and Analysis

The following equations were used to calculate the activity coefficients γ_i and fugacity coefficients ϕ_i

$$\gamma_i = Py_i\phi_i/[x_iP_i^0\phi_i^0 \exp\{V_i^0(P - P_i^0)/RT\}] \qquad (1)$$

$$\ln \phi_i = (2\sum_i y_jB_{ij} - \sum_i\sum_j y_iy_jB_{ij})P/RT \qquad (2)$$

where *P* is the total pressure, P_i^0 is the measured pure-component vapor pressure, and V_i^0 is the liquid molar volume calculated from a modified Rackett equation (Spencer and Danner, 1972), B_{ii} is the pure second virial coefficient taken from Smith and Srivastava (1986a,b), and B_{ij} is the unlike-interaction second virial coefficients estimated by the Hayden−O'Connell method (1975). Table 3 gives the values of P_i^0, V_i^0, and B_{ii} and B_{ij} which were used in the analysis of the experimental results. The differences of the pure second virial coefficients between the interpolated values of Smith and Srivastava (1986a,b) and those calculated by the Hayden−O'Connell method (1975) have little effect on the fugacity coefficient of eq 2 at the moderate pressures studied in this work. Table 4 shows the experimental results for 2-propanol + cyclohexane + toluene at 318.15 K.

The experimental VLE results were analyzed using the UNIQUAC associated-solution model (Nagata, 1985b) with binary parameters obtained from the binary VLE results. We assume that in a ternary mixture alkanol self-associates to form open chains of any length, which produce many chemical complexes with two other active nonassociated components. The equilibrium constants for chemical-complex formation are independent of the numbers of associated and solvated molecules, the association constant for 2-propanol being $K^0_A = 49.1$ at 323.15 K (Brandani, 1983); the enthalpy of a hydrogen bond is $h_A = -23.2$ kJ·mol^{-1} (Stokes et al., 1973). The temperature dependence of the equilibrium constants is fixed by the van't Hoff equation. The pure-component molecular-size and molecular-area parameters *r* and *q*, calculated from the method of Vera et al. (1977), are given in Table 3. The binary energy parameters of the model were obtained using a computer code based on the maximum-likelihood principle (Prausnitz et al., 1980). The standard deviations for the experimental values were taken as 0.13 kPa for pressure, 0.05 K for temperature, 0.001 for liquid mole fraction, and 0.003 for vapor mole fraction. Table 5 shows the solvation constant K^0_{AB}, the enthalpy h_{AB} of complex formation, the binary energy parameters a_{AB} and a_{BA}, and the root-mean-squared deviations between the experimental and the most probable calculated values: δP for pressure; δT for temperature; δx for liquid mole fraction; δy for vapor mole fraction. Table 6 shows the deviations between the ternary experimental results and those calculated from the UNIQUAC associated-solution model with only the binary parameters. Figure 1 shows the experimental and calculated tie lines. Agreement is good. The ternary VLE data for 2-propanol + cyclohexane + toluene at 318.15 K were well predicted by using the UNIQUAC associated-solution model and may be thermodynamically consistent.

Table 6. Deviations between Calculated and Experimental Vapor-Phase Mole Fractions and Pressures for 2-Propanol (1) + Cyclohexane (2) + Toluene (3) at 318.15 K

deviation	$10^3\delta y_1$	$10^3\delta y_2$	$10^3\delta y_3$	δP/kPa	$10^2\delta P/P$
mean	6.7	9.2	4.4	0.2112	0.70
root-mean-square	7.9	10.9	5.4	0.2383	0.81

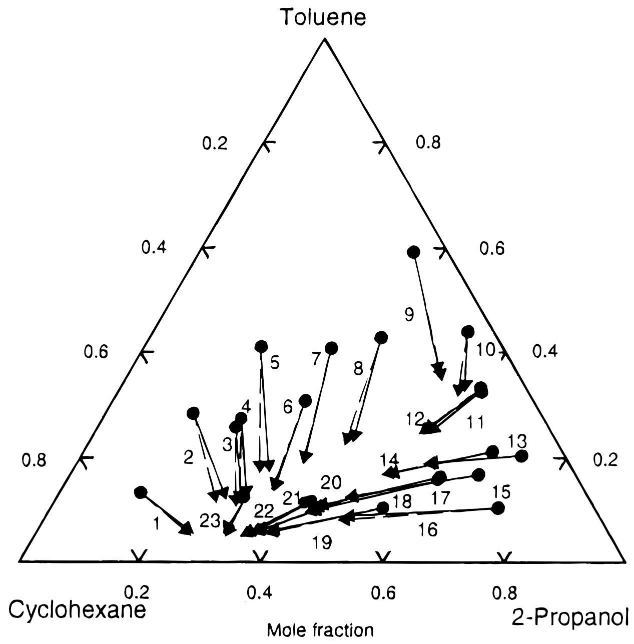

Figure 1. Equilibrium tie lines; (▲) vapor; (●) liquid; (—) experimental; (- - -) calculated.

Literature Cited

Ashcroft, S. T.; Clay, A. D.; Shearm, R. B. Isothermal Vapor-Liquid Equilibria for the Systems Toluene-n-Heptane, Toluene-Propan-2-ol, Toluene-Sulfolane, and Propan-2-ol-Sulfolane. *J. Chem. Eng. Data* **1979**, *24*, 195−199.

Brandani, V. A. Continuous Linear Association Model for Determining the Enthalpy of Hydrogen-Bonded Formation and the Equilibrium Association Constant for the Pure Hydrogen-Bonded Liquids. *Fluid Phase Equilib.* **1983**, *12*, 87−104.

Hayden, J. G.; O'Connell, J. P. A. Generalized Method for Predicting Second Virial Coefficients. *Ind. Eng. Chem. Process Des. Dev.* **1975**, *14*, 209−216.

Konakbaeva, E. G.; Anisimova, Z. K. H.; Shakhparonov, M. I. Precise Measurements of Vapor Pressure of Binary Solutions of Nonelectrolytes. *Vestn. Mosk. Univ. Khim.* **1974**, *15*, 30−36.

Nagata, I. Isothermal Vapor-Liquid Equilibria for the Ternary Methanol − Ethanol − Benzene System. *J. Chem. Eng. Data* **1985a**, *30*, 201−203.

Nagata, I. On the Thermodynamics of Alcohol Solutions. Phase Equilibria of Binary and Ternary Mixtures Containing Any Number of Alcohols. *Fluid Phase Equilib.* **1985b**, *19*, 153−174.

Nagata, I.; Ohta, T.; Uchiyama, Y. Excess Gibbs Free Energies for Binary Systems Isopropanol with Benzene, Cyclohexane, Methylcyclohexane. *J. Chem. Eng. Data* **1973**, *18*, 54−59.

Prausnitz, J. M.; Anderson, T. F.; Grens, E. A.; Eckert, C. A.; Hsieh, R.; O'Connell, J. P. *Computer Calculations for Multicomponent Vapor-Liquid and Liquid-Liquid Equilibria*; Prentice-Hall: Englewood Cliffs, NJ, 1980.

Riddick, J. A.; Bunger, W. *Organic Solvents*, 3rd ed.; Wiley-Interscience: New York, 1970.

Riddick, J. A.; Bunger, W. B.; Sakano, T. K. *Organic Solvents*, 4th ed.; Wiley-Interscience: New York, 1986.

Smith, B. D.; Srivastava, R. *Thermodynamic data for pure compounds. Part A. Hydrocarbons and ketones, Physical Sciences Series 25*; Elsevier: Amsterdam, 1986a.

Smith, B. D.; Srivastava, R. *Thermodynamic data for pure compounds. Part B. Halogenated hydrocarbons and alcohols, Physical Sciences Series 25*; Elsevier: Amsterdam, 1986b.

Spencer, C. F.; Danner, R. P. Improved Equation for Prediction of Saturated Liquid Density. *J. Chem. Eng. Data* **1972**, *17*, 236−241.

Stokes, R. H.; Burfitt, C. Enthalpies of dilution and transfer of ethanol in non-polar solvents. *J. Chem. Thermodyn.* **1973**, *5*, 623−631.

TRC. *Databases for Chemistry*; Texas A&M University: College Station, TX, 1996.

Vera, J. H.; Sayegh, S. G.; Ratcliff, G. A. A Quasi Lattice-Local Composition Model for the Excess Gibbs Free Energy of Liquid Mixtures. *Fluid Phase Equilib.* **1977**, *1*, 113−135.

Received for review June 3, 1996. Accepted August 13, 1996.[⊗]

JE960191E

[⊗] Abstract published in *Advance ACS Abstracts,* September 15, 1996.