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Vapor−Liquid Equilibria for Methanol + Acetone + Acetonitrile + Benzene at 328.15 K

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Vapor−liquid equilibria are reported for methanol + acetone + acetonitrile + benzene at 328.15 K. The results were obtained using a modified Boublik vapor-recirculating still, and they compare well with those calculated with the UNIQUAC formalism having only binary parameters.

Introduction

As part of our studies on isothermal vapor−liquid equilibria (VLE) for quaternary mixtures involving one alcohol, acetonitrile, and benzene, this paper reports the experimental VLE results for methanol + acetone + acetonitrile + benzene at 328.15 K. The measured quaternary results are compared with those calculated from the UNIQUAC formalism with only binary parameters, determined from binary VLE results for six systems: methanol + acetone at 328.15 K (Freshwater and Pike, 1967); methanol + acetonitrile at 328.15 K (Ohta and Nagata, 1983); methanol + benzene at 328.15 K (Scatchard et al., 1946); acetone + acetonitrile at 318.15 K (Brown and Smith, 1960); acetonitrile + benzene at 328.15 K (Ohta and Nagata, 1983); acetone + benzene at 318.15 K (Brown and Smith, 1957).

Experimental Section

Materials. All chemicals were supplied by Wako Pure Chemical Industries Ltd. Special grade acetone and methanol were fractionated after storage over anhydrous copper sulfate. Special grade acetonitrile was used directly. Chemically pure benzene was purified by repeated fractional crystallization. The purities of chemicals used were better than 99.9 mol % according to glc analysis. The densities of the chemicals used, measured with an Anton-Paar densimeter at 298.15 K, the vapor pressures, and the boiling points agreed well with literature values (Riddick and Bunger, 1970; Brown and Smith, 1954), as shown in Table 1.

Procedure. Quaternary VLE results measured at 328.15 K were obtained using a modified Boublik vapor-recirculating still as described previously (Nagata, 1985b). The liquid- and vapor-phase samples of quaternary equilibrated mixtures were withdrawn with preheated Hamilton syringes and their compositions were analyzed with a Shimadzu glc (GC-8A) equipped with an electronic integrator (Shimadzu Chromatopac, C-R6A). A good separation of the four 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 column temperature was 393 K. The detector current was 100 mA at a helium flow rate of 60 mL min^{-1}. The glc was calibrated with gravimetrically prepared mixtures. Three analyses were made to obtain a mean value for each sample solution. The experimental uncertainties of the measured variables were ±0.002 in liquid and vapor mole fractions, x_i and y_i, ±13.33 Pa in pressure, and ±0.05 K in temperature.

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

	d(298.15 K)/ g·cm^{-3}		P(328.15 K)/ kPa		T_b(101.325 kPa)/ K	
component	exptl	lit.	exptl	lit.	exptl	lit.
methanol	0.786 67	0.786 64[a]	68.314	68.289[a]	337.8	337.85[a]
acetone	0.784 42	0.784 40[a]	96.952	96.944[a]	329.3	329.44[a]
acetonitrile	0.776 62	0.776 60[a]	40.837	40.848[b]	354.7	354.72[b]
benzene	0.873 69	0.873 70[a]	43.610	43.592[a]	353.2	353.25[a]

[a] Riddick and Bunger, 1970. [b] Brown and Smith, 1954.

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

component	A	B	C
methanol[a]	7.022 40	1474.08	−44.02
acetone[a]	6.356 47	1277.03	−35.92
acetonitrile[b]	6.405 24	1420.20	−31.909
benzene[a]	6.030 55	1211.033	−52.36

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

[a] Riddick and Bunger, 1970. [b] Brown and Smith, 1954.

Results and Analysis

The activity coefficients γ_i and fugacity coefficients ϕ_i were calculated using the following equations:

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

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

where R is the gas constant, P is the total pressure, P_i° and V_i° are the pure-component vapor pressures obtained using the Antoine equation with coefficients in Table 2 and liquid molar volumes calculated from a modified Rackett equation (Spencer and Danner, 1972), and B are the pure and unlike-interaction second virial coefficients estimated by the method of Hayden−O'Connell (1975). The values of P_i°, V_i°, B, and pure-component molecular-size and molecular-area parameters r_i and q_i, estimated from the method of Vera et al. (1977), are summarized in Table 3. Table 4 shows the experimental results for methanol + acetone + acetonitrile + benzene at 328.15 K.

The experimental quaternary VLE results were analyzed using the UNIQUAC formalism (Nagata, 1985a) with only binary parameters obtained from the binary VLE results. We assume the self-association of alkanol (A), which forms open chains of any length, and a solvation equilibrium

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Table 3. Vapor Pressures P_i°, Liquid Molar Volumes V_i°, Structural Parameters r_i and q_i, and Second Virial Coefficients B_{ij} at 328.15 K

	methanol	acetone	acetonitrile	benzene
P_i°/kPa	68.289	96.944	40.848	45.592
V_i°/cm^3·mol^{-1}	40.97	77.59	54.61	92.73
r_i	1.15	2.06	1.50	2.56
q_i	1.12	1.85	1.40	2.05
$-B_{ii}$/cm^3·mol^{-1}	1437	1354	3787	1156
	methanol + acetone	methanol + acetonitrile	methanol + benzene	
$-B_{ij}$/cm^3·mol^{-1}	1004	1841	434	
	acetone + acetonitrile	acetone + benzene	acetonitrile + benzene	
$-B_{ij}$/cm^3·mol^{-1}	2125	1013	1099	

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 Methanol (1) + Acetone (2) + Acetonitrile (3) + Benzene (4) at 328.15 K

x_1	x_2	x_3	y_1	y_2	y_3	P/kPa	γ_1	γ_2	γ_3	γ_4	ϕ_1	ϕ_2	ϕ_3	ϕ_4
0.366	0.163	0.150	0.447	0.171	0.099	87.779	1.569	0.958	1.378	1.777	0.965	0.961	0.919	0.984
0.267	0.095	0.087	0.462	0.091	0.065	87.166	2.211	0.869	1.560	1.383	0.966	0.962	0.926	0.981
0.380	0.055	0.071	0.510	0.570	0.053	89.193	1.751	0.963	1.595	1.571	0.964	0.962	0.925	0.982
0.383	0.106	0.072	0.491	0.108	0.054	89.139	1.672	0.945	1.598	1.614	0.964	0.961	0.924	0.982
0.277	0.165	0.074	0.435	0.170	0.050	88.299	2.033	0.946	1.427	1.439	0.966	0.961	0.924	0.980
0.274	0.111	0.158	0.433	0.109	0.116	86.300	1.999	0.882	1.511	1.481	0.966	0.961	0.921	0.983
0.464	0.106	0.069	0.517	0.112	0.049	89.857	1.463	0.988	1.524	1.839	0.963	0.962	0.923	0.983
0.259	0.198	0.143	0.396	0.201	0.100	86.140	1.933	0.910	1.435	1.496	0.967	0.961	0.920	0.982
0.190	0.116	0.062	0.423	0.128	0.050	85.153	2.787	0.979	1.651	1.228	0.969	0.962	0.929	0.979
0.470	0.155	0.067	0.495	0.163	0.050	91.219	1.403	0.998	1.621	1.984	0.962	0.961	0.920	0.983
0.201	0.117	0.250	0.367	0.121	0.170	81.607	2.192	0.879	1.324	1.483	0.970	0.962	0.922	0.984
0.461	0.171	0.028	0.496	0.179	0.029	91.859	1.443	1.000	2.268	1.833	0.962	0.961	0.921	0.982
0.624	0.044	0.064	0.584	0.050	0.051	89.699	1.224	1.063	1.709	2.426	0.961	0.963	0.924	0.986
0.605	0.096	0.066	0.570	0.111	0.049	90.566	1.243	1.091	1.603	2.416	0.960	0.963	0.921	0.987
0.307	0.303	0.152	0.374	0.322	0.094	88.673	1.583	0.979	1.298	1.796	0.966	0.960	0.915	0.984
0.534	0.046	0.141	0.550	0.049	0.100	88.273	1.327	0.980	1.492	2.194	0.962	0.963	0.921	0.987
0.168	0.226	0.265	0.299	0.252	0.171	80.353	2.109	0.933	1.235	1.505	0.972	0.962	0.920	0.984
0.550	0.046	0.069	0.558	0.050	0.056	89.913	1.331	1.018	1.744	2.072	0.962	0.963	0.924	0.985
0.378	0.164	0.088	0.463	0.171	0.061	89.433	1.603	0.970	1.478	1.690	0.964	0.961	0.921	0.982
0.465	0.143	0.143	0.492	0.155	0.099	88.393	1.366	0.997	1.454	2.076	0.963	0.962	0.918	0.987

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 Associated-Solution Model for Binary Systems

binary system (A + B)	T/K	$K_{AB}(T)^a$	$-h_{AB}$/kJ·mol^{-1}	a_{AB}/K	a_{BA}/K	δP/kPa	δT/K	$10^3\delta x$	$10^3\delta y$
methanol + acetone	328.15	60.0	21.0	203.36	58.10	0.1893	0.09	0.5	4.5
methanol + acetonitrile	328.15	30.0	17.0	480.47	−113.06	0.1333	0.04	1.0	5.3
methanol + benzene	328.15	4.0	8.3	−71.04	220.25	0.1253	0.05	1.4	4.7
acetone + acetonitrile	318.15			−17.86	37.09	0.1067	0.03	0.3	1.5
acetone + benzene	318.15			−48.30	130.97	0.1307	0.04	0.4	2.7
acetonitrile + benzene	328.15			−37.07	313.15	0.2160	0.00	0.3	7.9

[a] T = 323.15 K.

between the terminal hydroxy group of alkanol chains and one solvating molecule (B or C or D). The general formulas of the chemical complexes are represented by A_i, A_iB, A_iC, and A_iD, where i ranges from 1 to ∞. The equilibrium constants are assumed to be independent of the chain size: the association constant for methanol $K_A = 173.9$ at 323.15 K (Brandani, 1983); the enthalpy of a hydrogen bond is $h_A = -23.3$ kJ·mol^{-1} (Stokes et al., 1973); solvation parameters were taken from Nagata (1985a). The temperature dependence of the equilibrium constants is fixed by the van't Hoff equation. An optimum set of the binary molar energy parameters of the model was obtained using a computer program based on the maximum likelihood principle (Prausnitz et al., 1980). In binary VLE data analysis pure-component vapor pressures were calculated from the Antoine equation (Riddick and Bunger, 1970; Brown and Smith, 1954). The standard deviations for the experimental values in obtaining the binary parameters were set as 0.133 kPa for pressure, 0.05 K for temperature, 0.001 for liquid mole fraction, and 0.003 for vapor mole fraction. Table 5 gives the solvation constant K_{AB}, the enthalpy h_{AB} of complex formation, the binary parameters a_{AB} and a_{BA}, and the root-mean square deviations between experimental and the most probable calculated values of the measured variables: δP for pressure, δT for temperature, δx for liquid mole fraction, and δy for vapor mole fraction. Table 6 shows the absolute arithmetic-mean and root-mean deviations of the vapor mole fractions and pressures between the quaternary experimental results and those calculated from the UNIQUAC formalism using the binary parameters from Table 5. Agreement is good in comparison with the results obtained for 14 quaternary systems (Nagata and Tamura, 1996).

Table 6. Deviations between Calculated and Experimental Vapor-Phase Mole Fractions and Pressures for Methanol (1) + Acetone (2) + Acetonitrile (3) + Benzene (4) at 328.15 K

	$10^3\delta y_1$	$10^3\delta y_2$	$10^3\delta y_3$	$10^3\delta y_4$	δP/kPa	$10^2\delta P/P$
mean	4.1	3.2	2.7	3.4	0.2653	0.30
root-mean square	4.9	3.9	3.3	4.0	0.2960	0.33

Conclusion

Quaternary VLE data for methanol + acetone + acetonitrile + benzene at 328.15 K compare well with those calculated using the UNIQUAC formalism having only binary parameters and are considered to be thermodynamically consistent.

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