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Isobaric Vapor–Liquid Equilibria of Binary Systems of Acetonitrile with Benzene, Toluene, and Methylcyclohexane

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Isobaric vapor–liquid equilibria have been measured at 760 mmHg pressure for the miscible binary systems benzene–acetonitrile and toluene–acetonitrile in a modified Othmer still and for the partially miscible system methylcyclohexane–acetonitrile in a Smith and Bonner still. The liquid-phase activity coefficients have been calculated by taking into account the nonideality in the vapor phase. The data have been correlated with Wilson's equation using a nonlinear least-squares method. The data satisfied Herington's consistency test.

The knowledge of vapor–liquid equilibria (VLE) is essential in the design of an azeotropic or extractive or simple distillation columns. These distillation processes generally operate at atmospheric pressure. Generation of VLE data at atmospheric pressure is, therefore, more desirable than obtaining data at constant temperature although the latter are preferred from a theoretical point of view.

In the present study isobaric VLE have been determined at 760 mmHg pressure for the binary systems benzene–acetonitrile and toluene–acetonitrile in a modified Othmer still (*6*) and for partially miscible binary methylcyclohexane–acetonitrile in a Smith and Bonner (*13*) still. This is a part of our study of the polar solvent–hydrocarbon systems for the separation of hydrocarbons and for testing the predictability of different methods. To our knowledge the VLE data for methylcyclohexane–acetonitrile binary are not reported in the literature. However, Horsley (*5*) has reported that this binary forms an azeotrope at 71.1 °C and 51 vol % (equivalent to 71.7 mol %) acetonitrile. For the benzene–acetonitrile binary, isothermal VLE data at 45 °C are reported by Palmer and Smith (*8*) and Brown and Smith (*2*) and isobaric data at 760 mmHg have been obtained by Boeuve (*1*) and calculated data using the NRTL equation (*11*) are reported by Tripathi and Asselineau (*15*). Isothermal VLE data for the toluene–acetonitrile system at 45 °C are reported by Orye and Prausnitz (*7*).

Experimental Section

(*a*) ***Material.*** Pure benzene, toluene, and methylcyclohexane, supplied by M/S Phillips, were used. The physical properties of these chemicals corresponded to minimum 99.9% purity. The chemicals were dried over 4-Å molecular sieves before use. Acetonitrile (obtained from M/S British Drug House, India), was dried over anhydrous calcium chloride and further purified by fractional distillation at high reflux ratio, using a Helipak packed column, by collecting a heart cut and discarding the first 10% distillate and last 15% residue. The important physical properties (density and refractive index) compare with the literature (*3*) values.

(*b*) ***Apparatus.*** The vapor–liquid equilibrium data for the partially miscible system methylcyclohexane–acetonitrile were obtained in a Smith and Bonner (*13*) type of still provided with a magnetic stirrer. The VLE data for benzene–acetonitrile and toluene–acetonitrile binaries were obtained in a modified Othmer still (*6*) with provision for the vapors to be stirred by a magnetic stirrer. The still was thoroughly lagged to avoid any loss of heat by conduction. The equilibrium vapor temperatures were measured by a mercury-in-glass thermometer within ±0.05 °C. The following stem corrections were also applied in cases of exposed stems:

$$t_c = t_o + 0.000158l(t_o - t_m) \tag{1}$$

where t_c is the corrected temperature, t_o and t_m are the observed and mean temperatures of the exposed stem, respectively, and l is the length of the mercury thread in °C. The pressure of the system was maintained at 760 ± 0.5 mmHg with the help of a suitable pressure regulating device. To establish the equilibrium time, we carried out a number of trial runs on each system for 2, 3, and 4 h. The results obtained in 3 and 4 h were the same. The stills were therefore operated for 4 h in all subsequent runs. At the end, about 2 mL of equilibrated sample was withdrawn in each case for analysis.

(*c*) ***Analysis.*** In all experiments about 650 mL of the liquid phase of known compositions was taken. This composition was considered as unaltered after the withdrawal of vapor sample. In the case of a partially miscible system, the vapor sample was collected in a microburet maintained at 20 °C. The procedure for analysis followed for this partially miscible vapor sample was described earlier (*15*). The vapor samples of benzene–acetonitrile and toluene–acetonitrile systems were analyzed by determining their densities at 20 °C with the help of a calibrated 1-mL pycnometer. From the densities, the compositions were determined from the density–composition calibration chart made earlier at 20 °C.

Results

The liquid-phase activity coefficients were calculated from the following equation (*17*) which takes into account the vapor-phase imperfections:

$$\ln \gamma_i = \ln \frac{y_i}{x_i}\frac{P}{p_i^s} + \frac{(B_{ii} - V_i^L)(P - p_i^s)}{RT} + \frac{P\delta_{ij}(1 - y_i)^2}{RT} \tag{2}$$

where

$$\delta_{ij} = 2B_{ij} - B_{ii} - B_{jj}$$

The second virial coefficients of the nonpolar components methylcyclohexane, benzene, and toluene and polar component acetonitrile were calculated by the correlations of Pitzer and Curl (*9*) and Tsonopoulos (*16*), respectively. However, the values of the constant K_{ij} were taken as zero in the calculation of the second virial cross coefficient, B_{ij}.

The critical constants and other parameters used in the above calculations of second virial coefficients were taken from the literature (*10*, *14*). The vapor pressure data were calculated from the Antoine equation

$$\log p^s = A - B/(C + t) \tag{3}$$

The constants A, B, and C were taken from the literature as reported by Dreisbach (*3*).

The VLE data for the partially miscible system methylcyclohexane (1)–acetonitrile (2) are given in Table I and Figure 1 along with the vapor-phase compositions calculated by the Wilson (*18*) three-parameter equation. The system forms a heteroazeotrope between x_1 = 0.205 and 0.705 and at 71.1 °C with a vapor-

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Table I. Isobaric VLE Data for the Methylcyclohexane (1)-Acetonitrile (2) System at 760 mmHg

no.	equilib temp, °C	liquid molar compn, x_1	vapor molar compn		activity coef			
					exptl		calcd^a	
			y_1 (exptl)	y_1 (calcd)^a	r_1	r_2	r_1	r_2
1	79.7	0.012	0.068	0.069	11.071	0.997	12.932	1.0006
2	75.0	0.049	0.228	0.223	10.457	0.987	9.820	1.009
3	73.1	0.077	0.285	0.283	8.732	1.000	8.128	1.022
4	72.2	0.090	0.298	0.308	8.056	1.023	7.509	1.029
5	72.1	0.098	0.308	0.313	7.632	1.022	7.142	1.035
6	71.1	0.212	0.316	0.357	3.748	1.192	4.061	1.146
7	71.1	0.316	0.316	0.363	2.514	1.373	2.746	1.309
8	71.1	0.391	0.316	0.363	2.032	1.542	2.220	1.470
9	71.1	0.514	0.316	0.360	1.546	1.933	1.678	1.852
10	71.1	0.644	0.316	0.361	1.234	2.639	1.341	2.521
11	72.2	0.823	0.350	0.405	1.027	4.887	1.079	4.553
12	75.7	0.883	0.413	0.438	1.004	6.002	1.035	5.777
13	76.6	0.902	0.436	0.475	1.003	6.742	1.025	6.285
14	78.3	0.913	0.460	0.483	0.990	6.920	1.020	6.603
15	81.4	0.928	0.525	0.494	1.004	6.743	1.014	7.073
16	88.3	0.962	0.662	0.610	0.986	7.558	1.004	8.356
17	93.5	0.982	0.791	0.759	0.991	8.545	1.0009	9.263

^{a} Wilson equation.

Table II. Isobaric VLE Data for the Benzene (1)-Acetonitrile (2) System at 760 mmHg

no.	equilib temp, °C	liquid molar compn, x_1	vapor molar compn		activity coef			
					exptl		calcd^a	
			y_1 (exptl)	y_1 (calcd)^a	r_1	r_2	r_1	r_2
1	80.6	0.020	0.048	0.051	2.545	1.0009	2.480	1.0003
2	80.4	0.027	0.062	0.063	2.355	1.001	2.456	1.0005
3	79.0	0.056	0.125	0.129	2.309	1.005	2.361	1.002
4	78.5	0.065	0.147	0.150	2.269	1.013	2.332	1.003
5	78.0	0.077	0.165	0.173	2.249	1.019	2.295	1.004
6	76.0	0.176	0.293	0.295	1.897	1.035	2.018	1.023
7	74.9	0.242	0.355	0.361	1.732	1.060	1.859	1.046
8	74.4	0.299	0.393	0.403	1.578	1.096	1.737	1.072
9	73.8	0.371	0.438	0.452	1.445	1.155	1.599	1.118
10	73.7	0.380	0.449	0.459	1.429	1.162	1.583	1.125
11	73.4	0.440	0.485	0.494	1.364	1.201	1.483	1.177
12	73.2	0.513	0.519	0.532	1.260	1.301	1.375	1.261
13	73.0	0.5294	0.5294	0.542	1.251	1.324	1.353	1.283
14	73.2	0.581	0.545	0.563	1.169	1.418	1.287	1.366
15	73.4	0.665	0.600	0.602	1.117	1.556	1.194	1.546
16	73.8	0.713	0.626	0.623	1.074	1.684	1.149	1.687
17	74.0	0.767	0.657	0.655	1.042	1.888	1.103	1.891
18	74.4	0.790	0.680	0.667	1.033	1.930	1.086	1.999
19	76.3	0.920	0.801	0.797	1.0002	2.644	1.015	3.013

^{a} Wilson equation.

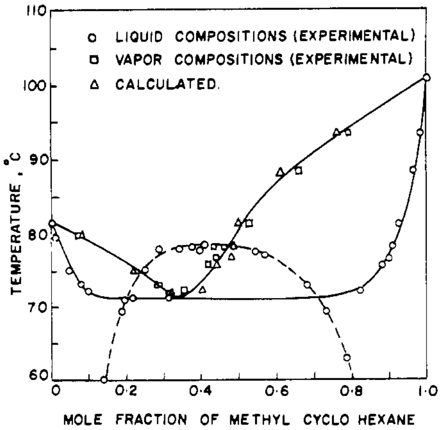

Figure 1. Vapor-liquid equilibrium data for the methylcyclohexane (1)-acetonitrile (2) system at 760 mmHg. Solubility envelope is shown with dotted line.

phase composition of y_1 = 0.316 mole fraction.

The VLE data for benzene (1)-acetonitrile (2) and toluene (1)-acetonitrile (2) systems are presented in Table II and Figure 2 and Table III and Figure 3 , respectively. Both binaries form minimum boiling azeotropes. The benzene-acetonitrile system forms an azeotrope at 73 °C and 52.9 mol % benzene whereas the toluene-acetonitrile system forms an azeotrope at 81.1 °C

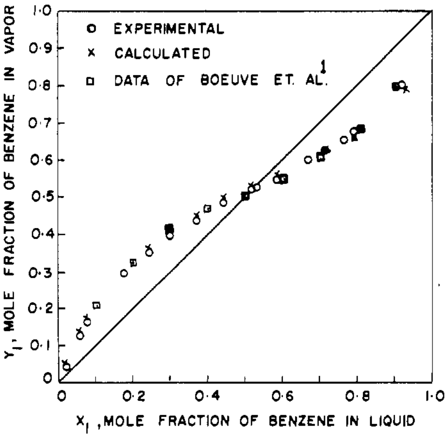

Figure 2. VLE data for the benzene (1)-acetonitrile (2) system at 760 mmHg.

Table III. Isobaric VLE Data for the Toluene (1)-Acetonitrile (2) System at 760 mmHg

no.	equilib temp, °C	liquid molar compn, x_1	vapor molar compn y_1 (exptl)	vapor molar compn y_1 (calcd)[a]	activity coef exptl r_1	activity coef exptl r_2	activity coef calcd[a] r_1	activity coef calcd[a] r_2
1	81.5	0.033	0.051	0.036	3.897	0.989	3.340	1.002
2	81.4	0.069	0.081	0.070	3.067	0.998	3.027	1.007
3	81.1	0.1218	0.1218	0.1174	2.611	1.017	2.642	1.022
4	81.3	0.182	0.154	0.153	2.214	1.047	2.299	1.047
5	81.4	0.221	0.172	0.173	2.026	1.071	2.118	1.069
6	81.8	0.284	0.195	0.198	1.763	1.120	1.878	1.114
7	82.7	0.375	0.230	0.225	1.527	1.193	1.615	1.199
8	84.4	0.533	0.284	0.275	1.253	1.406	1.313	1.424
9	85.6	0.605	0.315	0.298	1.176	1.531	1.219	1.572
10	91.1	0.785	0.417	0.387	1.002	2.034	1.064	2.143
11	93.4	0.840	0.473	0.451	0.986	2.296	1.044	2.408
12	95.6	0.876	0.526	0.507	0.983	2.484	1.022	2.616
13	101.2	0.929	0.665	0.623	0.984	2.637	1.007	2.988
14	103.6	0.956	0.738	0.736	0.988	3.089	1.003	3.214
15	106.7	0.977	0.836	0.837	1.000	3.419	1.0008	3.413
16	107.5	0.982	0.854	0.868	1.0001	3.471	1.0005	3.463

[a] Wilson equation.

Table IV. Constants for the Wilson Equation

system	constants	average/ absolute % error[a] in y_1
methylcyclohexane (1)-acetonitrile (2)	$\Lambda_{ij} = 0.280204$ $\Lambda_{ji} = 0.399257$ $c = 1.419686$	−5.4
benzene (1)-acetonitrile (2)	$\Lambda_{ij} = 0.810132$ $\Lambda_{ji} = 0.274742$	−1.8
toluene (1)-acetonitrile (2)	$\Lambda_{ij} = 0.458895$ $\Lambda_{ji} = 0.470035$	+2.6

[a] % error = (y(exptl) − y(calcd))/y(exptl) × 100.

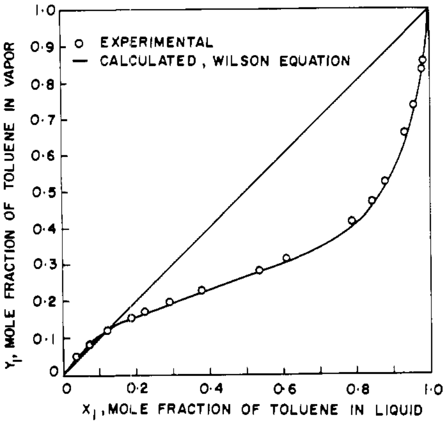

Figure 3. VLE data for the toluene (1)-acetonitrile (2) system at 760 mmHg.

and with 12.18 mol % toluene. These data agree fairly well with those reported in literature (*5*). The VLE data measured experimentally in the present study for the benzene (1)-acetonitrile (2) system are compared in Figure 2 with those reported in the literature (*1*). The two sets of data agree fairly well.

Further, the data have been correlated with Wilson (*18*) two- and three-constant (in case of a partially miscible system) equations by a least-squares fit of the experimental activity coefficient using a nonlinear multiple regression technique in an IBM 360 computer. Redlich-Kister (*12*) and Margules two- and three-constant equations have also been tried to correlate the data, but the deviations between experimental and calculated values were quite large. The best fit was obtained by the Wilson equation (Table IV). The maximum percent error between experimental and calculated values of y_1 was 6.2 for the benzene-acetonitrile system, 7.4 for the toluene-acetonitrile system, and 15 for methylcyclohexane-acetonitrile system in the heterogeneous region. The average percent errors are given in Table IV. The data of all the three systems satisfy Herington's test (*4*) of thermodynamic consistency.

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Glossary

A, B, C	Antoine constants
B_{11} and B_{22}	pure component second virial coefficient, cm^3/mol
B_{12}	second virial cross coefficients, cm^3/mol
P	total pressure
p_1^s and p_2^s	saturated vapor pressure of pure components, mmHg, 1 and 2
R	gas constant, cm^3 atm/(deg mol)
T	temperature, K
t	temperature, °C
V_1^L and V_2^L	liquid molar volumes of components 1 and 2, cm^3-/mol
x_1	liquid (molar composition) mole fraction
y_1	vapor (molar composition) mole fraction
γ_1 and γ_2	liquid-phase activity coefficients of component 1 and 2

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