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Thermodynamic Excess Property Measurements for Acetonitrile–Benzene–n-Heptane System at 45°C

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Vapor-liquid equilibrium, excess enthalpy, and excess volume data for the acetonitrile–benzene–n-heptane system at 45°C are reported. The vapor-liquid equilibrium measurements cover the three binaries, the ternary solubility envelope, and the miscible ternary region. A static equilibrium cell was used, and the phase compositions were obtained by gas-liquid chromatography. The excess enthalpy and excess volume measurements cover only the binaries. A Tronac isothermal titration calorimeter was used for the enthalpy measurements. Glass dilatometers were used to measure the excess volume directly.

The development of suitable equations for correlating the thermodynamic properties of partially miscible multicomponent systems has been hampered by a lack of experimental data. Consequently, a long-range program is under way to supply the needed data for a number of partially miscible ternary systems. To date, binary and ternary vapor-liquid equilibrium data have been reported for the sulfur dioxide–pentane–benzene system at −17.8°C (1).

Data have now been measured for the partially miscible acetonitrile–benzene–n-heptane system at 45°C. Included are vapor-liquid equilibrium (G^E) data for the three binary mixtures and for 51 points in the ternary region. Eighteen of the ternary points are vapor-liquid-liquid equilibria that produce nine tie lines. Excess enthalpy (H^E) and excess volume (V^E) data are also presented for the three binary mixtures. The new binary data compare favorably with literature data on the same systems, and the binary and ternary vapor-liquid equilibrium data

are thermodynamically consistent. Mutual thermodynamic consistency of G^E and H^E data has also been tested with the Gibbs-Helmholtz equation.

EXPERIMENTAL

The acetonitrile and benzene were obtained from Fisher Scientific Co. and the n-heptane from Phillips Petroleum Co. Analysis by gas-liquid chromatography showed the following ratios of impurity areas to total summed areas of the chromatograms: acetonitrile, 0.1%, benzene, 0.04%; n-heptane, 0.11%. Hence, all three compounds were used as received without further purification.

Vapor-Liquid Equilibrium. Figure 1 shows the equipment for the vapor-liquid and the vapor-liquid-liquid equilibrium measurements. The static equilibrium cell has been described previously (1). The water bath was maintained at 45°C by a Haake Unitherm Controller, Model A, sensitive to 0.01°C. Absolute bath temperature was measured with a NBS calibrated thermometer having 1/10°C divisions. Tempera-

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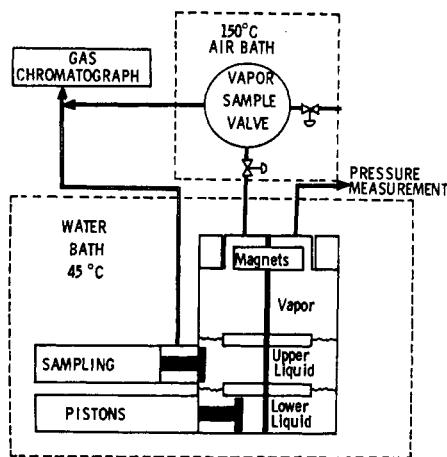
Figure 1. Schematic diagram of static equilibrium cell and accessories

ture fluctuations, monitored with a differential thermometer, were no greater than 0.02°C. If all measurement and control errors were present and in the same direction, the maximum absolute error in cell temperature would have been no more than 0.06°C.

Pressure was measured in an open-ended mercury manometer, 1.3 cm in i.d., connected to the equilibrium cell by a heated stainless steel tube. Mercury levels were read to ±0.05 mm with a Gaertner M911 cathetometer, barometric pressure was measured with a Princo Standard Mercurial Barometer, and all measurements were converted to standard gravity and 0°C. The estimated overall maximum uncertainty was 0.5 mm Hg, arising from two cathetometer readings (±0.05 mm each), possible meniscus deformations (±0.1 mm each), a monometer temperature gradient (±0.1 mm), and a barometer error (±0.1 mm).

In a typical run, the degassed liquids were added to the cell and stirred with magnetically driven paddles until equilibrium had been attained. After pressure measurement, vapor samples amounting to no more than 1% of the total vapor in the cell were drawn into the sampling valve. The latter was located in an air chamber held at 150°C to minimize adsorption losses. Then the liquid samples were captured by retracting the pistons into the position shown by the upper piston in Figure 1. The samples were displaced with mercury from the annular space in the sampling cylinders into a liquid sampling valve.

Both liquid and vapor compositions were determined in triplicate using a Perkin-Elmer 820 gas chromatograph with a thermal conductivity detector. Peak areas were measured with a Leeds-Northrup recorder having a Disc integrator. Complete separation of the three peaks was achieved on two $^1/_8$-in. columns connected in series—the first was 2 ft long and was packed with benzoquinoline (15%) on Chromosorb G; the second was 4 ft long and was packed with didecylphthalate (15%) on Chromosorb G. Matching sets of columns were used on the reference and sensing sides of the chromatograph. Compositions were calculated by a relative response factor technique which takes into account response factor variations due to changing ambient conditions (18).

Excess Enthalpy (Heat of Mixing). Excess enthalpies for each of the three binaries were measured in an isothermal titration calorimeter (Tronac, Inc.) similar to the one described by Christensen et al. (7). The instrument had an injection mechanism mounted inside a bath maintained within ±0.001°C. A piston driven by a synchronous motor injected the titrant at a constant rate through a tube into an "open" 41-cc reaction vessel equipped with a Peltier cooler that withdrew heat at a constant rate. During the titration, a constant temperature was maintained by a variable-input heater controlled

by a thermistor and an electronic circuit which measured differential heat input. Temperature changes ranging up to 0.05°C occurred in the reaction vessel at the start of injection and lasted about $^1/_{30}$ of the total injection time; thereafter, the temperature was controlled within ±0.002°C.

The instrument printed out the results at time intervals that were selected to produce an almost continuous H^E curve. The two halves of each curve were obtained in two separate runs, and the titrations were run to make the two branches overlap in the middle. When the instrument functions properly and the vaporization corrections are correct, the two branches coincide with each other in the overlap region.

Corrections were made for vaporization and condensation effects by assuming that the vapor was always in equilibrium with the liquid. The vaporization correction for an entire run was always less than 1% of the H^E value at the midpoint. However, the potentiometers in the calibration circuits were sensitive to small changes in room temperature, and there were excessive fluctuations in line voltage. Consequently, the instrument did not perform as expected, and the estimated errors of ±2% for the miscible systems and ±5% for the partially miscible systems are higher than normal. A complete description and error analysis of the instrument is available (10) and will be published soon.

Excess Volume (Volume of Mixing). Excess volume data were obtained with dilatometers such as the one shown in Figure 2. In a typical run, the cell was filled with clean, degassed mercury, and then weighed amounts of liquids A and B were injected into the two tips by a syringe with a long Teflon needle. If necessary, additional mercury was added to raise the level to a convenient point in the capillary at the bath temperature. The distance of the mercury surface from a mark was measured with a cathetometer before and after mixing, and the change in level was used to calculate V^E in cc/mol. Enough cells were used to cover the entire composition range in each run.

A detailed analysis of the errors involved in these measurements is available (19) and will be published soon. The errors arising from equipment limitations were estimated as: capillary calibrations (±0.4%), temperature variations (equivalent to 0.02 cc/mol), mercury height measurements (0.05 mm for each of four measurements), compressibility of liquid and cell (0.3%), specific volume of mercury displaced as it changes from the cell temperature to the temperature in the stem (maximum of 0.4% in V^E). Additively, these errors were estimated to be 0.006 cc/mol for acetonitrile–benzene, 0.009 cc/mol for acetonitrile–n-heptane, and 0.010 cc/mol for benzene–n-heptane. The RMSD values obtained when a polyno-
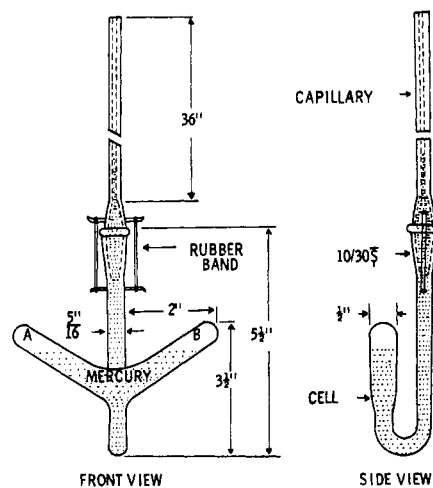

Figure 2. Dilatometer cell as it appears before A and B are mixed

mial was fitted to the various sets of data were well within these estimates.

DATA REDUCTION

The vapor-liquid equilibrium data were reduced to activity coefficients (γ_i) with the rigorous thermodynamic equation:

$$\gamma_i = \frac{y_i P}{x_i P_i'} \frac{\phi_{i,P}}{\phi_{i,P_i'}} \exp\left[\frac{(P_i' - P)V^L}{RT}\right] \qquad (1)$$

The standard state was the pure liquid i at the temperature and pressure of the system.

The vapor pressures (P_i'), obtained from a smoothing of literature data, were: 0.2749 atm for acetonitrile (15), 0.2939 atm for benzene (17), and 0.1501 atm for n-heptane (24).

The vapor pure component and mixture fugacity coefficients, represented in Equation 1 by $\phi_{i,P_i'}$ and $\hat{\phi}_{i,P}$, respectively, were approximated with the virial equation of state truncated after the second term, which should be accurate for this low-pressure system. Second virial coefficients for the mixture were related to the pair coefficients by (21)

$$B = \sum_i \sum_j y_i y_j B_{ij} \qquad (2)$$

The pair coefficients used in the data reduction were as follows:

$$B_{11} = -4797 \qquad B_{22} = -1298 \qquad B_{33} = -2345$$

$$B_{12} = -1167 \qquad B_{13} = -1639 \qquad B_{23} = -1765$$

The cross-coefficients were estimated with the O'Connell-Prausnitz correlation (12), but are not expected to be very accurate for the mixtures containing acetonitrile. The vapor molar volume was calculated from:

$$\frac{PV}{RT} = 1 + \frac{B}{V} \qquad (3)$$

The pure component fugacity coefficients were obtained from:

$$\ln \phi_{i,P_i'} = -\ln Z_i + \frac{2B_{ii}}{V_i} \qquad (4)$$

where the compressibility factor was given by:

$$Z = PV/RT \qquad (5)$$

The mixture fugacity coefficients were obtained from:

$$\ln \hat{\phi}_{i,P} = -\ln Z + \frac{2}{V} \sum_j y_j B_{ij} \qquad (6)$$

The excess Gibbs free energy was calculated from the activity coefficients using:

$$G^E = RT \sum_i x_i \ln \gamma_i \qquad (7)$$

The data were tested for thermodynamic consistency by plotting $\ln \gamma_1/\gamma_2$ vs. x_1. According to the Gibbs-Duhem equation, the ratio of areas above and below the curve should be unity because the volume correction term was negligible.

The maximum expected errors in activity coefficients (γ_i) and in G^E due to equipment limitations are given in Tables I and II, respectively. They are based on maximum possible errors in x, y, P, and t due to equipment inaccuracy.

RESULTS AND DISCUSSION

Binary Vapor-Liquid Equilibrium Data. The vapor-liquid equilibrium data at 45°C are given in Table III. (The tabulation of activity coefficients and excess free energy values has been deposited with the ACS Microfilm Deposi-

Table I. Maximum Percentage Error in Activity Coefficients Due to Equipment Limitations

System	γ	Liquid concentration of lower numbered component						
		0.05	0.10	0.20	0.50	0.80	0.90	0.95
Acetonitrile[1]–	γ_1	5.2	2.9	1.8	1.7	1.1	1.1	1.1
benzene[2]	γ_2	1.0	1.0	1.0	1.4	1.8	2.8	4.9
Acetonitrile[1]–	γ_1	4.2	2.4	Region of partial				1.1
n-heptane[3]	γ_3	1.8	1.9	miscibility				4.8
Benzene[2]–	γ_2	5.2	2.9	1.9	1.7	1.1	1.1	1.0
n-heptane[3]	γ_3	1.7	1.6	1.6	2.4	2.7	4.8	8.1

Table II. Maximum Error ($\pm$Cal/Mol) in G^E Values Due to Equipment Limitations

System	Liquid concentration of lower numbered component						
	0.05	0.10	0.20	0.50	0.80	0.90	0.95
Acetonitrile[1]– benzene[2]	4.8	4.3	3.5	2.5	3.8	4.5	5.0
Acetonitrile[1]– n-heptane[3]	9.7	9.6	Region of partial				5.3
Benzene[2]– n-heptane[3]	8.8	8.1	7.2	4.2	2.6	3.4	3.8

Table III. Binary Vapor-Liquid Equilibrium Data at 45°C

x_i	y_i	P	x_i	y_i	P
Acetonitrile($i = 1$)– Benzene[2]			Acetonitrile($i = 1$)– n-Heptane[3] Experimental Values		
0.0247	0.0682	0.3084	0.0213	0.4583	0.2671
0.0744	0.1531	0.3270	0.0471	0.5729	0.3295
0.2221	0.3018	0.3534	0.0813	0.6502	0.3987
0.3091	0.3670	0.3618	0.1016	0.6546	0.4124
0.4145	0.4361	0.3663	0.9372	0.6546	0.4124
0.5266	0.4962	0.3667	0.9646	0.7142	0.3759
0.5680	0.5146	0.3653	0.9755	0.7647	0.3524
0.6858	0.5987	0.3568	0.9761	0.7694	0.3517
0.7953	0.6759	0.3433	0.9854	0.8242	0.3279
0.8912	0.7749	0.3222			
0.9833	0.9516	0.2847			
Benzene($i = 2$)– n-Heptane[3]			Acetonitrile($i = 1$)– n-Heptane[3] Adjusted Data		
0.0604	0.1551	0.1664	0.002	0.0780	0.1626
0.1180	0.2645	0.1812	0.020	0.4343	0.2610
0.1432	0.3082	0.1882	0.030	0.5182	0.3038
0.2370	0.4396	0.2080	0.040	0.5698	0.3375
0.2841	0.4906	0.2182	0.050	0.6022	0.3626
0.3105	0.5237	0.2241	0.060	0.6222	0.3799
0.3777	0.5783	0.2358	0.070	0.6343	0.3910
0.4195	0.6157	0.2410	0.080	0.6416	0.3980
0.4798	0.6672	0.2528	0.090	0.6472	0.4035
0.5856	0.7288	0.2645	0.102	0.6567	0.4128
0.6412	0.7639	0.2713	0.937	0.6491	0.4124
0.6913	0.7893	0.2762	0.940	0.6505	0.4117
0.7738	0.8415	0.2853	0.950	0.6690	0.4017
0.9183	0.9288	0.2929	0.960	0.7019	0.3848
0.9779	0.9759	0.2962	0.970	0.7442	0.3648
			0.980	0.7973	0.3421
			0.990	0.8720	0.3140

tory Service.) The Gibbs-Duhem consistency test area ratio (smaller area to larger area regardless of sign) is 0.98 for the acetonitrile[1]–benzene[2] system. Except for the points at $x_1 = 0.5680$ and $x_1 = 0.9833$, the data fall within the bounds of maximum experimental error owing to equipment limitations. Furthermore, the data compare favorably with those by Brown and Smith (6) at the same temperature. There is an azeotrope in the system which falls at about $x_1 = 0.463$ at 45°C.

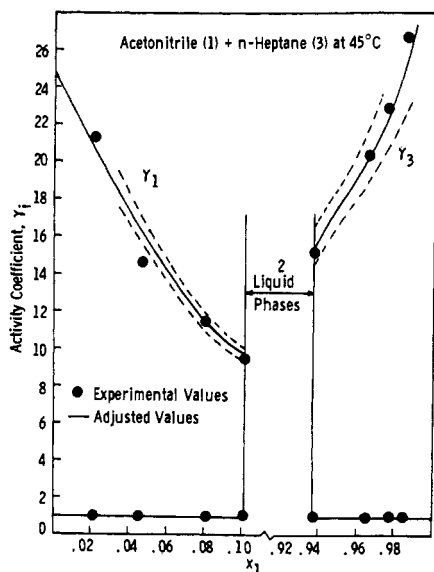The consistency test area ratio for the benzene[2]–n-heptane-

Figure 3. Experimental and adjusted activity coefficients for acetonitrile–n-heptane binary at 45°C

Dashed lines enclose possible error band due to equipment limitations
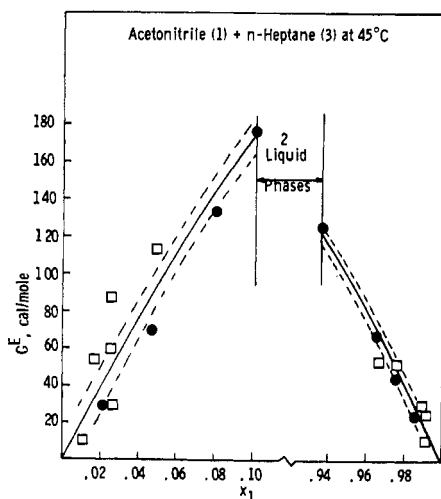

Figure 4. Comparison of experimental and adjusted G^E values for acetonitrile–n-heptane binary at 45°C with data of Werner and Schuberth at 20°C

Dashed lines enclose possible error band due to equipment limitations
□ 20° C (23). ● 45° C (this work). — 45° C (adjusted data)

Table IV. Vapor-Liquid and Vapor-Liquid-Liquid Equilibrium Data for the Acetonitrile[1]–Benzene[2]–n-Heptane[3] System at 45°C

N	x_1	x_2	y_1	y_2	P (atm)
1	0.1167	0.0342	0.6297	0.0321	0.4120
2	0.9129	0.0188	0.6297	0.0321	0.4120
3	0.1451	0.0562	0.6290	0.0504	0.4133
4	0.8954	0.0325	0.6290	0.0504	0.4133
5	0.1642	0.0907	0.6157	0.0741	0.4161
6	0.8605	0.0552	0.6157	0.0741	0.4161
7	0.1711	0.1104	0.6076	0.0889	0.4168
8	0.8406	0.0684	0.6076	0.0889	0.4168
9	0.2225	0.1455	0.5957	0.1146	0.4161
10	0.7810	0.1002	0.5957	0.1146	0.4161
11	0.2466	0.1727	0.5987	0.1323	0.4170
12	0.7529	0.1229	0.5987	0.1323	0.4170
13	0.2674	0.1709	0.5850	0.1355	0.4183
14	0.7235	0.1333	0.5850	0.1355	0.4183
15	0.2723	0.1771	0.5889	0.1367	0.4175
16	0.7025	0.1356	0.5889	0.1367	0.4175
17	0.4398	0.1882	0.5742	0.1521	0.4204
18	0.5803	0.1737	0.5742	0.1521	0.4204
19	0.0827	0.1417	0.5299	0.1384	0.3705
20	0.0686	0.2483	0.4422	0.2444	0.3567
21	0.0297	0.8648	0.0874	0.8367	0.3115
22	0.1460	0.7601	0.2816	0.6427	0.3557
23	0.8869	0.0991	0.7170	0.1810	0.3486
24	0.8018	0.1669	0.6234	0.2387	0.3772
25	0.7427	0.2339	0.5906	0.3092	0.3757
26	0.6497	0.3312	0.5445	0.3995	0.3732
27	0.5719	0.4120	0.5150	0.4453	0.3754
28	0.4733	0.5137	0.4688	0.5050	0.3734
29	0.4615	0.5030	0.4600	0.4774	0.3791
30	0.4393	0.4827	0.4649	0.4239	0.3887
31	0.3974	0.4407	0.4669	0.3589	0.3962
32	0.3527	0.3942	0.4810	0.3146	0.4011
33	0.0746	0.7427	0.2053	0.6738	0.3530
34	0.1345	0.6930	0.2855	0.5862	0.3663
35	0.2684	0.5872	0.3914	0.4766	0.3882
36	0.3470	0.5231	0.4395	0.4287	0.3961
37	0.4020	0.4791	0.4582	0.4024	0.3997
38	0.5212	0.3845	0.5056	0.3484	0.4018
39	0.6021	0.3219	0.5247	0.3228	0.4000
40	0.1177	0.3317	0.4487	0.2878	0.3887
41	0.2602	0.2766	0.5307	0.2152	0.4166
42	0.3790	0.2314	0.5608	0.1794	0.4167
43	0.4282	0.2123	0.5680	0.1678	0.4180
44	0.4779	0.2977	0.5262	0.2493	0.4078
45	0.6093	0.2229	0.5482	0.2082	0.4100
46	0.0622	0.5379	0.2555	0.5211	0.3400
47	0.1003	0.5151	0.3288	0.4549	0.3591
48	0.2648	0.4206	0.4603	0.3318	0.3970
49	0.3704	0.3597	0.4973	0.2884	0.4045
50	0.2958	0.1880	0.5795	0.1452	0.4163
51	0.4891	0.1970	0.5691	0.1622	0.4159

[3] data is 0.99. The azeotrope falls at about $x_2 = 0.965$ at 45°C.

The partially miscible acetonitrile[1]–n-heptane[3] mixture forms a heterogeneous azeotrope. At 45°C, the liquid-phase compositions are $x_1 = 0.1016$ and $x_1 = 0.9372$, with a corresponding vapor composition of $y_1 = 0.6546$. The "adjusted data" tabulated for this system were obtained by calculating thermodynamically consistent vapor compositions from experimental x-P-t data. The procedure was described by Van Ness (21) and programmed by Cunningham (8). Figure 3 shows both the experimental and "adjusted" activity coefficients, illustrating the thermodynamic consistency of the experimental data. Figure 4 presents a similar comparison for the G^E values and also shows how the new data compare with the data of Werner and Schuberth at 20°C (23).

Ternary Vapor-Liquid Equilibrium Data. The ternary vapor-liquid and vapor-liquid-liquid equilibrium data for

the acetonitrile[1]–benzene[2]–n-heptane[3] system at 45°C are given in Table IV (full table deposited with ACS Microfilm Depository Service includes γ and G^E values). The data point numbers are denoted by N. Points 1–18 are along the solubility envelope, and the connected points (such as 1–2 and 3–4) have identical vapor compositions because the vapor was measured in equilibrium with two liquid phases. The liquid compositions are the tie lines for the binodal curve.

Figure 5 shows the tie-line data plotted on both Hand and Othmer-Tobias coordinates. Since the data do not exhibit much scatter from straight lines, they are judged acceptable on an empirical basis.

An extrapolation to the plait point by the method of Treybal (20) gives the location of the plait point as $x_1 = 0.509$, $x_2 = 0.185$, and $x_3 = 0.306$.

Most of the data in the miscible ternary region were taken by adding a third component in increments to an original binary mixture to maintain a constant ratio of the two initial com-
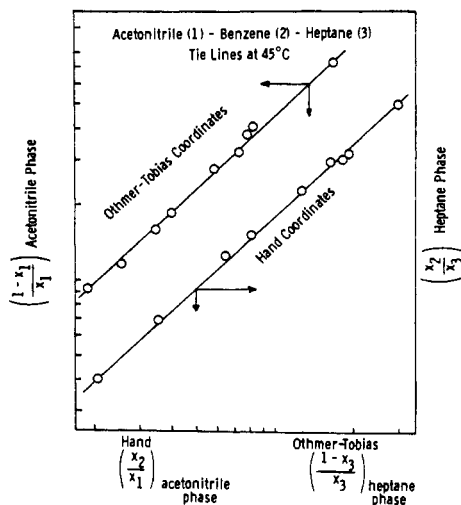
Figure 5. Tie-line data plotted on both hand and Othmer-Tobias coordinates

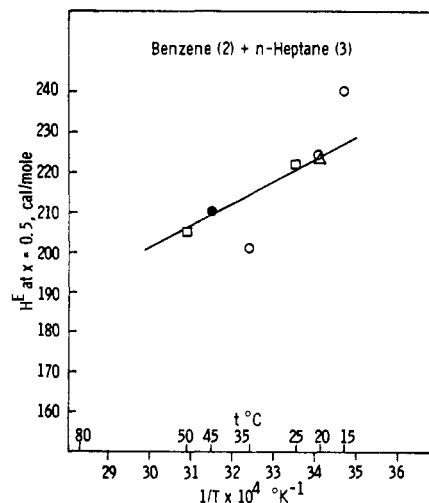**Figure 6. Comparison of midpoint H^E values at various temperatures for benzene–n-heptane system**

○ (22). △ (2). □ (11). ● This work

ponents. The thermodynamic consistency of most of the ternary data, except for the points along the solubility envelope, was tested directly using the equation:

$$\int_{x_k=0}^{x_k} \left(\ln \frac{\gamma_k{}^{r+1}}{\gamma_i \gamma_j{}^r} \right) dx_i - \left(\frac{G^E}{RT} \right)_{x_k=0} + \left(\frac{G^E}{RT} \right)_{x_k} = 0 \qquad (8)$$

which has been derived elsewhere (13). The integration is performed at constant ratio (r) of components i and j. All of the data thus analyzed were consistent, except for points 26, 33, and 35 in Table IV.

Binary H^E Data. Over 100 H^E points were obtained on each miscible binary; representative data are given in

Table V where some points were selected specifically to show any discrepancy in the overlap region. The complete tables are available elsewhere (13).

The acetonitrile[1]–benzene[2] data fall slightly lower than data by Brown and Fock (5) and slightly higher than data by Prausnitz and Anderson (14). The two branches of the H^E curve differ by 1.4 cal at $x_1 = 0.6431$. This discrepancy is believed due to a variation in calibration factor between runs.

The benzene[2]–n-heptane[3] H^E curves also had a discontinuity of 1.4 cal at $x_2 = 0.6434$. These data are in general agreement with the data at 25° and 50°C by Lundberg (11), and at 20°C by Brown (2), as shown in Figure 6. However, the data by Vilcu and Stanciu (22) do not show the same trend with temperature.

The acetonitrile[1]–n-heptane[3] data showed abrupt changes in slope at the solubility limits measured in the equilibrium cell, indicating that the calorimeter may be a useful device for measurement of solubilities.

Binary V^E Data. The excess volume data for the three binary systems are given in Table VI. The benzene–n-

Table V. Excess Enthalpy at 45°C, Cal/Mol

Acetonitrile[1]–Benzene[2]

x_1	H^E	x_1	H^E
0.0848	33.0	0.6025	117.5
0.1778	59.7	0.6460	115.2
0.2537	78.1	0.6431	114.4
0.3309	94.0	0.6805	111.3
0.4048	105.8	0.7408	102.9
0.4812	114.1	0.8016	89.1
0.5403	117.4	0.8669	67.8
0.5708	117.9	0.9361	36.6

Benzene[2]–n-Heptane[3]

x_2	H^E	x_2	H^E
0.0779	48.1	0.5991	212.1
0.1446	87.1	0.6245	209.9
0.2022	117.3	0.6226	208.9
0.2828	153.4	0.6875	197.9
0.3487	177.2	0.7557	177.4
0.4034	192.7	0.8250	145.4
0.4819	207.6	0.8919	102.3
0.5646	213.2	0.9519	51.4

Acetonitrile[1]–n-Heptane[3]

x_1	H^E	x_1	H^E
0.0171	44.8	0.9301	166.2
0.0337	90.9	0.9327	166.2
0.0465	125.0	0.9353	165.9
0.0590	155.6	0.9380	163.9
0.0682	184.5	0.9460	147.9
0.0801	209.5	0.9652	99.5
0.0917	230.8	0.9823	52.5

Table VI. Excess Volume Data at 45°C, cc/mole

Acetonitrile[1]–Benzene[2]

x_1	V^E	x_1	V^E
0.088	−0.086	0.505	−0.098
0.094	−0.093	0.615	−0.047
0.146	−0.125	0.658	−0.035
0.193	−0.141	0.696	−0.022
0.313	−0.154	0.793	+0.006
0.388	−0.140	0.903	+0.017

Benzene[2]–n-Heptane[3]

x_2	V^E	x_2	V^E
0.064	0.124	0.502	0.579
0.187	0.325	0.699	0.516
0.302	0.452	0.802	0.399
0.412	0.539	0.894	0.250

Acetonitrile[1]–n-Heptane[3]

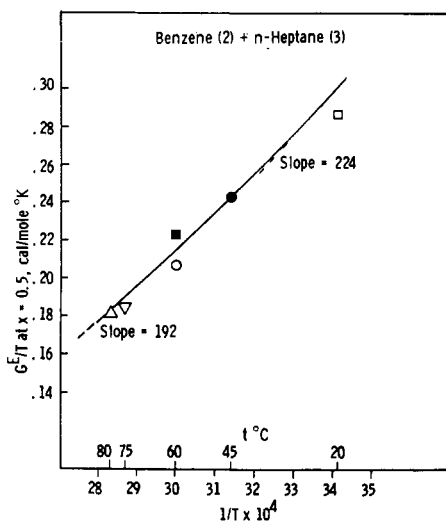| x_1	V^E	x_1	V^E
0.037	0.190	0.955	0.139
0.057	0.293	0.963	0.118
0.072	0.356	0.973	0.088
0.079	0.361	0.980	0.066
0.090	0.428	0.996	0.009

Figure 7. Gibbs-Helmholtz test for benzene–n-heptane data

■ (4). ▽ (9). ○ (16). △ (3). ● This work. □ (23)

heptane data compare favorably with the data by Brown and Ewald (4) at 25°C and by Yaun (25) at 60°C. Temperature has little effect on V^E for this binary.

Mutual Consistency of G^E and H^E Data. Any G^E data available at more than one temperature were tested for mutual consistency with H^E data by using the Gibbs-Helmholtz equation:

$$(H^E)_{x_1} = \left[\frac{\partial(G^E/T)}{\partial(1/T)}\right]_{x_1} \tag{9}$$

This equation relates the slope of the G^E/T curve, with respect to reciprocal temperature, to the excess enthalpy.

For the acetonitrile–n-heptane system, the only other reported G^E data are at 20°C (23) and they scatter too much to permit the test.

For acetonitrile–benzene, the test was performed at $x = 0.5$ using G^E data at 20°C (23) and 45°C. The slope of the line at 45°C was based on the midpoint valve of H^E at 45°C, and was drawn as a straight line because the temperature dependence of H^E was unknown. Both sets of G^E data appeared consistent with the H^E data because the line passed very close to the G^E/T point at 20°C.

Figure 7 shows the Gibbs-Helmholtz test for the benzene–n-heptane system. The curve was drawn in both directions from the 45°C point (which had an area ratio of 0.99), and the slope was varied to be compatible with the H^E curve in Figure 6. The data at 45°C are consistent with the data at 80°C (3) which had the next best area ratio of 0.91. Data at 60°C by Renon (16) were insufficient to obtain an area ratio. Data of Brown and Ewald (4) at 60°C had an area ratio of 0.73, and data by Fu and Lu (9) at 75°C had an area ratio of 0.87. Data by Werner and Schuberth at 20°C (23) also had an area ratio of 0.87.

Miscellaneous Observations. All three binary mixtures form azeotropes at 45°C.

The excess entropy and excess volume are positive for the benzene–n-heptane and acetonitrile–n-heptane systems.

The excess entropy for acetonitrile–benzene is negative, though at high values of x_1 it is small and could even be positive. The excess volume is negative except at high values of x_1.

The trend of the ternary G^E data indicates that the region of the plait point has the highest excess free energy in the ternary system. It also appears to be the point with the highest pressure and thus would be a ternary azeotrope.

NOMENCLATURE

B	= second virial coefficient (cc/mol)
G^E	= excess Gibbs free energy (cal/mol)
H^E	= excess enthalpy (cal/mol)
P	= pressure (atm)
P'	= vapor pressure (atm)
R	= gas constant (1.9872 cal/mol °K)
T	= temperature (°K)
V	= vapor molar volume (cc/mol)
V^L	= liquid molar volume
V^E	= excess volume (cc/mol)
x_i	= liquid molar composition of component i
y_i	= vapor molar composition of component i
Z	= compressibility factor

GREEK LETTERS

γ	= activity coefficient
$\hat{\phi}_{i,P}$	= fugacity coefficient in a mixture
$\phi_{i,P_i'}$	= pure component fugacity coefficient

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