Excess Thermodynamic Functions for Ternary Systems. 4. Total-Pressure Data and G^E for Acetonitrile–Ethanol–Water at 50 °C

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Isothermal $P-X$ data for the ternary system acetonitrile–ethanol–water at 50 °C are reported. Data are also presented for the constituent binaries at 50 °C. Reduction of the data by Barker's method allows calculation of G^E.

The data set reported here comprises VLE measurements for the system acetonitrile (1)–ethanol (2)–water (3) at 50 °C. Experimental results are presented for the three constituent binaries and for six runs on ternary mixtures formed by additions of each pure constituent to mixtures of the other two in molar proportions of 2 to 1.

Data were taken with the total-pressure apparatus of Gibbs and Van Ness (*7*), modified as described briefly in part 3 (*5*) of this series of papers.

The acetonitrile was chromatoquality reagent from Matheson Coleman and Bell; the reagent-grade ethanol was supplied by U.S. Industrial Chemicals, and the water was doubly deionized. Except for degassing, all reagents were used as received, with indicated purities of at least 99.8 mol %. Vapor pressures of the pure constituents as measured during the course of these experiments and their comparison with literature values are reported in Table I. Because of the excellent reproducibility of these measurements, P_i^{sat} values in all calculations are fixed at average values.

Results and Correlations

Tables II through IV give experimental values of total pressures for the three constituent binaries, and Table V contains all data for the six runs made with ternary mixtures. Data reduction is by Barker's method, with analytical expressions for G^E provided by Margules or modified Margules expressions for the binary systems and by the Wohl equation for the ternary data. The procedures are fully described elsewhere (*1*, *2*).

Table I. Vapor Pressures of Pure Constituents at 50 °C in kPa

	acetonitrile (1)	ethanol (2)	water (3)
present work	33.859	29.490	12.363
	33.860	29.491	12.342
	33.864	29.494	12.348
	33.864	29.496	12.349
av value	33.862	29.493	12.350
lit. values	33.845 (*8*)	29.481 (*11*)	12.345 (*3*, *11*)
	33.872 (*6*)	29.494 (*4*)	12.349 (*9*)
		29.507 (*10*)	

Table II. Total-Pressure Data for Acetonitrile (1)-Ethanol (2) at 50 °C

x_1	x_2	P/kPa
0.0	1.0000	29.496
0.0518	0.9482	33.343
0.1418	0.8582	38.000
0.2169	0.7831	39.878
0.3163	0.6837	41.203
0.4065	0.5935	41.952
0.4864	0.5136	42.313
0.5642	0.4358	42.395
0.6391	0.3609	42.239
0.7063	0.2937	41.851
0.7923	0.2077	40.854
0.8724	0.1276	39.204
0.9500	0.0500	36.499
1.0000	0.0	33.864

Table III. Total-Pressure Data for Acetonitrile (1)-Water (3) at 50 °C

x_1	x_3	P/kPa
0.0	1.0000	12.348
0.0328	0.9672	22.829
0.0974	0.9026	32.279
0.1699	0.8301	35.358
0.2261	0.7739	36.180
0.2846	0.7154	36.672
0.3556	0.6444	37.009
0.4215	0.5785	37.262
0.5041	0.4959	37.527
0.5748	0.4252	37.777
0.6687	0.3313	38.020
0.7418	0.2582	38.146
0.8330	0.1670	37.971
0.9026	0.0974	37.149
0.9472	0.0528	36.146
1.0000	0.0	33.860

Table IV. Total-Pressure Data for Ethanol (2)-Water (3) at 50 °C

x_2	x_3	P/kPa
0.0	1.0000	12.363
0.0325	0.9675	16.247
0.0575	0.9425	18.518
0.0920	0.9080	20.686
0.1244	0.8756	22.344
0.1587	0.8413	23.393
0.2007	0.7993	24.303
0.2388	0.7612	25.005
0.2813	0.7187	25.514
0.3598	0.6402	26.258
0.4403	0.5597	27.030
0.5214	0.4786	27.658
0.6405	0.3595	28.495
0.7701	0.2299	29.121
0.8726	0.1274	29.474
0.9589	0.0411	29.518
1.0000	0.0	29.490

In particular, the data for the acetonitrile (1)–ethanol (2) and the ethanol (2)–water (3) binaries are correlated by the Margules equation:

$$g_{ij} \equiv \frac{G^E_{ij}}{RT} = [(A_{ji}x_i + A_{ij}x_j) - (\lambda_{ji}x_i + \lambda_{ij}x_j)x_ix_j]x_ix_j \quad (1)$$

Four parameters are required for acetonitrile–ethanol but only three for ethanol–water. In the latter case

$$\lambda_{ij} = \lambda_{ji}$$

For acetonitrile (1)–water (3) the five-parameter modified Margules equation is required for correlation of the data:

$$g_{13} \equiv \frac{G^E_{13}}{RT} = \left[(A_{31}x_1 + A_{13}x_3) - \frac{\alpha_{13}\alpha_{31}x_1x_3}{\alpha_{13}x_1 + \alpha_{31}x_3 + \eta x_1x_3}\right]x_1x_3 \quad (2)$$

0021-9568/79/1724-0130$01.00/0

Table V. Total-Pressure Data for Acetonitrile (1)-Ethanol (2)-Water (3) at 50 °C

x_1	x_2	x_3	P/kPa
1.0000	0.0	0.0	33.864
0.3326	0.6674	0.0	41.361
0.3273	0.6570	0.0157	41.326
0.3153	0.6327	0.0520	41.033
0.3002	0.6025	0.0973	40.639
0.2838	0.5695	0.1467	40.194
0.2639	0.5297	0.2064	39.521
0.2507	0.5031	0.2462	39.072
0.2341	0.4699	0.2960	38.477
0.2172	0.4358	0.3470	37.828
0.0	1.0000	0.0	29.491
0.6694	0.3306	0.0	42.089
0.6546	0.3233	0.0221	42.060
0.6310	0.3116	0.0574	41.948
0.6010	0.2969	0.1021	41.749
0.5687	0.2809	0.1504	41.434
0.5291	0.2613	0.2096	40.999
0.5023	0.2481	0.2496	40.641
0.4696	0.2319	0.2985	40.177
0.4295	0.2121	0.3584	39.580
1.0000	0.0	0.0	33.859
0.6700	0.0	0.3300	38.007
0.6543	0.0234	0.3223	38.460
0.6314	0.0576	0.3110	38.988
0.6036	0.0991	0.2973	39.526
0.5704	0.1487	0.2809	40.025
0.5305	0.2082	0.2613	40.451
0.5040	0.2478	0.2482	40.635
0.4705	0.2977	0.2318	40.785
0.4378	0.3465	0.2157	40.833
0.0	0.0	1.0000	12.342
0.3366	0.0	0.6634	36.996
0.3296	0.0208	0.6496	37.116
0.3177	0.0561	0.6262	37.286
0.3022	0.1022	0.5956	37.416
0.2842	0.1559	0.5599	37.493
0.2646	0.2140	0.5214	37.483
0.2511	0.2544	0.4945	37.447
0.2341	0.3048	0.4611	37.269
0.2174	0.3544	0.4282	37.250
0.0	1.0000	0.0	29.494
0.0	0.3433	0.6567	26.187
0.0211	0.3360	0.6429	28.164
0.0575	0.3235	0.6190	30.845
0.1056	0.3070	0.5874	33.390
0.1560	0.2897	0.5543	35.219
0.2186	0.2683	0.5131	36.894
0.2596	0.2542	0.4862	37.637
0.3103	0.2368	0.4529	38.370
0.3614	0.2193	0.4193	38.930
0.0	0.0	1.0000	12.349
0.0	0.6697	0.3303	28.608
0.0203	0.6561	0.3236	30.229
0.0565	0.6318	0.3117	32.436
0.1028	0.6008	0.2964	34.684
0.1537	0.5667	0.2796	36.676
0.2137	0.5266	0.2597	38.160
0.2541	0.4995	0.2464	39.008
0.3161	0.4580	0.2259	39.995
0.3514	0.4344	0.2142	40.359

The ternary data are well fit by the simple equation

$$g_{123} = g_{12} + g_{13} + g_{23} + Cx_1x_2x_3 \qquad (3)$$

Correlations for the g_{ij} are provided by the binary data alone; the parameter C is found by regression of just the ternary data.

Second virial coefficients B_{ij} required to account for vapor-phase nonidealities are estimated by the method of Tsonopoulos (*12*).

Results of the correlations of data for the binary systems, together with all ancillary information, are summarized in Table VI. Correlation of the data for the ternary system, with binary parameters fixed at values as given in Table VI, yields for the ternary parameter the value

$$C = 3.686 \pm 0.007$$

The root-mean-square ΔP for the ternary data is 0.056 kPa; the maximum $|\Delta P|$ is 0.120 kPa. Inclusion of higher order ternary terms in eq 3 results in no significant improvement in the quality of correlation.

Table VI. Summary of Results for Binary Systems at 50 °C[a]

	acetonitrile (1)-ethanol (2)	acetonitrile (1)-water (3)	ethanol (2)-water (3)
P_i^{sat}, kPa	33.862	33.862	29.493
P_j^{sat}, kPa	29.493	12.350	12.350
V_i^L, cm³/mol	54.71	54.71	60.36
V_j^L, cm³/mol	60.36	18.23	18.23
B_{ii}, cm³/mol	−4036	−4036	−1706
B_{jj}, cm³/mol	−1706	−1674	−1674
B_{ij}, cm³/mol	−1142	−287	−948
A_{ij}	1.292 ± 0.029	2.587 ± 0.007	1.697 ± 0.007
A_{ji}	1.235 ± 0.030	2.000 ± 0.009	0.929 ± 0.012
λ_{ij}	0.047 ± 0.143		0.313 ± 0.034
λ_{ji}	0.615 ± 0.150		0.313 ± 0.034
α_{ij}		1.202 ± 0.071	
α_{ji}		0.578 ± 0.044	
η		−0.679 ± 0.079	
RMS ΔP, kPa	0.079	0.032	0.054
max $\|\Delta P\|$, kPa	0.176	0.063	0.134
x_i^{az}	0.5454	0.7560	0.9439
P^{az}, kPa	42.419	38.140	29.537

[a] Pairs of components are listed in the order i, j.

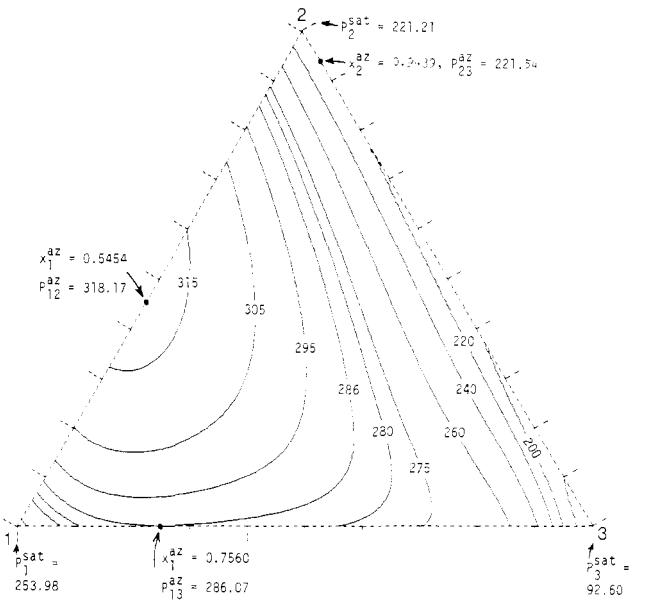

Figure 1. Computer-generated contour diagram showing lines of constant P (in mmHg) on a liquid-mole-fraction grid for acetonitrile (1)-ethanol (2)-water (3) at 50 °C.

Discussion

The ethanol-water binary is the only system for which literature values are available for comparison with our results. Pemberton and co-workers (*10*, *11*) report total-pressure values at 50 °C as part of an extensive data set for both VLE and H^E taken over a wide temperature range. Comparison of total pressures calculated from our correlation with their smoothed values shows only fair agreement:

$$\text{RMS } \Delta P = 0.10 \text{ kPa}$$

$$\text{max } |\Delta P| = 0.26 \text{ kPa}$$

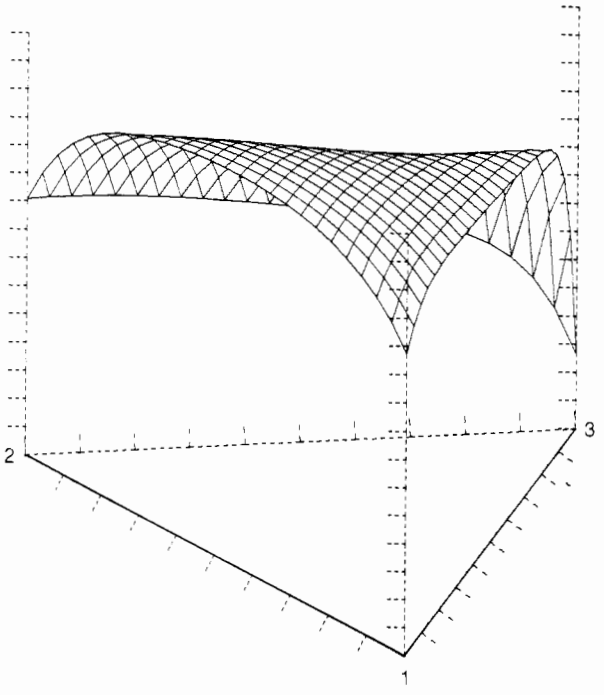

Figure 2. Computer-generated pictorial view of the $P-x$ surface for acetonitrile (1)–ethanol (2)–water (3) at 50 °C.

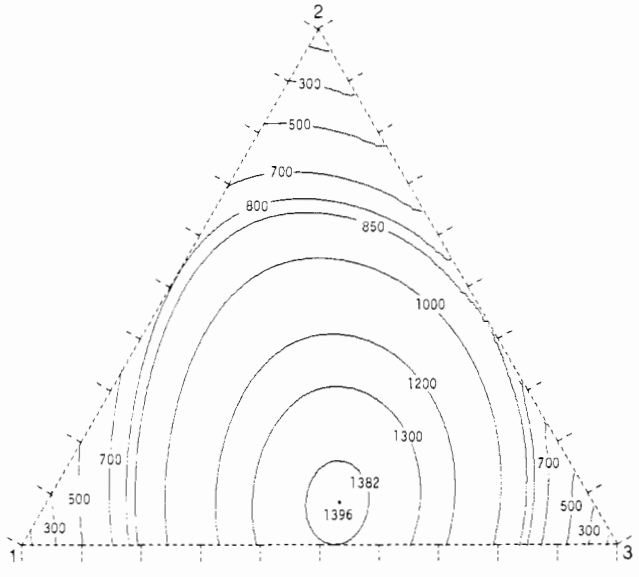

Figure 3. Computer-generated contour diagram showing lines of constant G^E_{123} (in J/mol) on a liquid-mole-fraction grid for acetonitrile (1)–ethanol (2)–water (3) at 50 °C.

The results of this study are displayed pictorially by Figures 1 through 4. It is evident from Figure 1 that each binary system contains a maximum-pressure azeotrope. There is, however, no ternary azeotrope or other singular point on the pressure–composition surface.

Glossary

A_{ij}, A_{ji}	parameters in eq 1 and 2
B_{ij}	second virial coefficient
C	parameter in eq 3

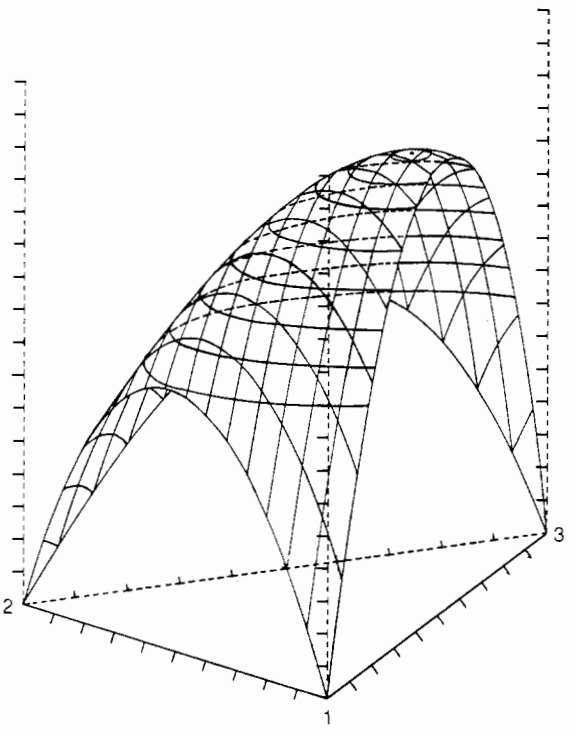

Figure 4. Computer-generated pictorial view of the $G^E_{123}-x$ surface for acetonitrile (1)–ethanol (2)–water (3) at 50 °C.

G^E	excess Gibbs function, liquid phase
g	G^E/RT
P	total pressure
p^{az}	azeotropic pressure
P_i^{sat}	vapor pressure of pure i
R	universal gas constant
T	absolute temperature
V_i^L	molar volume of pure liquid i
x	mole fraction, liquid phase
x^{az}	azeotropic composition

Greek Letters

α_{ij}, α_{ji}	parameters in eq 2
η	parameter in eq 2
$\lambda_{ij}, \lambda_{ji}$	parameters in eq 1
Δ	signifies a difference

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Received for review August 4, 1978. Accepted January 8, 1979. Partial support (about 20%) for this work came from National Science Foundation Grant No. ENG75-17367 and the remainder from the Department of Chemical and Environmental Engineering, Rensselaer Polytechnic Institute.