J. Chem. Eng. Data 1983, 28, 410–412

Excess Thermodynamic Functions for Ternary Systems. 9. Total-Pressure Data and G^E for Water/Ethylene Glycol/Ethanol at 50 °C

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Isothermal P–x data for the ternary system water/ethylene glycol/ethanol at 50 °C are reported, together with data for the constituent binaries. Data reduction by Barker's method provides a correlation for G^E.

Reported here are vapor/liquid equilibrium (VLE) measurements for the water (1)/ethylene glycol (2)/ethanol (3) system at 50 °C. Experimental values of total vapor pressure are given over the full composition range of the three constituent binaries and for five runs with ternary mixtures formed by addition of a pure species to mixtures of the other two. The apparatus is that of Gibbs and Van Ness (*1*) as modified by DiElsi et al. (*2*).

Table I. P–x Data for Water (1)/Ethylene Glycol (2) at 50 °C

x_1	x_2	P, kPa	x_1	x_2	P, kPa
0.0185	0.9815	0.316	0.5494	0.4506	6.589
0.0479	0.9521	0.634	0.5994	0.4006	7.224
0.0991	0.9009	1.185	0.6494	0.3506	7.858
0.1500	0.8500	1.753	0.6995	0.3005	8.494
0.1990	0.8010	2.315	0.7498	0.2502	9.156
0.3006	0.6994	3.524	0.8000	0.2000	9.798
0.3506	0.6494	4.157	0.8501	0.1499	10.440
0.4009	0.5991	4.758	0.8999	0.1001	11.094
0.4506	0.5494	5.411	0.9502	0.0498	11.745
0.5006	0.4994	6.023	0.9803	0.0197	12.082
0.5020	0.4980	5.978			

Table II. P–x Data for Water (1)/Ethanol (3) at 50 °C

x_1	x_3	P, kPa	x_1	x_3	P, kPa
0.0499	0.9501	29.523	0.5006	0.4994	27.521
0.1004	0.8996	29.516	0.5508	0.4492	27.113
0.1500	0.8500	29.447	0.6007	0.3993	26.665
0.2002	0.7998	29.314	0.6513	0.3487	26.182
0.2508	0.7492	29.120	0.7004	0.2996	25.680
0.3003	0.6997	28.878	0.7507	0.2493	25.010
0.3503	0.6497	28.589	0.8006	0.1994	24.185
0.4010	0.5990	28.241	0.8508	0.1492	22.993
0.4507	0.5493	27.909	0.8720	0.1280	22.274
0.5004	0.4996	27.540	0.9488	0.0512	17.821

Table III. P–x Data for Ethylene Glycol (2)/Ethanol (3) at 50 °C

x_2	x_3	P, kPa	x_2	x_3	P, kPa
0.0203	0.9797	28.900	0.5004	0.4996	17.861
0.0504	0.9496	28.090	0.5495	0.4505	16.707
0.1093	0.8907	26.567	0.5994	0.4006	15.454
0.1492	0.8508	25.625	0.6494	0.3506	14.115
0.1982	0.8018	24.502	0.7002	0.2998	12.665
0.2474	0.7526	23.418	0.7501	0.2499	11.137
0.2974	0.7026	22.337	0.8003	0.1997	9.412
0.3470	0.6530	21.278	0.8464	0.1536	7.613
0.3968	0.6032	20.210	0.8995	0.1005	5.308
0.4465	0.5535	19.128	0.9420	0.0580	3.277
0.4962	0.5038	18.027	0.9790	0.0210	1.333

Table IV. P–x Data for Water (1)/Ethylene Glycol (2)/Ethanol (3) at 50 °C

x_1	x_2	x_3	P, kPa
0.4926	0.0204	0.4870	26.813
0.4744	0.0510	0.4746	26.145
0.4498	0.1006	0.4496	25.048
0.4244	0.1513	0.4243	23.903
0.3994	0.2014	0.3992	22.707
0.3745	0.2512	0.3744	21.574
0.3493	0.3015	0.3492	20.358
0.3239	0.3523	0.3238	19.132
0.2991	0.4019	0.2990	17.903
0.2742	0.4517	0.2741	16.637
0.2492	0.5016	0.2492	15.333
0.0304	0.6487	0.3209	13.768
0.0638	0.6264	0.3099	14.012
0.1251	0.5853	0.2896	14.467
0.1835	0.5462	0.2703	14.895
0.2405	0.5081	0.2514	15.290
0.2969	0.4704	0.2327	15.665
0.3527	0.4331	0.2142	16.024
0.4068	0.3968	0.1963	16.340
0.4593	0.3618	0.1790	16.617
0.5106	0.3274	0.1620	16.851
0.5605	0.2941	0.1455	17.015
0.0499	0.3137	0.6364	21.870
0.1002	0.2971	0.6027	22.155
0.1504	0.2805	0.5691	22.362
0.2005	0.2640	0.5355	22.568
0.2507	0.2474	0.5019	22.739
0.3003	0.2310	0.4687	22.876
0.3501	0.2146	0.4353	23.049
0.4003	0.1980	0.4017	23.076
0.4502	0.1815	0.3683	23.097
0.4990	0.1654	0.3356	23.060
0.6627	0.3266	0.0107	9.144
0.6517	0.3211	0.0272	10.572
0.6327	0.3118	0.0555	12.713
0.6124	0.3018	0.0858	14.515
0.5913	0.2914	0.1174	16.090
0.5691	0.2804	0.1504	17.428
0.5459	0.2690	0.1851	18.591
0.5212	0.2568	0.2220	19.621
0.4950	0.2439	0.2611	20.551
0.4547	0.2241	0.3212	21.748
0.4378	0.2157	0.3464	22.188
0.3250	0.6595	0.0155	4.879
0.3173	0.6438	0.0389	6.407
0.3042	0.6172	0.0786	8.692
0.2909	0.5904	0.1187	10.645
0.2773	0.5627	0.1600	12.360
0.2633	0.5344	0.2023	13.890
0.2488	0.5050	0.2462	15.264
0.2341	0.4750	0.2909	16.507
0.2188	0.4440	0.3372	17.655
0.2033	0.4125	0.3842	18.638
0.1873	0.3800	0.4328	19.773

Reagent-quality ethanol with an indicated purity of 99.9 mol % was supplied by U.S. Industrial Chemicals. The ethylene glycol was a chromatoquality reagent with a purity >99.5 mol % from Matheson Coleman and Bell. The water was doubly deionzed. All reagents were thoroughly degassed.

0021-9568/83/1728-0410$01.50/0

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

	water (1)/ ethylene glycol (2)	water (1)/ ethanol (3)	ethylene glycol (2)/ ethanol (3)
P_i^{sat}, kPa	12.345	12.345	0.116
P_j^{sat}, kPa	0.116	29.476	29.476
V_i^L, cm³/mol	18	18	57
V_j^L, cm³/mol	57	60	60
B_{ii}, cm³/mol	−1137	−1137	−1970
B_{jj}, cm³/mol	−1970	−1400	−1400
B_{ij}, cm³/mol	−1246	−1168	−1729
A_{ij}	−0.14939	0.93116	0.83640
A_{ji}	−0.14939	1.59918	0.70498
λ_{ij}		0.32660	0.20563
λ_{ji}		−0.32480	0.05615
η_{ij}		0.54830	
η_{ji}		−1.87888	
rms δP, kPa	0.025	0.012	0.019
max $\lvert\delta P\rvert$, kPa	0.048	0.024	0.048

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

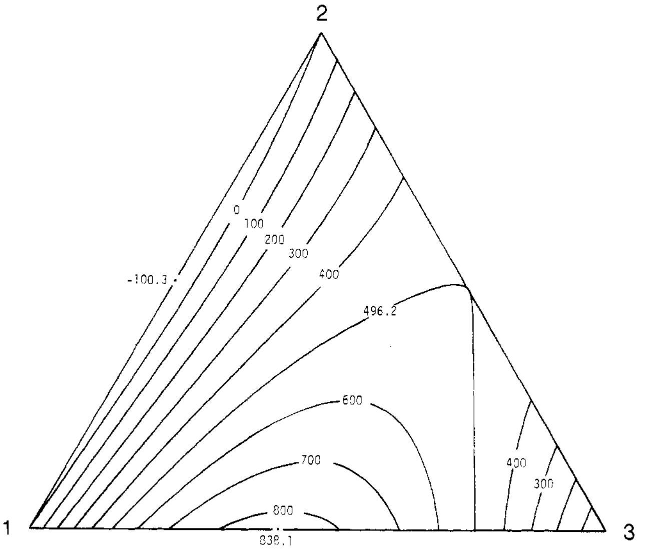

Figure 1. Lines of constant G^E (J/mol) for the water (1)/ethylene glycol (2)/ethanol (3) system at 50 °C.

Results and Correlations

Tables I–III give experimental values of total pressure for the three constituent binary systems, and Table IV presents the data for ternary mixtures. Data reduction is by Barker's method, as described earlier (*3*, *4*). For the binary systems, the Margules equation with up to six parameters provides suitable expression of G^E.

$$g_{ij} \equiv G^E_{ij}/RT = [A_{ji}x_i + A_{ij}x_j - (\lambda_{ji}x_i + \lambda_{ij}x_j)x_ix_j + (\eta_{ji}x_i + \eta_{ij}x_j)(x_ix_j)^2]x_ix_j \quad (1)$$

For the water (1)/ethanol (3) system, correlation requires all six parameters; for ethylene glycol (2)/ethanol (3), $\eta_{23} = \eta_{32} = 0$; and for water (1)/ethylene glycol (2), $\eta_{12} = \eta_{21} = \lambda_{12} = \lambda_{21} = 0$ and $A_{12} = A_{21}$.

Data for the ternary system are adequately correlated by the three-parameter Wohl equation:

$$g_{123} = g_{12} + g_{13} + g_{23} + (C_0 + C_1x_1 + C_2x_2)x_1x_2x_3 \quad (2)$$

Correlations for the g_{ij} are given by eq 1; parameters C_0, C_1, and C_2 result from regression of just the ternary data.

Second virial coefficients B_{ij} required for estimation of vapor-phase nonidealities come from the correlation of Hayden and O'Connell (*5*).

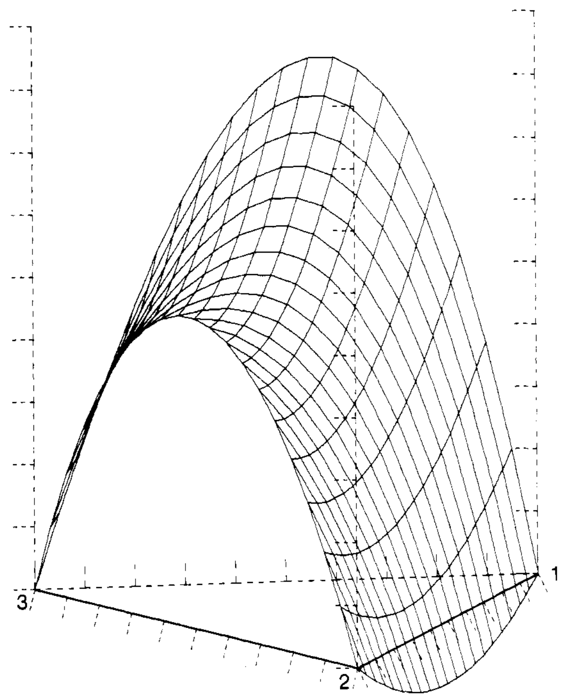

Figure 2. Pictorial view of the G^E–x surface for the water (1)/ethylene glycol (2)/ethanol (3) system at 50 °C.

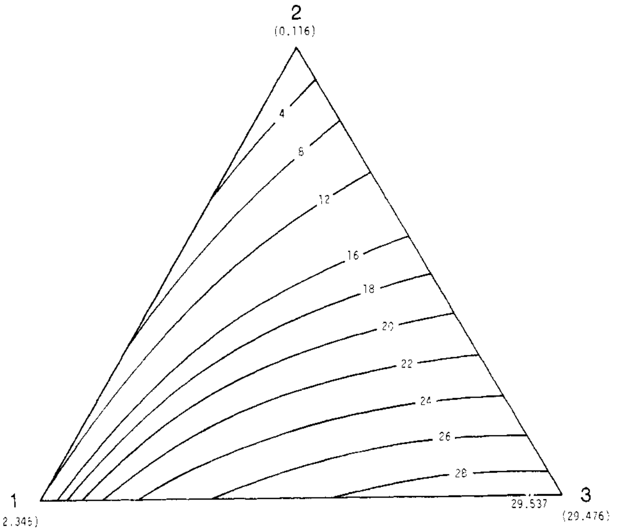

Figure 3. Lines of constant P (kPa) for the water (1)/ethylene glycol (2)/ethanol (3) system at 50 °C.

Results of correlation for the binary systems, together with all ancillary information, are summarized in Table V. With parameters for the binary systems fixed at the values of Table V, the ternary-mixture data are correlated when the parameters of eq 2 have the following values: $C_0 = 1.1616$; $C_1 = 0.6820$; $C_2 = 0.5229$. The root-mean-square (rms) value of δP for the ternary data is 0.081 kPa; the maximum value of $|\delta P|$ is 0.235 kPa.

Discussion

No data comparable with ours for the water/ethylene glycol and ethylene glycol/ethanol binary systems or for the ternary system appear in the literature. The data of Pemberton and Mash (*6*) for water/ethanol at 50 °C are in almost perfect agreement with ours.

The results of this study are shown in Figures 1–3. Figure 1 is a contour diagram showing lines of constant G^E on a triangular mole fraction grid. Figure 2 is an oblique view of the same surface, and Figure 3 is a contour diagram showing lines of constant P.

The only azeotrope is for the water/ethanol binary system at x_1 = 0.0641 and P^{az} = 29.537 kPa.

Glossary

A_{ij}, A_{ji}	parameters in eq 1
B_{ij}	second virial coefficient
C_0, C_1, C_2	parameters in eq 2
G^E	excess Gibbs function, liquid phase
g	G^E/RT
P	total 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

Greek Letters

λ_{ij}, λ_{ji}, η_{ij}, η_{ji}	parameters in eq 1
δ	denotes the difference, calculated − experimental

Registry No. Ethylene glycol, 107-21-1; ethanol, 64-17-5.

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Received for review January 17, 1983. Accepted March 18, 1983.

Total-Pressure Vapor–Liquid Equilibrium Data for Binary Systems of Dichloromethane with Pentane, Acetone, Ethyl Acetate, Methanol, and Acetonitrile

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Total-pressure vapor–liquid equilibrium (VLE) data are reported at approximately 298, 348, and 398 K for dichloromethane with pentane, acetone, ethyl acetate, methanol, and acetonitrile. The experimental *PTx* data were reduced to y_i, γ_i, and G^E values by both the Mixon–Gumowski–Carpenter and the Barker methods and the results compared. Six G^E correlations were tested in the Barker data reduction; the five-constant Redlich–Kister equation gave the best results. The Peng–Robinson equation of state was used for all the data reduction calculations.

Introduction

This paper presents total-pressure vapor–liquid equilibrium (VLE) data for five binary systems for dichloromethane with pentane, acetone, ethyl acetate, methanol, and acetonitrile. Data for each binary were measured at approximately 298, 348, and 398 K. The techniques and apparatus used to measure these data have been described previously along with the defining equation for the activity coefficient and the standard states used (*1*).

Chemicals Used

The sources and the purities of the chemicals used are given in Table I. Activated molecular sieves (either 3A or 4A) were put into the chemical containers as they were received. Just prior to being loaded in the VLE cells, each chemical was poured into a distillation flask and distilled through a Vigreux column (25-mm o.d. and 470 mm long). The first and last portions of each distillate were discarded. The retained portions were caught in amber bottles and back-flushed with dry nitrogen for transfer to the cell-loading operation. The stated purities of the chemicals were confirmed by gas–liquid chromatography.

Table I. Chemicals Used

component	vendor	stated purity, %
ethyl acetate	Burdick and Jackson	99.9
acetone	Burdick and Jackson	99.9+
methanol	Fisher Scientific	99.9
pentane	Burdick and Jackson	99.9
acetonitrile	Burdick and Jackson	99.9+
dichloromethane	Burdick and Jackson	99.9

Table II. Experimental P vs. x_1 Data for the Pentane (1) + Dichloromethane (2) System

298.19 K			348.17 K			398.16 K		
	P, KPA			P, KPA			P, KPA	
X1	EXPTL	SMOOTH	X1	EXPTL	SMOOTH	X1	EXPTL	SMOOTH
0.0	58.35	58.36	0.0	308.1	308.1	0.0	1030.1	1030.2
0.0331	63.98	63.95	0.0329	325.8	325.8	0.0329	1061.4	1061.4
0.0857	69.49	69.56	0.0854	343.2	343.3	0.0853	1097.1	1097.4
0.1510	74.24	74.18	0.1506	358.5	358.3	0.1504	1131.6	1130.9
0.2213	77.46	77.49	0.2209	369.6	369.7	0.2207	1157.1	1157.3
0.3012	79.84	79.84	0.3009	377.9	378.1	0.3007	1176.0	1176.6
0.4097	81.74	81.74	0.4095	384.2	384.1	0.4097	1187.6	1187.1
0.5011	82.46	82.45	0.5012	385.4	385.2	0.5016	1184.2	1183.7
0.5970	82.39	82.42	0.5975	382.6	382.9	0.5987	1169.3	1169.8
0.6945	81.61	81.58	0.6948	377.3	377.2	0.6954	1147.1	1147.3
0.7792	79.90	79.90	0.7796	368.8	368.8	0.7801	1121.4	1120.9
0.8185	78.73	78.73	0.8189	363.4	363.5	0.8194	1105.9	1105.9
0.8998	75.30	75.33	0.9002	349.5	349.4	0.9005	1066.8	1067.1
0.9497	72.45	72.43	0.9500	338.0	338.1	0.9502	1037.5	1037.3
1.0000	68.41	68.41	1.0000	323.9	323.9	1.0000	1003.3	1003.3

None of the compounds exhibited any degradation during the VLE measurements. The cell pressures were stable with re-

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