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Ebulliometric Determination of *PTx* Data and G^E for Acetone + Methyl Acetate from 20 to 60 °C

James D. Olson

Research and Development Department, Union Carbide Corporation, South Charleston, West Virginia 25303

An ebulliometer was used to measure total vapor-pressure (*Px*) data on 21 mixtures of acetone + methyl acetate (and the pure components) at 5 °C intervals between 20 and 60 °C. A two-parameter Redlich–Kister G^E model fit the individual isotherms via Barker's method with an average standard error of 0.05% in pressure. Equimolar G^E values thus derived vary 33% depending on which virial coefficient correlation is used to calculate the mixture fugacity coefficients. Use of the Hayden–O'Connell virial correlation yields G^E values whose temperature dependence is consistent with calorimetrically determined H^E data. The azeotropic composition decreases from 0.78 mole fraction acetone at 20 °C to 0.57 at 60 °C.

Measurement of *PTx* data as a route to vapor–liquid equilibria is an alternative to direct measurement of *PTxy* data in equilibrium stills. Use of *PTx* data requires rigorous and complete thermodynamic analysis of the equations and methods used to compute G^E and y (*1*, *16*). This is possible with the advent of digital computers.

Px data are usually measured isothermally in a static vapor-pressure apparatus (tensimeter). However, in this work, data were obtained from experiments in an ebulliometer which is a one-stage total-reflux boiler equipped with a vapor-lift pump to spray slugs of equilibrated liquid and vapor upon a thermometer well. Swietoslawski showed (*14*) that, although ebulliometry uses steady-state boiling rather than gradient-free static equilibrium, vapor-pressure data measured in an ebulliometer for pure components agree well with data from isothermal static measurements. The purpose of this work is twofold: (i) to compare ebulliometrically determined *Px* data at 50 °C for the system acetone (1) + methyl acetate (2) with recent measurements of DiElsi, Patel, Abbott, and Van Ness (*6*) which were determined isothermally in a static tensimeter and (ii) to present *Px* data and G^E for this system in 5 °C increments from 20 to 60 °C. Heat-of-mixing data, H^E, computed from the temperature slope of the G^E data are compared to calorimetric H^E data to test thermodynamic consistency.

Experimental Section

The acetone and methyl acetate were chromatoquality (99.5+ mol %) reagents from Matheson Coleman and Bell used as received. No volatile impurities were detected in the acetone by our own gas chromatography (FID) analysis; however, a small peak (0.1 area %) was detected from the methyl acetate. This impurity was found by GC/MS to be benzene. Karl Fischer titration revealed 0.053 wt % water present in the acetone and 0.27% in the methyl acetate. Care was taken during the experiments not to expose the chemicals to the humid laboratory atmosphere. Of course, no degassing is necessary for experiments in an ebulliometer.

The ebulliometer (*9*) is shown in Figure 1. The boiler, which was constructed from concentric pieces of glass tubing, has sintered glass fused to the heated surface to promote smooth ebullition. A nichrome wire heats the boiler electrically. Twin vapor-lift pumps spray liquid and vapor slugs on the thermometer well which is wrapped with a glass spiral to promote thermal equilibrium. The ebulliometer is connected to the manostat through a standard condenser which is cooled with a −20 °C glycol–water mixture. The entire apparatus is insulated except the condenser and condensed-vapor return. Finally, the side view shows a septum-covered stopcock where materials can be introduced into the apparatus.

Table I. Vapor Pressures (torr) of Acetone and Methyl Acetate[a]

T, °C	acetone[b]	methyl acetate[c]
20.000	185.373	172.450
25.000	230.677	216.278
30.000	285.423	269.695
35.000	349.110	332.225
40.000	424.747	406.823
45.000	512.497	493.835
50.000	615.340	596.524
55.000	732.397	713.700
60.000	868.087	850.190

[a] Antoine equation constants ($\log_{10} P_i^{\text{sat}} = A_i - [B_i/(C_i + T(°\text{C}))]$: acetone, $A_1 = 7.10485$, $B_1 = 1202.05$, $C_1 = 228.510$, $\hat{\sigma}_P = 0.28$ torr; methyl acetate, $A_2 = 7.15892$, $B_2 = 1202.20$, $C_2 = 224.246$, $\hat{\sigma}_P = 0.36$ torr. [b] Mean of three replicates, standard error at each temperature, 0.02–0.06%. [c] Mean of five replicates, standard error at each temperature, 0.02–0.07%.

The pressure was controlled with a Mensor Model 10205 quartz manometer/manostat. This instrument is equipped with a direct-reading option for 0–1000 torr (1 torr = 133.3224 Pa) with resolution of 0.01 torr. Pressures derived from the dial reading and the calibration chart are accurate to ±(0.01% + 0.02 torr) for a recently calibrated instrument.

Temperatures on the IPTS-68 scale were measured with a Hewlett-Packard Model 2801A quartz thermometer. This thermometer was calibrated at each of the experimental temperatures by comparison to a Leeds and Northrup primary-standard platinum resistance thermometer traceable to NBS.

Experimental Procedure. The ebulliometer was flushed with dry nitrogen, and the condenser coolant circulation started. A Hamilton gas-tight syringe (capacity = 50 cm^3) was flushed with nitrogen, and a sample of methyl acetate was drawn from the reagent container through a septum. The methyl acetate was then injected into the ebulliometer through the septum-covered port. This procedure was repeated with a clean syringe for the desired amount of acetone. The syringes were weighed on a Voland balance to ±1 mg before and after each addition which gave the total mass of each component added to the ebulliometer. The ebulliometer was then connected to the manostat which was set at the approximate vapor pressure of mixture at 20 °C, and the electrical heater turned on. After steady-state boiling was observed (30–45 min), the manostat dial was adjusted until the ebulliometer temperature read exactly 20.000 ± 0.0005 °C. The corrected manostat reading was then recorded as the solution vapor pressure. Data were obtained similarly at 5 °C increments to 60 °C by manipulation of the manostat control pressure. Equilibration was rapid (10–15 min) at each new point. In this fashion, data for two mixtures were measured per 8-h day.

Results

Table I contains vapor-pressure data from measurements on the pure components. These data are essential for meaningful

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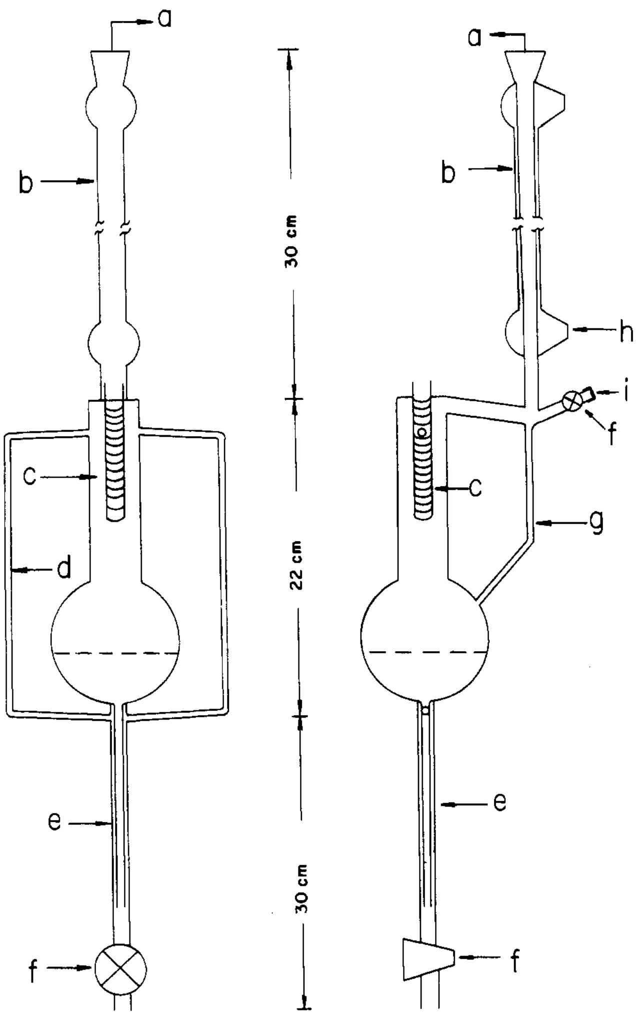

Figure 1. Front and side cross-sectional views of ebulliometer: (a) to manostat; (b) condenser; (c) thermometer well; (d) vapor-lift pump (two-arm); (e) boiler; (f) stopcock; (g) condensed vapor return; (h) condenser coolant inlet; (i) septum; (- - -) indicates liquid level ≃75 cm^3.

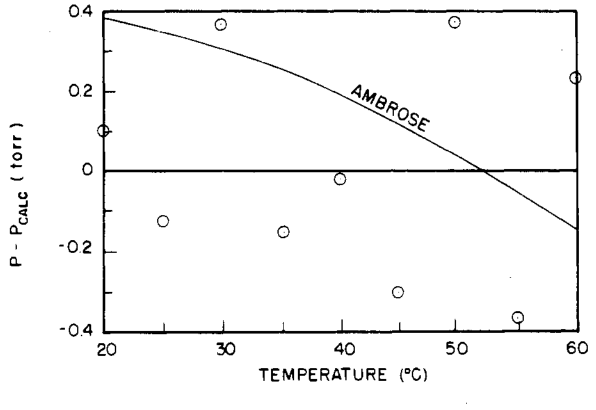

Figure 2. Acetone vapor pressure residual from Antoine equation: (⊙) experimental point; (—) indicates deviation from data of ref *2*.

mixture experiments to insure that the derived G^E represents only the mixture nonideality, not systematic errors in the pure-component vapor pressures (*1*, *16*). Note the agreement between the vapor pressures of acetone and the data of Ambrose et al. (*2*) as shown in Figure 2. No such definitive reference data are available for methyl acetate.

Table II. Experimental Data for Composition Calculations

run^a	m_1, g	m_2, g	z_1
1	24.070	42.889	0.4172
2	47.396	15.236	0.7987
3	34.965	29.023	0.6058
4	6.853	65.550	0.1177
5	25.048	39.752	0.4456
6	40.219	23.190	0.6887
7	16.644	51.354	0.2925
8	11.588	56.287	0.2080
9	53.893	8.358	0.8916
10	31.818	32.955	0.5519
11	28.680	36.256	0.5022
12	37.498	26.092	0.6470
13	56.960	5.729	0.9269
14	3.925	66.740	0.0698
15	9.494	60.808	0.1661
16	50.048	12.127	0.8404
17	14.488	53.870	0.2554
18	41.962	18.577	0.7423
19	14.967	53.006	0.2648
20	55.960	5.741	0.9256
21	19.849	47.271	0.3488

[a] Chronological order of experiments. $V^T = 210$ cm^3. $V^{CV} = 2.0$ cm^3.

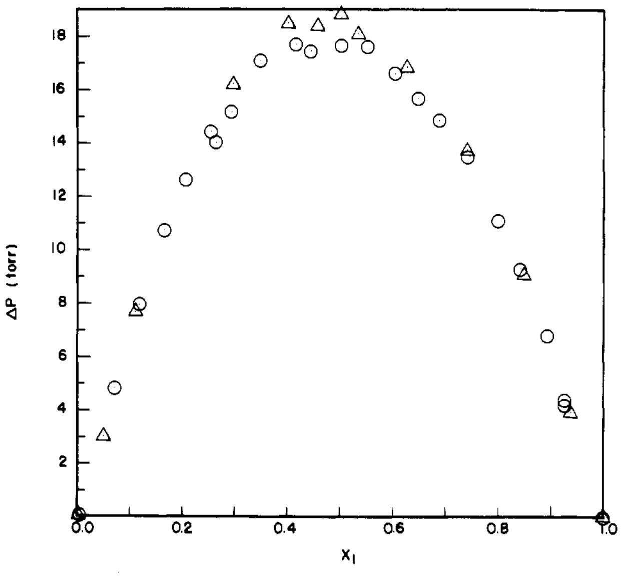

Figure 3. Pressure deviation from Raoult's law for acetone (1) + methyl acetate (2) at 50 °C: (⊙) this work; (△) ref *6*.

Raw data for calculation of the liquid-phase mole fraction, x, are given in Table II. These data are essential to compute x from z, the overall mole fraction charged to the ebulliometer. A material-balance correction was computed to take into account the composition change due to the vapor space and the presence of a film of condensed vapor (holdup) on the upper walls of the ebulliometer (*7*). This correction is small, as seen by comparing z in Table II to x in Table III. The vapor-liquid equilibrium model used to compute this correction was obtained from a preliminary analysis of the data in which $x = z$.

Results for 188 PTx measurements are shown in Table III. Note that y, *the vapor-phase composition, is a calculated value* based on the Redlich-Kister G^E model and the Hayden-O'-Connell virial correlation. The PTx data at 50 °C may be compared to the results of DiElsi et al. (*6*) by computing ΔP, the difference between the measured mixture vapor pressure and the pressure predicted by Raoult's law ($x_1P_1^{sat} + x_2P_2^{sat}$). This deviation-pressure comparison minimizes the effect of small differences in the measured pure-component vapor pressures. Figure 3 is a plot of ΔP vs. x. Note that the two sets of data agree within experimental error except near the equimolar point where differences of 4–6% in ΔP are observed.

Values of G^E and y were computed by a Gauss–Newton nonlinear least-squares fit to the experimental mixture vapor

Table III. Pressure–Temperature–Composition Data

x_1	P, torr	y_1[a]	x_1	P, torr	y_1[a]
	$T = 20\ °C$			$T = 35\ °C$	
0.0	172.45	0.0	0.0	332.23	0.0
0.069 41	174.81	0.0823	0.069 46	336.20	0.0802
0.117 14	176.54	0.1359	0.117 21	338.83	0.1327
0.165 43	178.23	0.1881	0.165 53	341.47	0.1840
0.207 25	179.36	0.2319	0.207 37	343.31	0.2272
0.254 68	180.61	0.2803	0.254 80	345.11	0.2751
0.264 04	180.45	0.2897	0.264 17	344.98	0.2845
0.291 74	181.17	0.3173	0.291 88	346.01	0.3119
0.348 07	182.52	0.3724	0.348 21	348.29	0.3667
0.416 57	183.63	0.4380	0.416 72	349.75	0.4322
0.444 99	183.86	0.4649	0.445 14	350.03	0.4592
0.501 74	184.66	0.5182	0.501 89	351.17	0.5127
0.551 48	185.31	0.5647	0.551 62	351.92	0.5594
0.605 49	185.76	0.6151	0.605 63	352.25	0.6102
0.646 82	185.86	0.6539	0.646 95	352.31	0.6493
0.688 55	186.19	0.6930	0.688 68	352.49	0.6889
0.742 29	186.50	0.7439	0.742 40	352.69	0.7404
0.798 70	186.32	0.7981	0.798 81	352.22	0.7953
0.840 41	186.26	0.8387	0.840 48	351.85	0.8362
0.891 66	186.17	0.8893	0.891 71	351.29	0.8877
0.925 62	185.75	0.9235	0.925 65	350.29	0.9224
0.926 97	185.81	0.9248	0.927 01	350.41	0.9238
1.000 00	185.37	1.000	1.000 00	349.11	1.0000
	$T = 25\ °C$			$T = 40\ °C$	
0.0	216.28	0.0	0.0	406.82	0.0
0.069 43	219.13	0.0815	0.069 48	411.50	0.0795
0.117 17	221.03	0.1348	0.117 24	414.50	0.1317
0.165 46	223.09	0.1867	0.165 55	417.53	0.1828
0.207 30	224.40	0.2303	0.207 40	419.66	0.2259
0.254 72	225.84	0.2785	0.254 84	421.71	0.2737
0.264 09	225.69	0.2879	0.264 21	421.46	0.2830
0.291 79	226.51	0.3154	0.291 92	422.81	0.3103
0.348 12	228.13	0.3704	0.348 26	425.23	0.3651
0.416 62	229.39	0.4360	0.416 76	426.69	0.4307
0.445 04	229.66	0.4629	0.445 18	427.20	0.4576
0.501 80	230.67	0.5163	0.501 94	428.41	0.5112
0.551 53	231.27	0.5628	0.551 66	429.18	0.5580
0.605 54	231.69	0.6134	0.605 67	429.46	0.6089
0.646 86	231.80	0.6522	0.646 98	429.54	0.6480
0.688 59	232.05	0.6916	0.688 68	429.64	0.6877
0.742 34	232.30	0.7428	0.742 43	429.73	0.7394
0.798 75	232.15	0.7971	0.798 83	428.98	0.7944
0.840 43	232.01	0.8379	0.840 50	428.46	0.8357
0.891 68	231.78	0.8888	0.891 73	427.64	0.8873
0.925 63	231.23	0.9231	0.925 67	426.36	0.9220
0.926 98	231.30	0.9245	0.927 02	426.51	0.9234
1.000 00	230.68	1.000	1.000 00	424.75	1.000
	$T = 30\ °C$			$T = 45\ °C$	
0.0	269.70	0.0	0.0	493.84	0.0
0.069 45	273.05	0.0808	0.069 49	499.24	0.0790
0.117 19	275.34	0.1337	0.117 25	502.70	0.1309
0.165 50	277.66	0.1853	0.165 58	506.05	0.1817
0.207 34	279.25	0.2287	0.207 43	508.46	0.2247
0.254 76	280.87	0.2767	0.254 87	510.86	0.2723
0.264 13	280.70	0.2861	0.264 24	510.65	0.2816
0.291 84	281.64	0.3135	0.291 95	512.03	0.3088
0.348 17	283.51	0.3685	0.348 29	514.61	0.3635
0.416 67	284.92	0.4340	0.416 80	516.72	0.4291
0.445 09	285.18	0.4609	0.445 23	516.84	0.4560
0.501 85	286.30	0.5144	0.501 98	518.10	0.5096
0.551 58	286.96	0.5611	0.551 70	518.92	0.5565
0.605 58	287.36	0.6118	0.605 71	519.18	0.6076
0.646 91	287.45	0.6507	0.647 02	519.11	0.6468
0.688 63	287.62	0.6902	0.688 73	519.07	0.6867
0.742 34	288.02	0.7415	0.742 46	519.13	0.7385
0.798 78	287.64	0.7962	0.798 86	517.95	0.7938
0.840 46	287.35	0.8371	0.840 52	517.27	0.8352
0.891 70	286.99	0.8883	0.891 74	516.16	0.8869
0.925 64	286.22	0.9227	0.925 68	514.56	0.9218
0.926 99	286.34	0.9241	0.927 03	514.71	0.9232
1.000 00	285.42	1.000	1.000 00	512.50	1.000

Table III. (*Continued*)

x_1	P, torr	y_1[a]
	$T = 50$ °C	
0.0	596.52	0.0
0.069 50	602.68	0.0784
0.117 27	606.69	0.1300
0.165 60	610.38	0.1806
0.207 46	613.10	0.2234
0.254 90	615.72	0.2709
0.264 28	615.51	0.2802
0.291 98	617.17	0.3075
0.348 33	620.12	0.3621
0.416 84	622.04	0.4277
0.445 27	622.33	0.4547
0.502 02	623.61	0.5084
0.551 74	624.51	0.5553
0.605 77	624.54	0.6065
0.647 02	624.42	0.6457
0.688 77	624.34	0.6857
0.742 50	624.02	0.7377
0.798 89	622.64	0.7930
0.840 54	621.62	0.8345
0.891 76	620.09	0.8865
0.925 67	618.11	0.9215
0.927 04	618.37	0.9229
1.000 00	615.34	1.0000
	$T = 55$ °C	
0.0	713.70	0.0
0.069 51	721.73	0.0780
0.117 29	725.37	0.1293
0.165 62	729.39	0.1798
0.207 49	732.54	0.2224
0.254 93	735.59	0.2698
0.264 31	735.24	0.2790
0.292 02	737.11	0.3062
0.348 36	740.38	0.3608
0.416 87	742.85	0.4262
0.445 30	742.49	0.4532
0.502 06	743.90	0.5069
0.551 78	744.72	0.5540
0.605 77	744.50	0.6052
0.647 09	744.28	0.6446
0.688 80	743.97	0.6847
0.742 53	743.48	0.7368
0.798 91	741.67	0.7924
0.840 57	740.40	0.8341
0.891 77	738.26	0.8862
0.925 70	735.74	0.9213
0.927 05	736.55	0.9227
1.000 00	732.40	1.0000
	$T = 60$ °C	
0.0	850.19	0.0
0.117 30	863.34	0.1287
0.165 64	868.20	0.1789
0.207 51	871.35	0.2214
0.254 96	875.10	0.2687
0.264 33	874.70	0.2779
0.292 04	876.63	0.3051
0.348 40	880.04	0.3596
0.416 91	882.44	0.4250
0.445 34	882.16	0.4520
0.502 09	883.79	0.5058
0.551 82	884.49	0.5527
0.605 82	884.14	0.6042
0.647 13	883.74	0.6437
0.688 84	882.79	0.6838
0.742 56	882.49	0.7361
0.798 94	879.74	0.7918
0.840 59	878.19	0.8336
0.891 79	875.90	0.8858
0.925 71	872.22	0.9210
0.927 06	873.02	0.9224
1.000 00	868.09	1.0000

[a] Calculated by Barker's method.

pressures coupled with a bubble-point calculation during each iteration (Barker's method). No attempt was made to correct for the presence of the trace water. The equation which describes the thermodynamic equilibrium between the phases at a particular temperature T and equilibrium pressure P is eq 1,

$$\phi_i y_i P = \gamma_i x_i P_i^{\text{sat}} \phi_i^{\text{sat}} \exp[(P - P_i^{\text{sat}}) V_i/(RT)] \qquad i = 1, 2 \tag{1}$$

where ϕ is the vapor-phase fugacity coefficient, γ is the liquid-phase activity coefficient (reference state: pure liquid at system T and P), P^{sat} is the pure-component vapor pressure, and V is the pure-component saturated-liquid molar volume. The exponential pressure correction terms contain usual approximations (*12*) for the pressure dependence of the volumetric properties of the liquid phase.

The G^{E} model was the Redlich–Kister equation

$$G^{\text{E}} = x_1 x_2[A + B(x_1 - x_2) + C(x_1 - x_2)^2 + \ldots] \tag{2}$$

$$RT \ln \gamma_i = G^{\text{E}} + x_j(\partial G^{\text{E}}/\partial x_i)_{TP} \qquad i, j = 1, 2 \tag{3}$$

where A, B, C, ... are parameters to be estimated in the least-squares fit.

The equation of state for the vapor-phase mixture was the pressure-explicit virial equation truncated to the first correction term

$$Z = 1 + B_{\text{M}} P/(RT) \tag{4}$$

$$B_{\text{M}} = y_1^2 B_{11} + 2y_1 y_2 B_{12} + y_2^2 B_{22} \tag{5}$$

where B_{11}, B_{22}, and B_{12} are the pure-component and mixed second virial coefficients. The vapor-phase fugacity coefficients may be calculated from eq 6. Two correlations were used to

$$\ln \phi_i = (2 \sum_{j=1}^{2} y_j B_{ij} - B_{\text{M}})[P/(RT)] \tag{6}$$

estimate the second virial coefficients: the method of Tsonopoulos (*15*) and the method of Hayden and O'Connell (*8*). Data used in these correlations and liquid density data are listed in Table IV.

Table IV. Physical Properties and Virial Correlation Data for the Acetone (1) + Methyl Acetate (2) System[a]

compd	T_c, K	P_c, atm	V_c, cm^3 mol^{-1}	ρ^{20}, g cm^{-3}	$(d\rho/dT)^{20}$
			Physical Property Data		
1	508.1	46.4	209	0.7900	−0.001 00
2	506.8	46.3	228	0.9339	−0.001 30
		ω	a	b	k_{ij}
			Tsonopoulos Correlation Parameters		
1		0.309	−0.0309	0.0	0.10
2		0.324	−0.0109	0.0	0.10
		$10^{25}\mu$, (J M^3)$^{1/2}$	$10^8 R'$, cm	η_{ii}	η_{ij}
			Hayden–O'Connell Correlation Parameters		
1		9.044	2.740	0.900	1.10
2		5.534	2.862	0.850	1.10

[a] Molecular weights of acetone and methyl acetate are 58.080 and 74.080, respectively.

The PTx data at 50 °C were fit with the one-, two-, and three-constant Redlich–Kister models as shown in Table V. Two parameters are sufficient to describe G^{E}, as was found by DiElsi et al. (*6*). The two parameters from their Margules model

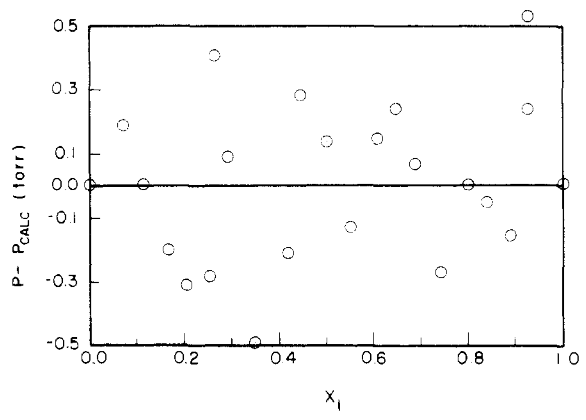

Figure 4. Mixture pressure residual for acetone (1) + methyl acetate (2) at 50 °C.

Table V. Redlich-Kister Parameters at 50 °C

no. parm[a]	A, J mol^{-1}	B, J mol^{-1}	C, J mol^{-1}	$\hat{\sigma}_P$, torr
1	275.948			0.447
2	275.666	−21.484		0.250
3	274.982	−21.866	2.79	0.258

[a] Number of Redlich-Kister parameters, eq 2.

Table VI. Redlich-Kister Parameters for Acetone (1) + Methyl Acetate (2)

T, °C	A, J mol^{-1}	B, J mol^{-1}	$\hat{\sigma}_P$, torr	max P_{dev}, torr
20	290.070	−21.909	0.123	0.232
25	286.979	−22.963	0.136	0.237
30	284.461	−22.781	0.169	0.291
35	282.428	−22.893	0.186	0.366
40	280.732	−22.256	0.207	0.413
45	277.740	−24.462	0.232	0.449
50	275.666	−21.484	0.250	0.510
55	275.391	−25.986	0.368	0.731
60	274.976	−25.730	0.430	0.982

may be calculated from the Redlich–Kister A and B constants by eq 7 and 8. Subsequent fitting used only the two-parameter

$$A_{12} = (A - B)/(RT) \tag{7}$$

$$A_{21} = (A + B)/(RT) \tag{8}$$

model. The pressure-residual scatter plot shown in Figure 4 indicates that the residuals are free from systematic runs.

Table VI contains results from fitting the two-parameter Redlich–Kister model to Px data at each temperature. Goodness of fit is indicated by the standard root-mean-square error in the calculated pressures and the maximum $(P - P_{\text{calcd}})$. Other models were tested, including the Wilson and van Laar equations, but they offered no particular advantage over the two-parameter Redlich–Kister equation.

Data given in Table VII compare the thermodynamic results at 50 °C of DiElsi et al. (*6*) and our data using (i) the Tsonopoulos correlation and (ii) the Hayden–O'Connell correlation. The equimolar G^E values computed from these two choices of virial correlation differ by $\sim$33%. Although there is no reason to pick one method over the other for data at a single temperature, the G^E vs. T data computed by using the Hayden–O'Connell correlation are more consistent with H^E, the heat-of-mixing, known from calorimetry as discussed in the next section.

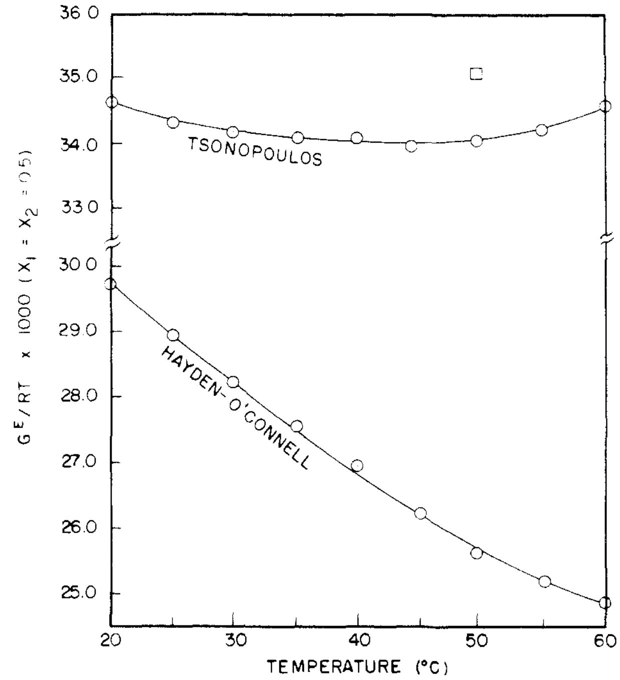

Figure 5. $G^E/(RT)$ from Barker's method analysis. (□) ref *6*.

Discussion

The precision of the results is indicated by (i) the root-mean-square standard error for replicates during the pure-component vapor-pressure experiments (Table I), (ii) the fitting error of the Antoine equation (Table I), and (iii) the fitting error for the mixture data (Table VI). On this basis the precision expressed as standard error at each temperature is $\sim$0.04% in pressure. The overall (between temperatures) standard error is probably 0.05–0.1%.

The evaluation of the accuracy of experimental measurements in the absence of exactly known reference values is a difficult and ill-defined process (*10*). If systematic errors (bias) are absent, the experimental uncertainty is the same as the uncertainty expected from random errors, 0.05–0.1%. The overall integrity of the experimental method is shown by (i) the agreement of the acetone vapor-pressure data with the reference data of Ambrose et al. (*2*) and (ii) the agreement of the 50 °C mixture data with the data of DiElsi et al. (*6*). These comparisons indicate that serious systematic errors are absent from the procedure.

The thermodynamic consistency of the temperature dependence of the G^E values can be tested by comparison to calorimetrically determined H^E data according to eq 9, where $g = G^E/(RT)$.

$$H^E = -RT^2(\partial g/\partial T)_x \tag{9}$$

The value of the equimolar H^E determined from calorimetry at 50 °C is 86.5 J mol^{-1} (*17*). Figure 5 shows g vs. T from analysis of our PTx data which used, in the one case, the Tsonopoulos virial coefficient correlation and, in the other,

Table VII. Effect of Virial Correlation on G^E at 50 °C

	$\hat{\sigma}_P$, torr	max P_{dev}, torr	G^E,[c] J mol^{-1}	γ_1^∞	γ_2^∞	y_1[d]
this work[a]	0.250	0.510	68.9	1.1169	1.0992	0.508 35
this work[b]	0.251	0.539	91.6	1.1547	1.1374	0.508 53
ref *6*[b]	0.29	0.71	94.1	1.1588	1.1421	

[a] Used Hayden–O'Connell virial correlation. [b] Used Tsonopoulos virial correlation. [c] Equimolar value, $x_1 = x_2 = 0.5$. [d] Calculated value for experimental point, $x_1 = 0.50202$.

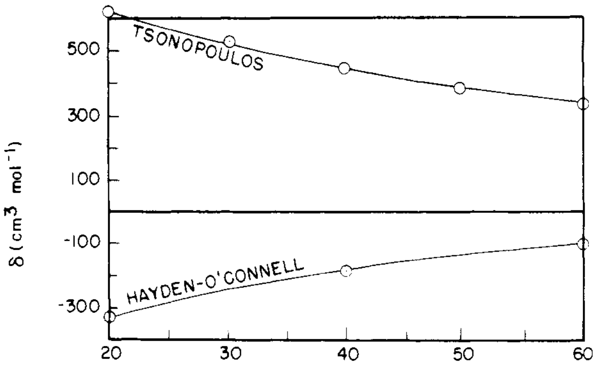

Figure 6. Calculated excess second virial coefficient of acetone (1) + methyl acetate (2).

Table VIII. Acetone (1) + Methyl Acetate (2) Azeotrope

	this work		lit.		
T, °C	x_1^{AZ}	P^{AZ}, torr	x_1^{AZ}	P^{AZ}, torr	ref
20	0.7788	186.36	0.7960	182.2	*4*
25	0.7539	232.19			
30	0.7202	287.79	0.6880	282.3	*4*
35	0.6949	352.58			
40	0.6686	429.70	0.5935[b]	423.7	*4*
45	0.6427	519.27			
50	0.6204	624.66	0.6272	624.40	*6*
50	0.6214[a]	624.67[a]	0.78		*13*
50			0.6555[c]	623.81[c]	*5*
55	0.5934	744.78			
60	0.5727	884.38			

[a] Calculated with Tsonopoulos virial correlation. [b] Estimated value; $x = y$ data point not given. [c] Data of Severns et al. reanalyzed by DiElsi, ref *5*.

the Hayden–O'Connell virial coefficient correlation. Use of the Hayden–O'Connell method leads to a value of ~88 J mol⁻¹ for the 50 °C equimolar H^E while use of the Tsonopoulos method gives an athermal or slightly exothermic equimolar H^E at 50 °C. On this basis, I conclude that use of the Hayden–O'Connell virial correlation leads to a more realistic representation of the vapor-phase mixture properties.

The difference between mixture virial coefficients predicted by the Tsonopoulos and Hayden–O'Connell methods can be seen by plotting the temperature dependence of the excess second virial coefficient δ, defined by eq 10, as shown in Figure 6.

$$\delta = B_{12} - (B_{11} + B_{22})/2 \tag{10}$$

As seen, $d\delta/dT$ is negative for Tsonopoulos and positive for Hayden–O'Connell. This is the reason for the dramatically different G^E vs. T plots in Figure 5. Note also that Hayden–O'Connell predicts negative values of δ, which indicates chemical interaction (solvation) between acetone and methyl acetate in the vapor phase. A k_{ij} value of -0.04 used in the Tsonopoulos method gives approximately the same δ vs. T as Hayden–O'Connell. Moreover, the rough guide for prediction of k_{ij} given by Tsonopoulos (*15*) does not include ketone + ester systems; the most chemically similar choice is ketone + ether where $k_{ij} = 0.13$. A value of 0.10 is the k_{ij} used for data shown in Figure 6 and apparently also used by DiElsi et al. (*6*). Tsonopoulos points out that a negative k_{ij} is observed in systems when chemical effects are present.

A direct measurement of δ, perhaps by the Knobler method (*11*), would eliminate the possibility that the more realistic G^E temperature dependence obtained from use of the Hayden–O'Connell method is an artifact. Finally, note that, even though the equimolar G^E values are 33% different for the different choices of virial correlation, the goodness of fit to pressure and the calculated y values are virtually unaffected (Table VII).

Table VIII contains calculated azeotrope compositions and pressures from 20 to 60 °C based on a second-order Lagrangian interpolation of the data of Table III and the calculated pressures. These data are compared with previous work (*4*, *6*, *13*).

Acknowledgment

M. R. Bent performed the experimental measurements.

Glossary

a, b	polar contribution parameters, Tsonopoulos virial correlation, ref 15
A_{12}, A_{21}	Margules G^E model parameters
A, B, C, ...	Redlich–Kister G^E model parameters, J mol⁻¹
A_i, B_i, C_i	Antoine vapor-pressure equation parameters, log₁₀, torr, °C
B_{ij}	second virial coefficient, interaction between molecules i and j, cm³ mol⁻¹
B_M	mixture second virial coefficient, cm³ mol⁻¹
g	$G^E/(RT)$
G^E	liquid-phase molar excess Gibbs energy, J mol⁻¹
H^E	liquid-phase excess enthalpy (heat of mixing), J mol⁻¹
k_{ij}	interaction parameter, Tsonopoulos virial correlation, ref *15*
m_i	mass of component i added to ebulliometer, g
P	pressure, torr
P_{calcd}	pressure calculated from Antoine equation (Figure 2) or from Barker method fit to mixture data (Figure 4)
P_{dev}	$P - P_{calcd}$
R	gas constant, 8.31433 J mol⁻¹
R'	radius of gyration, Hayden–O'Connell virial correlation, ref *8*, cm
T	absolute temperature, K
V^i	volume of phase i, cm³
V_i	saturated liquid molar volume of component i, cm³ mol⁻¹
x_i	liquid-phase mole fraction of component i
y_i	vapor-phase mole fraction of component i
z_i	total mole fraction of component i added to ebulliometer
Z	compressibility factor of vapor

Greek Letters

γ_i	liquid-phase activity coefficient of component i (reference state: pure liquid at system T and P)
δ	excess second virial coefficient, cm³ mol⁻¹
ΔP	difference of mixture pressure from Raoult's law, torr
η_{ij}	chemical interaction parameter, Hayden–O'Connell virial correlation, ref *8*
μ	molecular dipole moment, Hayden–O'Connell virial correlation, ref *8*, (J m³)$^{1/2}$
ρ	liquid-phase density, g cm³
$\hat{\sigma}_P$	standard root-mean-square error of least-squares fit to pressure, torr
ϕ_i	fugacity coefficient of component i
ω	acentric factor, Tsonopoulos virial correlation, ref 15

Subscripts

1	of component 1, acetone
2	of component 2, methyl acetate
M	of the mixture
c	at the liquid-vapor critical point

Superscripts

AZ	at azeotrope
CV	in the condensed vapor phase
T	total in system (ebulliometer)

sat	pure saturated liquid
∞	at infinite dilution
20	value at 20 °C

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Ultrasonic Velocities, Densities, and Viscosities of Triethylamine in Methanol, Ethanol, and 1-Propanol

A. Kumar, O. Prakash, and S. Prakash*
Chemical Laboratories, University of Allahabad, Allahabad, India

Ultrasonic velocities, densities, and viscosities of triethylamine in methanol, ethanol, and 1-propanol have been measured at 25 °C. From experimental data isentropic compressibility, molar volume, and their excess values along with excess viscosity and excess molar Gibbs free energy for the activation of flow have been computed and presented as functions of composition. The parameter *d* of the Grunberg and Nissan expression has also been calculated. The results indicate A–B-type interaction which decreases in strength with an increase in the chain length of alcohols.

Introduction

Considerable interest has been stimulated by the ultrasonic and viscosity investigations of binary liquid mixtures. The nonideal behavior of liquid mixtures has been predicted by Tuomikoski and Nurmi (*1*), Fort and Moore (*2*, *3*), Flory and coworkers (*4*, *5*), Prakash et al. (*6*), Nigam and Singh (*7*), and Raman and Naidu (*8*). The deviations from the law of additivity in the values of various parameters indicate the existence of specific interaction between unlike molecules. Triethylamine (TEA) is a weakly polar liquid, whereas alcohols are polar and associating. The present work deals with the study of ultrasonic velocity, isentropic compressibility, molar volume, viscosity, and excess values along with excess molar Gibbs free energy for activation of flow and the Grunberg and Nissan (*9*) term *d* for the systems (I) triethylamine (TEA)–methanol, (II) TEA–ethanol, and (III) TEA–1-propanol at 25 °C.

Experimental Section

Ultrasonic velocity at 2 MHz was measured by a single-crystal variable-path interferometer. The transducer was a gold-plated quartz cyrstal. The accuracy of velocity measurement was ±0.18%.

Density was determined by a double-walled pycnometer having capillaries of narrow bore provided with well-fitted glass caps in order to avoid changes in composition due to evaporation of the more volatile liquid. The accuracy in density is of the order of 0.03%. (See Table I.)

Table I. Densities of Chemicals

compd	density at 25 °C exptl	density at 25 °C lit.	ref
triethylamine	0.7255	0.7254	*16*
methanol	0.7868	0.7870	*3*
ethanol	0.7851	0.78506	*17*
propanol	0.7996	0.79968	*18*

The suspended level Ostwald viscometer calibrated with benzene and double-distilled water was used for determining the viscosities. The values are accurate to 0.001 cP. The temperature was maintained constant by a thermostatic bath.

Ethanol (BCPW) and TEA, methanol, and 1-propanol (all BDH AR grade) were purified by Copp and Findlay's method (*10*). The mixtures were prepared by mixing weighed amounts of pure liquids and left for 2 h.

The isentropic compressibility β_s is given by

$$\beta_s = v^{-2}\rho - 1 \qquad (1)$$

where v is the ultrasonic velocity and ρ is the density. The molar volume V of a mixture is defined as

$$V = \bar{M}/\rho \qquad (2)$$

where $\bar{M} = xM_1 + (1 - x)M_2$, M_1 and x being the molecular weight and the mole fraction of the first component, respectively, and M_2 and $(1 - x)$ the molecular weight and the mole fraction of the second component, respectively. The viscosity was determined from eq 3, where t and η represent the time

$$\nu = \text{kinematic viscosity} = \eta/\rho = at - b/t \qquad (3)$$

of flow in seconds and the viscosity in centipoise, respectively, of the mixtures, whereas a and b are the constants of the

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