intersect at singular end points with critical identity of the liquid and vapor phases. The experimental data given here are for the solid–liquid or solid–vapor two-phase regions. The measured solubilities are therefore both temperature and pressure dependent; the pressure dependence is considerably weaker below the critical temperature of the solvent. The solubility at a given temperature was found to be a linear function of the pressure and the value at a corresponding saturated pressure (*3*) was obtained by extrapolation. Since the solute concentration is quite low the saturated pressure of pure oxygen is a reasonable approximation to the actual triple point pressure.

The precision of the data ranges from a few tenths of a percent at the higher concentrations to 27.8% in the worst case. The accuracy can be assumed to follow accordingly except for a systematic difference between data obtained at different periods in the study. Methylene chloride data taken with the 10-cm^3 sample loop and a Tenax-GC separation column were 3.8–5.5% greater than similar data obtained with a 5-cm^3 sample loop and a Carbowax 400 on Chromosorb T column. Time and funds did not allow resolution of this descrepancy.

Acknowledgment

The authors appreciate the work of D. T. Buss, H. L. Donat, and D. S. Cunningham and especially the analytical support provided by J. B. Wallace.

Glossary

L	liquid phase
S	solid phase
V	vapor phase
x_{exptl}	experimental solute concentration
$x_{\text{sat.}}$	solute concentration in the saturated liquid

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Excess Thermodynamic Functions for Ternary Systems. 3. Total Pressure Data and G^E for Acetone–Acetonitrile–Methyl Acetate at 50 °C

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Isothermal P–x data for the ternary system acetone–acetonitrile–methyl acetate at 50 °C are reported. Data are also presented for the constituent binaries at 50 °C. Reduction of the data via Barker's method allows calculation of G^E.

In parts 1 (*6*) and 2 (*9*) of this series of papers we presented data and correlations of H^E, G^E, and S^E for two highly nonideal ternary systems. Here we report VLE data for a much more nearly ideal system, acetone (1)–acetonitrile (2)–methyl acetate (3) at 50 °C. Because of the relatively simple behavior of this system, much less experimental information is required for the ternary mixtures. Thus the data set comprises VLE measurements for the three constituent binaries and for but three runs on the ternary mixtures formed by addition of each pure constituent to an approximately equimolar mixture of the other two.

Data were taken on the total-pressure apparatus described by Gibbs and Van Ness (*5*), modified for ternary systems by the addition of a third piston injector. Several refinements in experimental technique were also adopted for this work. Minor changes in equipment design have made it possible to zero the differential-pressure null indicator and the Texas Instruments pressure gauge between data points and to incorporate into the raw data corrections for the drift in the zeros of these instruments. Additionally, the time required for degassing of the pure chemicals has been greatly reduced by use of a novel distillation degassing technique (*11*).

The acetone, acetonitrile, and methyl acetate were chromatoquality reagents supplied by Matheson Coleman and Bell. Except for degassing, all reagents were used as received, with indicated purities of at least 99.5 mole %.

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

x_1	x_2	P, mmHg
0.0000	1.0000	253.89
0.0824	0.9176	283.94
0.1600	0.8400	311.02
0.2531	0.7469	346.15
0.3451	0.6549	379.82
0.4314	0.5686	411.59
0.4754	0.5246	425.83
0.5077	0.4923	438.83
0.5517	0.4483	453.07
0.6350	0.3650	482.21
0.7386	0.2614	519.07
0.8138	0.1862	546.56
0.8996	0.1004	578.20
0.9581	0.0419	599.34
1.0000	0.0000	615.16

Results and Correlations

Tables I through III contain experimental total-pressure data for the three constituent binaries; Table IV contains results for the three ternary runs.

Except for the acetone (1)–acetonitrile (2) system, whose P–x behavior closely follows Raoult's law, all data were reduced by Barker's method (*2*). Liquid-phase nonidealities for the binary systems are adequately described by the two-parameter Margules equation

$$g_{ij} \equiv G^{E}{}_{ij}/RT = x_i x_j (A_{ji} x_i + A_{ij} x_j) \qquad (1)$$

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Table II. Total Pressure Data for Acetone (1)-Methyl Acetate (3) at 50 °C

x_1	x_3	P, mmHg
0.0000	1.0000	594.56
0.0464	0.9536	598.62
0.1100	0.8900	604.51
0.2980	0.7020	616.87
0.4024	0.5976	621.25
0.4549	0.5451	622.23
0.5019	0.4981	623.58
0.5361	0.4639	623.59
0.6290	0.3710	624.23
0.7408	0.2592	623.41
0.8491	0.1509	620.97
0.9386	0.0614	617.69
1.0000	0.0000	614.95

Table III. Total Pressure Data for Acetonitrile (2)-Methyl Acetate (3) at 50 °C

x_2	x_3	P, mmHg
0.0000	1.0000	595.23
0.0475	0.9525	583.46
0.1081	0.8919	567.38
0.1932	0.8068	544.57
0.2884	0.7116	518.08
0.3829	0.6171	490.53
0.4578	0.5422	467.45
0.5022	0.4978	453.83
0.5427	0.4573	439.99
0.5742	0.4258	430.14
0.6547	0.3453	401.86
0.7417	0.2583	368.87
0.8313	0.1687	332.23
0.9082	0.0918	298.44
0.9642	0.0358	271.89
1.0000	0.0000	253.73

Table IV. Total Pressure Data for Acetone (1)-Acetonitrile (2)-Methyl Acetate (3) at 50 °C

x_1	x_2	x_3	P, mmHg
0.0000	0.0000	1.0000	594.74
0.0000	0.5004	0.4996	453.62
0.0290	0.4859	0.4851	458.55
0.0893	0.4557	0.4550	468.46
0.1804	0.4100	0.4096	483.60
0.2689	0.3657	0.3654	497.83
0.3678	0.3162	0.3160	514.15
0.4623	0.2689	0.2688	529.58
0.5490	0.2255	0.2255	543.73
1.0000	0.0000	0.0000	614.97
0.4935	0.0000	0.5065	623.58
0.4751	0.0371	0.4878	610.34
0.4478	0.0925	0.4597	590.87
0.4058	0.1776	0.4166	561.45
0.3583	0.2739	0.3678	528.09
0.3105	0.3708	0.3187	494.65
0.2661	0.4607	0.2732	463.01
0.2251	0.5439	0.2310	433.35
0.0000	1.0000	0.0000	253.87
0.4996	0.5004	0.0000	434.75
0.4783	0.4791	0.0426	445.35
0.4450	0.4455	0.1095	461.56
0.4027	0.4030	0.1943	480.35
0.3567	0.3570	0.2863	499.13
0.3098	0.3099	0.3803	516.80
0.2646	0.2646	0.4708	531.89
0.2242	0.2242	0.5516	544.51

The ternary data were correlated with an equation due to Wohl (*13*)

$$g_{123} = g_{12} + g_{13} + g_{23} + Cx_1x_2x_3 \qquad (2)$$

Table V. Results of Data Reduction for the Binary Systems at 50 °C: Pure Component Vapor Pressures, Virial Coefficients, Parameters for Equation 1, and Pressure Deviations[a]

	Acetone (1)-acetonitrile (2)	Acetone (1)-methyl acetate (3)	Acetonitrile (2)-methyl acetate (3)
P_i^{sat}, mmHg	614.97	614.97	253.87
P_j^{sat}, mmHg	253.87	594.74	594.74
B_{ii}, cm³/mol	−1435	−1435	−4020
B_{jj}, cm³/mol	−4020	−1175	−1175
B_{ij}, cm³/mol	−2465	−905	−2280
A_{ij}		0.1474 ± 0.0026	0.2712 ± 0.0026
A_{ji}		0.1329 ± 0.0024	0.2386 ± 0.0039
RMS ΔP, mmHg	1.10	0.29	0.38
Max ΔP, mmHg	2.40	0.71	0.88

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

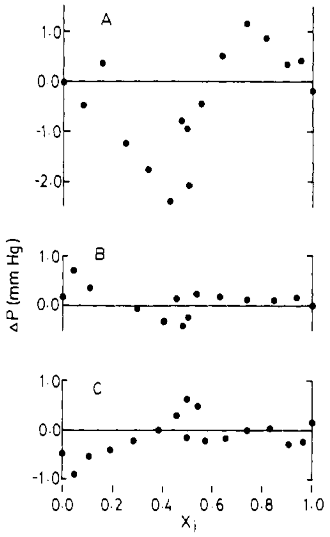

Figure 1. Pressure residuals for the three binary systems: (A) acetone–acetonitrile, (B) acetone–methyl acetate, (C) acetonitrile–methyl acetate. For each binary, species i is first-named substance.

Correlations for the g_{ij} were obtained from the binary data alone; thus only the empirical parameter C in eq 2 was found by regression of the ternary data. The data-reduction procedure incorporated corrections for nonidealities in the vapor phase (assumed described by the two-term virial equation) and for the pressure effect on liquid-phase fugacities. Second virial coefficients B_{ij} were estimated by the method of Tsonopoulos (*10*). Details of the data-reduction technique are described elsewhere (*1*).

Results of the binary correlations are summarized in Table V; the quality of these correlations is indicated by the pressure-residual scatter plots of Figure 1. The pure-component vapor pressures P_i^{sat} used for regression of the binary data were those values determined as part of the ternary runs. Thus, the binary scatter plots show small values of ΔP at the composition extremes $x_i = 0$ and $x_i = 1$. The root-mean-square values of ΔP are small (less than 0.5 mmHg) for the 13 and 23 binaries; for acetone–acetonitrile, the root mean square ΔP is larger, about 1.1 mmHg. The data for this system were also reduced by Barker's method, with liquid-phase nonidealities assumed described by eq 1. However, values of Margules parameters so determined are smaller than their estimated errors and hence statistically insignificant in magnitude. Evidently, liquid mixtures of acetone and acetonitrile are nearly ideal solutions at 50 °C and low pressures.

Correlation of the ternary data, with binary parameters fixed at values as given in Table V, yielded for the ternary parameter the value

$$C = 0.3283 \pm 0.0058$$

The root mean square ΔP for the ternary data is 0.41 mmHg; the maximum ΔP is 0.82 mmHg. Inclusion of higher order ternary terms in eq 2 gave no significant improvement in the

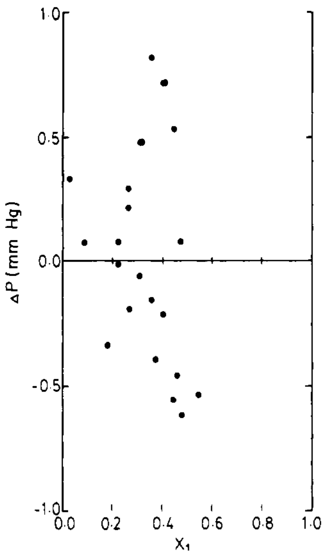

Figure 2. Pressure residuals for the ternary system. Species 1 is acetone.

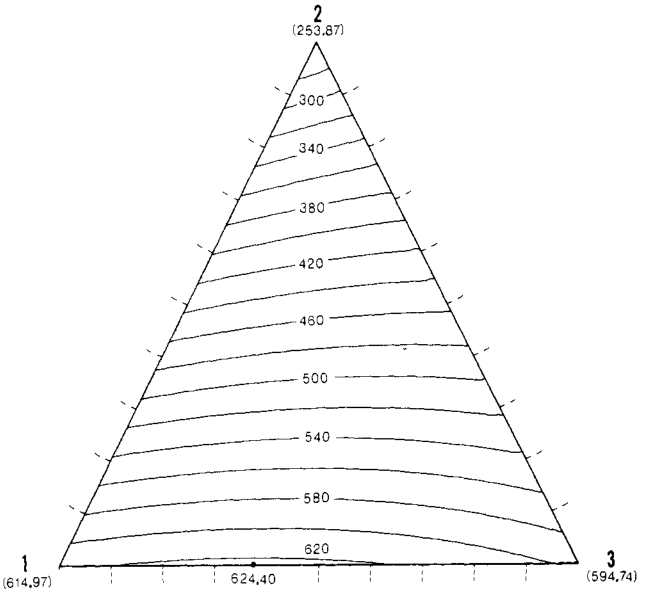

Figure 3. Lines of constant P (mmHg) for the acetone (*1*)-acetonitrile (2)-methyl acetate (3) system at 50 °C. Azeotrope for the 13 binary is at x_1 = 0.6272.

quality of the correlation. Figure 2 is a pressure-residual scatter plot for the correlation of the ternary data.

Discussion

The pure-component vapor pressures selected for reduction of our data were those measured as part of the ternary runs. However, values (given in Tables I-III) were also determined as end points in the binary experiments. In all cases, the three values for each substance (two from binary runs and one from a ternary run) agree to within estimated experimental error. They are also in substantial agreement with data from the literature.

The acetone-acetonitrile system has been studied by other workers (*4*, *7*, *12*) who also observed linear P-x behavior. Isothermal P-x-y data for acetone-methyl acetate have been reported at 50 °C by Severns et al. (*8*) and at 20, 30, and 40 °C by Bekarek (*3*); our work is in qualitative agreement with the results of these studies. No isothermal data could be found for the acetonitrile-methyl acetate system.

We believe the ternary data reported in this paper to be the first such results for the acetone-acetonitrile-methyl acetate system at 50 °C. Given the correlation for G^E_{123}/RT represented by eq 1 and 2, one can determine lines of constant G^E_{123} and lines of constant P for display on triangular diagrams with a grid representing liquid composition. Such computer-generated diagrams are shown in Figures 3 and 4. Figures 5 and 6,

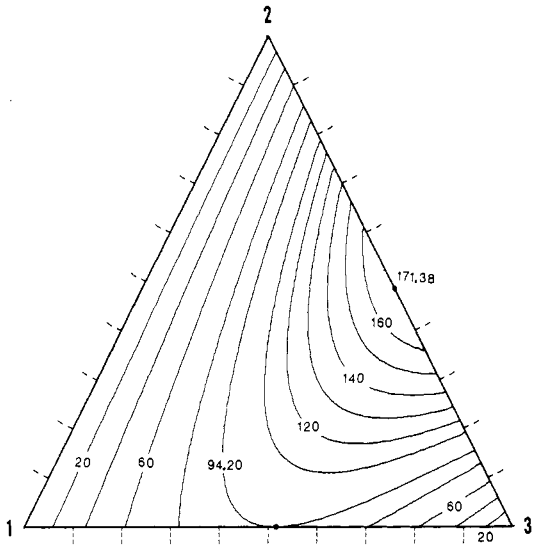

Figure 4. Lines of constant G^E_{123} (J/mol) for the acetone (1)-acetonitrile (2)-methyl acetate (3) system at 50 °C.

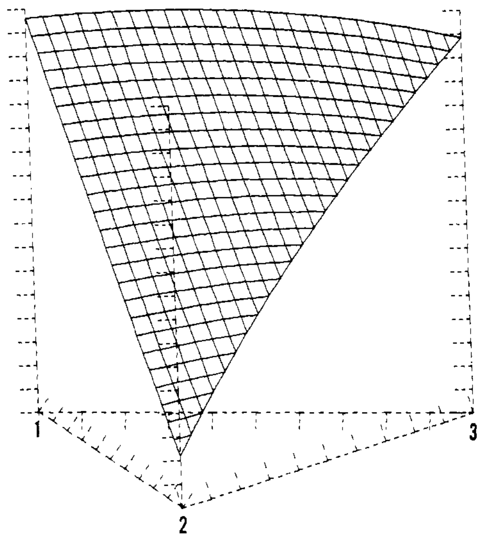

Figure 5. Oblique view of the P-x surface for acetone (1)-acetonitrile (2)-methyl acetate (3) at 50 °C.

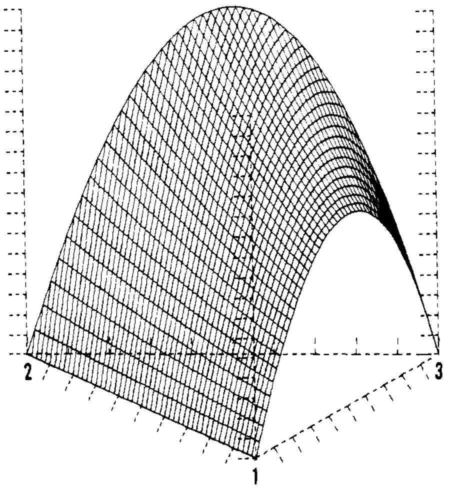

Figure 6. Oblique view of the G^E_{123}-x surface for acetone (1)-acetonitrile (2)-methyl acetate (3) at 50 °C.

computer-generated oblique views of the $P-x$ and $G^E{}_{123} - x$ surfaces, provide more graphic representations of the behavior of this ternary system.

Glossary

A_{ij}, A_{ji}	parameters in eq 1
B_{ij}	second virial coefficient
C	parameter 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
x	mole fraction, liquid phase
y	mole fraction, vapor phase
ΔP	difference between calculated and experimental pressures

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Enthalpies of Solution of Some Salts in Water

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Using the apparatus and procedure described in a recent report, with the energy equivalent of the calorimeter system determined with standard substances, enthalpies of solution in water at 298.15 K were measured for the following salts, as ΔH in kJ mol^{-1}: RbCl(c), in 1500 mol of H_2O, 17.225 ± 0.019; CsCl(c), in 800 mol of H_2O, 17.438 ± 0.014; CsBr(c), in 900 mol of H_2O, 26.146 ± 0.043; CsI(c), in 1500 mol of H_2O, 33.239 ± 0.030; Li_2CO_3(c), in 725 mol of H_2O, −14.800 ± 0.021.

1. Introduction

Measurements of the enthalpies of solution of several salts in water have been made, using the apparatus and procedure recently described, with the energy equivalent of the calorimeter being determined with standard substances (*12*).

The molecular weights used in this work are as follows (*3*): CsBr, 212.8094; CsCl, 168.3584; CsI, 259.8099; H_2O, 18.0152; Li_2CO_3, 73.8912; RbCl, 120.9208.

2. Experimental Section

Materials. The salts measured in this investigation are described as follows.

Rubidium chloride, National Bureau of Standards, Washington, D.C., Reference Material No. 984. The stated purity was 99.90 ± 0.02%. Prior to measurement, this material was dried at 873 K for 24 h.

Cesium chloride, Sample A, Harshaw Chemicals Co., Cleveland, Ohio. The purity was given as 99.96% (Gerald K. Johnson, Argonne National Laboratory, Argonne, Illinois, provided the sample and the assay of impurities) with the impurities being, in ppm, as follows: Mg, 5; Rb, 200; Na, 60; K, 5; Li, 4; Si, 30; Cs_2CO_3, 120. Prior to measurement, this material was dried at 645 K for 4 h.

Cesium chloride, Sample B, Alfa Inorganics, Beverly, Mass., Lot No. 87640. The purity was determined (Analysis provided by Gerald K. Johnson, Argonne National Laboratory, Argonne, Ill.) to be 99.99%, with the impurities being as follows, in ppm: Mg, 12; Rb, 10; Na, 5; K, 5; Cs_2CO_3, 56. Prior to measurement, this material was dried at 823 K for 24 h.

Cesium bromide, Alfa Inorganics, Beverly Mass., Lot No. 31672. The impurities were reported as follows, in ppm: Ba, 10; Sr, 5; Rb, 10; Na, 5; K, 5. Prior to measurement, this material was dried at 523 K for 8 h.

Cesium iodide, Alfa Inorganics, Beverly Mass., Lot No. 82473. The impurities were given as follows, in ppm: Ba, 50; Sr, 5; Na, 5; K, 5; Rb, 10. Prior to measurement, this material was dried at 523 K for 8 h.

Lithium carbonate, J. T. Baker, Ultrex, Phillipsburg, N.J. The purity was given as 99.98%, with total metallic impurities being 22 ppm. This material was heated at 523 K for 140 h. Within ±0.01% there was no loss in weight of the material from the 4th, to the 140th h. Prior to measurement, this material was heated again to 523 K for 22 h.

Potassium chloride, National Bureau of Standards, Standard Reference Material 918.

Tris(hydroxymethyl)aminomethane, National Bureau of Standards, Standard Reference Material 724a.

Following the drying procedure, the salts to be measured were placed in ampules in a dry atmosphere, except for lithium

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