Compressibility Factor as Functions of Temperature and Density

433° K.		453° K.				473° K.				493° K.			
P_{calc}	Z_{calc}	P_{corr}	Z_{corr}	P_{calc}	Z_{calc}	P_{corr}	Z_{corr}	P_{calc}	Z_{calc}	P_{corr}	Z_{corr}	P_{calc}	Z_{calc}
154	0.542	178	0.599	179	0.602	201	0.647	201	0.648	226	0.698	227	0.701
165	0.515	196	0.586	194	0.579	218	0.624	220	0.629	249	0.684	249	0.685
176	0.496	209	0.562	209	0.562	240	0.618	239	0.616	274	0.677	274	0.677
189	0.484	227	0.555	226	0.553	264	0.618	261	0.612	304	0.683	301	0.676
204	0.479	246	0.552	246	0.552	289	0.621	287	0.616	335	0.690	332	0.684
224	0.484	272	0.563	271	0.561	320	0.634	318	0.630	368	0.700	369	0.702
248	0.498	301	0.578	302	0.581	353	0.650	356	0.655	413	0.729	414	0.731
280	0.525	341	0.612	342	0.614	397	0.682	403	0.693	467	0.770	468	0.772
321	0.565	390	0.656	393	0.660	462	0.744	463	0.745	533	0.824	536	0.828
376	0.622	456	0.722	457	0.723	537	0.814	536	0.813	613	0.891	608	0.884
446	0.698	537	0.803	539	0.806	628	0.899	629	0.901	714	0.981	722	0.992
538	0.796	644	0.913	642	0.909	742	1.006	732	0.992	852	1.108	848	1.103
654	0.920	778	1.046	771	1.037	889	1.145	886	1.141	1018	1.258	1002	1.238
801	1.074	934	1.197	931	1.193	1071	1.314	1060	1.301	1202	1.415	1188	1.399
987	1.263	1123	1.373	1129	1.381	1273	1.491	1273	1.491	1402	1.575	1415	1.590
1220	1.493	1372	1.605	1372	1.605	1525	1.708	1532	1.716	1684	1.810	1688	1.814

tions. This is evident from the pattern of coefficients for the isotherms at higher temperatures.

Agreement between the corrected pressures observed during this investigation and the pressures calculated from the compressibility chart of Nelson and Obert (*4*) based on the theorem of corresponding states is excellent over the pressure and temperature range investigated (Figure 3).

NOMENCLATURE

P_{corr} = observed pressure, atmospheres.
Z_{corr} = compressibility factor calculated from the observed values of the pressure at the given temperature and density.
P_{calc} = pressure calculated from the virial expressions for the given density and temperature.
Z_{calc} = compressibility factor calculated from the virial expressions at the given temperature and density.

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Ternary Systems

Water-Acetonitrile-Salts

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Effectiveness in salting water out of acetonitrile was determined for 23 salts. Seven were effective, seven were ineffective, and nine precipitated the salt. Solubility data, equilibrium tie lines, and the plait point were determined for water-acetonitrile with four of these salts at 25° C.: sodium bromide, sodium nitrate, ammonium nitrate, and diammonium phosphate. A novel method of correlating the tie lines is proposed, applying the principle of rectilinear diameters to the equilibrium tie lines.

IN A CONTINUING study of water-acetonitrile-salt systems (*2, 3, 4*), salting-out effectiveness of nine salts of potassium, eight of ammonium, and seven of sodium was studied. Salts which bring about formation of two liquid phases upon addition of acetonitrile to the saturated salt solution are held to be effective in salting water out of acetonitrile. Binodal curves and equilibrium tie lines were determined experimentally for water-acetonitrile-sodium bromide, water-acetonitrile-sodium nitrate, water-acetonitrile-ammonium nitrate, and water-acetonitrile-diammonium phosphate.

EXPERIMENTAL

Results of salting-out effectiveness studies are given in Table I. Ineffective salts are those which failed to form two liquid phases. In some cases, the acetonitrile caused precipitation of the salt.

Binodal curves were determined by the well-known cloud point method. Starting in each case with a sample of approximately 1.5 grams of saturated salt solution, acetonitrile was added dropwise from a buret until a cloud point was reached. Water was added dropwise from a buret to clarify the solution and this initial clarification point was taken as the saturated salt-rich phase terminal composition on the binodal curve. This procedure was repeated until the graphical addition line for acetonitrile on the triangular diagram was coincidental with the binodal curve. The binodal data are given in Table II and in Figures 1 and 2.

All work was done in a laboratory controlled at 25° C. Weighings were made on a Mettler balance to ±0.1 mg. with samples in closed containers. The clarification points were determined to within one drop (±38 mg.) of water, resulting in a maximum uncertainty in binodal curve compositions of ±0.5%.

Table I. Effectiveness of Salts with Acetonitrile

Effective	Ineffective	Precipitated
K tetraborate	K metraperiodate	K iodate
NH_4 nitrate	K chlorate	K bromate
NH_4 citrate, dibasic	K nitrate	K bitartrate
NH_4 phosphate, dibasic	NH_4 metavanadate	K phosphate
Na chromate	NH_4 persulfate	NH_4 iodate
Na bromide	Na bisulfate	NH_4 oxalate
Na nitrate	Na iodate	K oxalate
		Na oxalate
		Na phosphate

Table II. Binodal Data at 25° C.

(Weight per cent)

System			System		
CH_3CN	NH_4NO_3	H_2O	CH_3CN	$NaNO_3$	H_2O
15.0	55.1	29.9	14.3	37.7	48.0
15.7	53.7	30.6	18.9	30.3	50.8
16.4	51.6	32.0	23.1	24.6	52.3
18.6	47.2	34.2	25.0	22.2	52.8
23.0	38.3	38.7	28.3	19.6	52.1
23.9	36.8	39.3	32.7	15.7	51.6
25.5	34.0	40.5	38.3	12.1	49.6
27.5	31.2	41.3	43.1	10.2	46.7
32.2	25.7	42.1	46.0	9.2	44.8
34.5	23.1	42.4	50.3	8.0	41.7
39.6	18.7	41.7	54.0	7.2	38.8
50.5	12.7	36.8	59.8	5.6	34.6
59.2	9.5	31.3	66.0	4.5	29.5
69.4	6.5	24.1	74.9	3.1	22.0
75.1	5.1	19.8	80.0	2.2	17.8
81.0	3.7	15.3	86.0	1.7	12.3
83.0	3.2	13.8	87.3	1.5	11.2
89.0	2.1	8.9	88.5	1.4	10.1
92.5	1.5	6.0			
CH_3CN	NaBr	H_2O	CH_3CN	$(NH_4)_2HPO_4$	H_2O
15.1	40.1	44.8	1.9	34.6	63.5
15.5	38.1	46.4	4.7	26.7	68.7
16.2	36.0	47.8	7.0	22.3	70.7
16.9	33.4	49.7	8.3	20.4	71.3
18.2	30.3	51.5	9.7	18.5	71.8
19.2	27.9	52.9	10.9	16.9	72.2
20.2	25.5	54.3	12.2	15.4	72.4
21.6	23.5	54.9	13.5	13.9	72.6
22.7	21.3	56.0	14.8	12.7	72.5
24.1	19.3	56.6	16.1	11.6	72.3
25.9	17.5	56.6	17.7	10.4	71.9
27.7	15.5	56.8	19.6	9.0	71.4
29.8	13.7	56.5	28.1	5.1	66.8
31.7	12.5	55.8	43.0	2.1	54.9
40.6	8.0	51.4	50.9	1.1	48.0
60.0	4.1	35.9	58.4	0.5	41.1
70.5	2.6	26.9	65.7	0.2	34.1
77.8	1.9	20.4	84.8	0.0	15.2
80.4	1.6	18.0			
86.8	1.2	12.0			
90.0	1.1	8.9			
95.8	0.8	3.4			

Equilibrium tie lines were determined by preparing a mixture of the three components of the system having a concentration in the two-phase region, closer to the acetonitrile-rich portion of the binodal curve than to the salt-rich portion. This mixture was shaken for 10 minutes to ensure complete solution of the salt, then held at 25° C. in a water bath controlled at 25° ± 0.05° C. to allow the mixture to form two layers. The layers were separated and analyzed for salt by vacuum drying to constant weight. Weighings were made to 0.1 mg. (Mettler balance). Water and acetonitrile compositions in the salt-rich phase were then obtained from the binodal curve, and the composition of the organic-rich phase was obtained by a material balance in conjunction with the binodal curve. The gravimetric analysis for salt in the organic-rich phase served as a check on the procedure and calculations. The plait point was determined (±2%) by the method of rectilinear diameters of Renard and Heichelheim (*3*) and the equilibrium tie line for the initial cloud point composition (the last tie line) was obtained by a novel method outlined below. Equilibrium tie lines are given in Table III.

MATERIALS

The salts used (99.7% purity) were Mallinckrodt analytical reagents. The acetonitrile was high-purity spectro grade (Matheson, Coleman, and Bell) with a refractive index at 20° C. of 1.3440 (literature value 1.3441) (*5*). Distilled water was used in all experimental work.

RESULTS

The data for the four systems show that ammonium nitrate has the greatest salting out power, followed closely and successively by sodium bromide, sodium nitrate, and diammonium phosphate. However, the latter has by far the lowest solubility in the concentrated salt solution which increases successively from diammonium phosphate, sodium nitrate, ammonium nitrate, to sodium bromide.

CORRELATIONS

In a previous paper (*3*), a novel method was employed, utilizing the principle of rectilinear diameters (*1*), to find the plait point. Equilibrium tie lines close to the plait point and close to the last tie line are subject to considerable uncertainty. We now extend the rectilinear diameters principle to determine the last tie line, and generalize it to give a computational correlation for the binodal curve and equilibrium tie lines.

The experimental tie lines were plotted on a triangular diagram as shown in Figure 1. The intersection of the locus of the midpoints of the tie lines with the binodal curve was taken to be the plait point. The midpoint locus was then extended away from the plait point and used as a conjugation line. The last tie line was found by trial. A tie line between the salt-rich phase at the initial cloud point and the organic-rich phase was assumed. If the midpoint of this tie line coincided with the locus of the midpoints of the other tie lines, it was correct; if not, it was adjusted until it was correct.

For each of the organic-water-salt systems studied in our laboratory, the symmetry of the two halves of the binodal curve suggests that each portion might be represented by

$$\frac{X_{ij} - S_{ij}}{X_{ip} - X_{ij}} = \alpha_j \frac{X_{kj} - S_{kj}}{X_{kp} - X_{kj}} \qquad (1)$$

where

X_{ij} = weight per cent of component *i* in phase *j*
X_{kj} = weight per cent of component *k* in phase *j*
S_{ij} = weight per cent of component *i* in phase *j* at saturation
S_{kj} = weight per cent of component *k* in phase *j* at saturation
X_{ip} = weight per cent of component *i* at the plait point
X_{kp} = weight per cent of component *k* at the plait point
α_j = constant for phase *j*

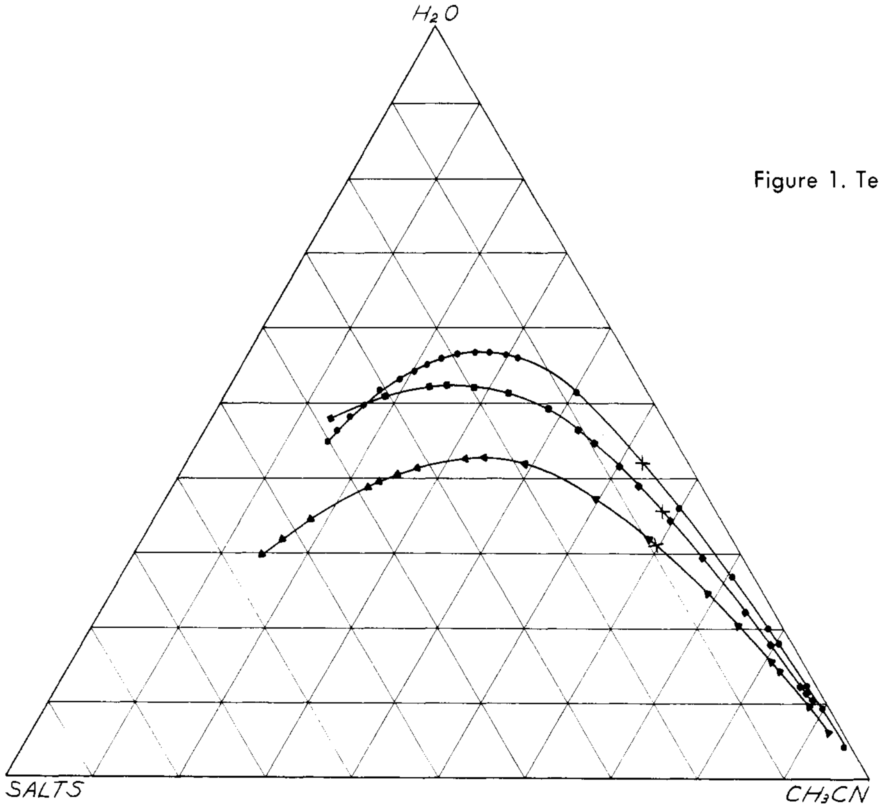

Figure 1. Ternary diagram for H_2O–CH_3CN–$(NH_4)_2HPO_4$
———Tie lines
------Locus of midpoints

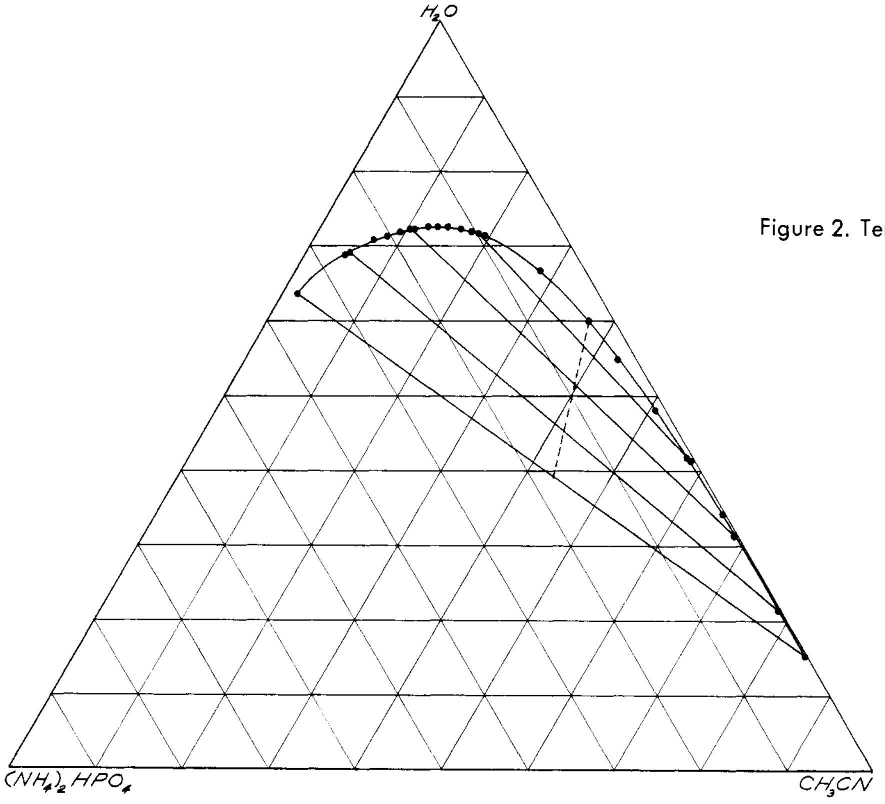

Figure 2. Ternary diagrams for H_2O–CH_3CN–salts
▲ NH_4NO_3
■ $NaNO_3$
● NaBr
X Plait points

Components 1, 2, and 3 are acetonitrile, salt, and water, respectively. Phases 1 and 2 are the acetonitrile-rich and salt-rich phases, respectively.

The principle of rectilinear diameters implies that the compositions of any two components in the two phases at equilibrium are related by

$$\frac{X_{ip} - \dfrac{X_{i1} + X_{i2}}{2}}{X_{jp} - \dfrac{X_{j1} + X_{j2}}{2}} = M \qquad (2)$$

where

$$M = \frac{X_{ip} - \dfrac{S_{i1} + S_{i2}}{2}}{X_{jp} - \dfrac{S_{j1} + S_{j2}}{2}}$$

These equations can be combined to give any composition in a phase as a function of a composition in the other phase. An algebraic solution is possible for any compositions; however, the resulting equation is an extremely com-

Table III. Tie-Line Data at 25° C.

(Weight per cent)

Salt-Rich Phase			Acetonitrile-Rich Phase		
NH_4NO_3	H_2O	CH_3CN	CH_3CN	H_2O	NH_4NO_3
55.1	29.9	15.0	92.5	6.0	1.5
49.8	32.9	17.3	91.8	6.5	1.7
36.8	39.4	23.8	88.1	9.4	2.5
24.6	42.8	33.1	84.4	12.4	3.2
			P.P.[a] 59.8	30.9	9.3
$NaNO_3$	H_2O	CH_3CN	CH_3CN	H_2O	$NaNO_3$
37.7	48.0	14.3	88.5	10.1	1.4
32.3	50.2	17.5	87.3	11.2	1.5
25.9	52.2	21.9	86.0	12.3	1.7
18.5	52.5	29.0	83.0	15.0	2.0
			P.P.[a] 58.0	36.0	6.0
NaBr	H_2O	CH_3CN	CH_3CN	H_2O	NaBr
40.1	44.8	15.1	95.8	3.4	0.8
29.6	52.0	18.4	89.9	9.1	1.0
22.8	55.5	21.7	86.8	12.0	1.2
14.3	56.7	29.0	76.7	21.3	2.0
			P.P.[a] 52.6	42.1	5.3
$(NH_4)_2HPO_4$	H_2O	CH_3CN	CH_3CN	H_2O	$(NH_4)_2HPO_4$
34.6	63.5	1.9	84.8	15.2	0.0
26.0	69.0	5.0	78.4	21.6	0.0
17.5	72.2	10.3	68.5	31.3	0.2
9.6	71.6	18.8	58.0	41.5	0.5
			P.P.[a] 37.2	60.0	2.8

[a] Plait point.

Table IV. Summary of Correlation Results

	Salt			
	NaBr	$NaNO_3$	NH_4NO_3	$(NH_4)_2$ HPO_4
α_1 (organic phase)	0.922	0.942	0.906	0.923
Deviation from binodal curve in organic phase, wt. %				
Max.	0.1	0.2	0.1	0.2
Av.	0.1	Nil	Nil	0.1
α_2 (salt phase)	0.209	0.305	0.328	0.255
Deviation from binodal curve in salt phase, wt. %				
Max.	0.8	1.4	1.7	0.7
Av.	0.3	0.6	0.8	0.3
Deviation in equilibrium tie lines, wt. %				
Max.	1.5	6.9	5.5	0.8
Av.	0.9	3.8	3.6	0.5
M	−0.8417	−1.9496	−1.4672	−0.7022

plicated quadratic, leading to severe uncertainties from roundoff. A search algorithm is recommended.

Although any combination of components can be used in the above equations, the choice of components in each equation can affect the outcome of the search. Applying Equation 1 to phase 1, the acetonitrile-rich phase, it is observed that the salt composition is very small and almost constant. For this reason, for $j = 1$ in Equation 1, let $i = 1$ and $k = 3$. In the salt-rich phase, the water composition goes through a maximum, which is not predicted by Equation 1. Therefore, for $j = 2$ in Equation 1, let $i = 1$ and $k = 2$. Applying these subscripts to Equation 1 and rearranging, we get

$$X_{31} = \frac{(\alpha_1 X_{1p} S_{31} - S_{11} X_{3p}) - (\alpha_1 S_{31} - X_{3p}) X_{11}}{(\alpha_2 X_{1p} - S_{11}) - (\alpha_1 - 1) X_{11}} \tag{3}$$

$$X_{22} = \frac{(\alpha_2 X_{1p} S_{22} - S_{12} X_{2p}) - (\alpha_2 S_{22} - X_{2p}) X_{12}}{(\alpha_2 X_{1p} - S_{12}) - (\alpha_2 - 1) X_{12}} \tag{4}$$

The locus of the midpoints of the tie lines, as represented by Equation 2, is more or less parallel to the acetonitrile axis for our data. This would tend to make M either very large or very small if acetonitrile were used in Equation 2. We therefore let $i = 2$ and $j = 3$ in Equation 2. Applying these subscripts to Equation 2 and rearranging, we get

$$X_{32} = \frac{2X_{2p} - X_{21} - X_{22} - M(2X_{3p} - X_{31})}{-M} \tag{5}$$

Equation 3 relates water to acetonitrile, Equation 4 salt to acetonitrile, and Equation 5 salt to water.

These equations have been used in the following iterative routine to determine the compositions of both phases in equilibrium, given only the acetonitrile composition in the acetonitrile-rich phase, (X_{11}).

(1) Compute X_{31} from Equation 3.
(2) Compute $X_{21} = 1 - X_{11} - X_{31}$.
(3) Approximate X_{12}. We used;

$$X_{12} = \frac{X_{1p}(X_{11} - S_{11}) + S_{12}(X_{1p} - X_{11})}{X_{1p} - S_{11}}$$

(4) Compute X_{22} from Equation 4.
(5) Compute X_{32} from Equation 5.
(6) Compute the sum of the compositions in the salt-rich phase, $SUMX = X_{12} + X_{22} + X_{32}$. If $SUMX = 1.00 \pm 0.001$, the solution has been reached. If not, set $X_{12} = X_{12}/SUMX$ and repeat steps 4 to 6.

CONCLUSIONS

The four systems reported in this study were treated by the method described above. Computations were carried out on an IBM 7040/7044. Results are shown in Table IV. The correlation is good for $|M| < 1$, but not so good for $|M| > 1$. The acetonitrile-rich portion of the binodal curve correlated extremely well for all four systems, with a maximum deviation of 0.2 weight % water. Maximum deviation for the salt-rich portion of the binodal curve was 1.7 weight % salt in the ammonium nitrate system. The worst deviation in a computed equilibrium tie line was 6.9 weight % sodium nitrate in the salt-rich phase. Average deviation in the salt-rich binodal curve computations was 1.2 weight % salt, while the average deviation for the equilibrium tie line computations was 2.2 weight % salt.

The correlations given herein can be used in the computational design of a stagewise dehydrator for acetonitrile. Similar correlations could be used for other salt-water-organic mixtures. If further precision were needed, equations for the binodal curve employing more than one parameter could be used. Work is continuing on these correlations, particularly taking into account curvatures which have heretofore been ignored.

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