166 J. Chem. Eng. Data 1985, 30, 166–171

Liquid–Liquid Equilibria for the System Ethyl Acetate–Acetic Acid–Water in the Presence of Dissolved Inorganic Salts

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A study has been made of the salting-out effect as applied to solvent extraction systems. The effect of the addition of three salts, viz., potassium chloride, sodium sulfate, and sodium chloride on the liquid–liquid equilibrium data of the ternary solutropic system ethyl acetate–acetic acid–water has been experimentally investigated at 30 °C with both the solubility (binodal) curve and the tie-line data determined for three concentrations of each of the aforementioned salts. In all three cases, the addition of salt enhances the distribution of acetic acid in the ester layer and the region of heterogeneity increases compared to the no-salt condition. The selectivity also has been found to increase as a result of salt addition. The tendency to exhibit a solutropic behavior ceases to exist on the addition of these salts. The tie-line data have been correlated by the Eisen–Joffe equation besides the frequently employed Othmer–Tobias and Hand plots.

There is hardly any chemical process that does not involve separation of liquid mixtures or recovery of valuable components from reaction products. Solvent extraction techniques have been increasingly employed with a decisive advantage in these operations. While one assesses the performance of a solvent for possible use in any such extraction technique, it is of paramount importance and significance to ascertain the extent to which the material being extracted distributes itself between the raffinate and solvent phases, as this is likely to reflect on the number of extraction stages required for the desired degree of separation. The decrease in solubility of a nonelectrolyte, called the "salting-out" effect, which has been known for many years, has potentially wide applications in solvent extraction for increasing the recovery of organic liquids from aqueous solutions. A survey of the literature, however, indicates that only fragmentary work has been done in this area (*1–7*).

This investigation, which forms a part of our continuing program on the study of the effect of dissolved salts on the distribution of a solute between the raffinate and extract phases, reports the experimental observations of the effect of addition of three inorganic salts, viz., potassium chloride, sodium sulfate, and sodium chloride at three concentrations, on the distribution of the solute acetic acid between the ethyl acetate and water phases. Both the solubility curves and the tie-line data have been determined, the temperature of experimentation being 30 °C. The system ethyl acetate–acetic acid–water has been particularly chosen because it tends to exhibit a solutropic behavior and it was felt that since in the case of vapor–liquid equilibria the addition of a properly selected salt either breaks or shifts an azeotrope in azeotropic systems, a salt could be expected to play a similar role in liquid–liquid equilibrium relationships of such a solutropic system also. The solubility and the tie-line data at 30 °C for this ternary system in the absence of salt used for comparison in this work have been taken from the literature (*8*). Our earlier findings with respect to a few other systems have been reported in the literature (*6*, *7*).

Experimental Section

Chemicals. The acetic acid used in this work had a minimum purity of 99.5% and was of SD reagent grade. The ethyl acetate supplied by the BDH Laboratory, was distilled again before use. The physical properties of these two components were measured and checked with the corresponding literature values to establish their purity. The three salts used were of laboratory reagent grade supplied by BDH Laboratory, Bombay, India. As for water, the laboratory supply of distilled water was used.

Table I. Ethyl Acetate–Acetic Acid–5% KCl Solution

(a) Binodal Curve Data

concn, wt %			
ethyl acetate	acetic acid	water	KCl salt
69.43	21.63	8.4835	0.4465
64.55	23.83	11.039	0.581
57.79	27.34	14.117	0.743
54.3	28.2	16.587	0.873
39.2	27.15	31.948	1.6815
25.7	24.5	47.215	2.485
13.65	20.48	62.567	3.293
12.98	20.22	63.507	3.34
10.87	19.21	66.416	3.4956
8.04	14.38	73.6915	3.8785
4.67	5.17	85.6425	4.5075

(b) Tie-Line Data—Salt-Free Basis

ethyl acetate phase			water phase		
X_C	X_S	X_A	X_C	X_S	X_A
9.76	84.75	5.49	9.5	5.9	84.6
12.07	81.75	6.18	11.68	7.02	81.3
16.85	76.35	6.8	17.06	9.94	73.5
21.57	69.5	8.93	20.72	13.07	66.2
27.86	58.25	13.89	25.23	26.27	48.5

Experimental Procedures. The solubility (binodal curve) and the tie-line data were determined at 30 ± 0.1 °C and at atmospheric pressure, viz., 760 ± 3 torr by the procedure detailed elsewhere (*6*, *7*). The analysis for the determination of acetic acid content of the two layers was done by direct titrations of a weighted sample against 0.5 N sodium hydroxide with phenolphthalein as the indicator. The salt concentrations were 5%, 10%, and 15% by weight, which are well within the saturation limit. The concentration measurements for all of the systems studied were generally accurate to ±0.005 weight fraction and the thermostatic bath temperature could be controlled to ± 0.1 K. Special precaution was taken to keep the ethyl acetate layer in an ice bath while titrating (in acetic acid determination) against sodium hydroxide, as acetate hydrolyzes to acid at room temperature.

Presentation and Discussion of the Results

The experimental ternary solubility data (i.e., the points on the binodal curve) and the tie-line data all in weight percentage for the system ethyl acetate–acetic acid–water in the presence of dissolved potassium chloride, sodium sulfate, and sodium chloride all at 5%, 10%, and 15% concentrations are presented in Tables I–IX. The binodal curves for the nine situations, i.e., three salts each at three concentrations, are plotted in Figures 1–3. The literature solubility data at 30 °C for this ternary system without salt (*8*) have also been shown in these figures for comparison. As could be observed from these diagrams the region of heterogeneity, i.e., the two-phase region, in-

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Table II. Ethyl Acetate–Acetic Acid–10% KCl Salt Solution

(a) Binodal Curve Data

concn, wt %			
ethyl acetate	acetic acid	water	KCl salt
81.72	11.6	6.48	0.72
61.04	28.176	9.693	1.077
52.02	30.76	15.489	1.721
51.81	29.89	16.452	1.828
44.85	31.39	21.366	2.374
36.9	30.52	29.304	3.256
24.5	26.85	43.776	4.864
12.24	22.80	58.365	6.485
10.5	19.83	62.676	6.964
7.55	17.43	67.5	7.5
4.45	7.17	79.515	8.835

(b) Tie-Line Data—Salt-Free Basis

ethyl acetate phase			water phase		
X_C	X_S	X_A	X_C	X_S	X_A
10.13	83.5	6.37	10.58	4.92	84.5
12.16	80.75	7.09	13.1	5.9	81
17.20	75	7.80	16.87	6.88	76.25
22.15	69	8.85	20.27	9.98	69.75
28.10	61	10.9	24.02	15.48	60.5

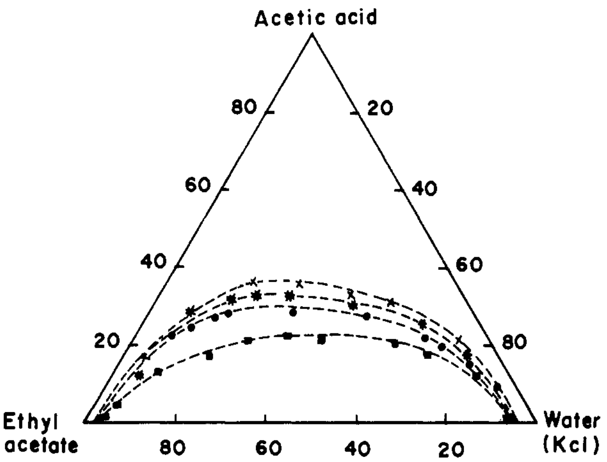

Figure 1. Binodal curves for the system ethyl acetate–acetic acid–water with and without KCl salt—concentrations on salt-free basis: (■) no-salt binodal curve, (●) 5% KCl binodal curve, (•) 10% KCl binodal curve, (X) 15% KCl binodal curve.

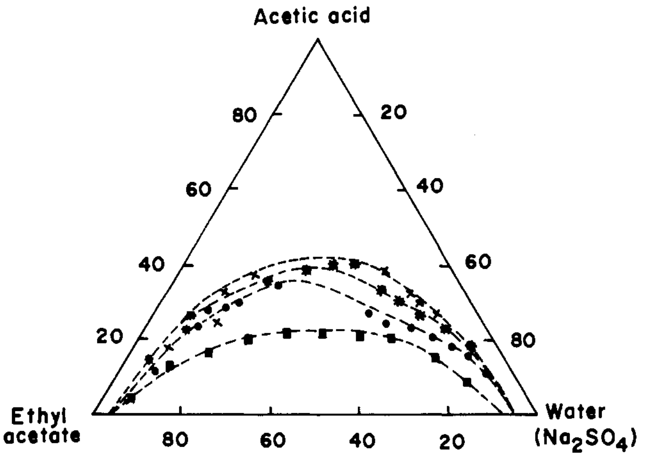

Figure 2. Binodal curves for the system ethyl acetate–acetic acid–water with and without Na_2SO_4 salt—concentrations on salt-free basis: (■) no-salt binodal curve, (●) 5% Na_2SO_4 binodal curve, (•) 10% Na_2SO_4 binodal curve, (X) 15% Na_2SO_4 binodal curve.

Table III. Ethyl Acetate–Acetic Acid–15% KCl Solution

(a) Binodal Curve Data

concn, wt %			
ethyl acetate	acetic acid	water	KCl salt
79.67	13.01	6.2135	1.0965
64.22	23.97	10.0215	1.7685
57.90	26.12	13.5575	2.3925
52.15	30.08	15.0875	2.6625
48.59	29.10	18.955	3.345
41.31	32.13	22.525	3.975
34.98	33.23	27.0045	4.7655
22.79	30.68	39.576	6.984
15.89	29.56	46.3505	8.1795
12.12	25.65	52.887	9.333
11.65	24.87	53.949	9.5205
7.42	16.70	64.481	11.379
4.20	8.83	73.9075	13.0425

(b) Tie-Line Data—Salt-Free Basis

ethyl acetate phase			water phase		
X_C	X_S	X_A	X_C	X_S	X_A
10.78	83.25	5.97	10.48	6.02	83.5
18.00	74.5	7.5	16.09	6.41	77.5
22.38	67.5	10.12	19.87	7.88	72.25
27.12	59.9	12.98	23.39	9.61	67

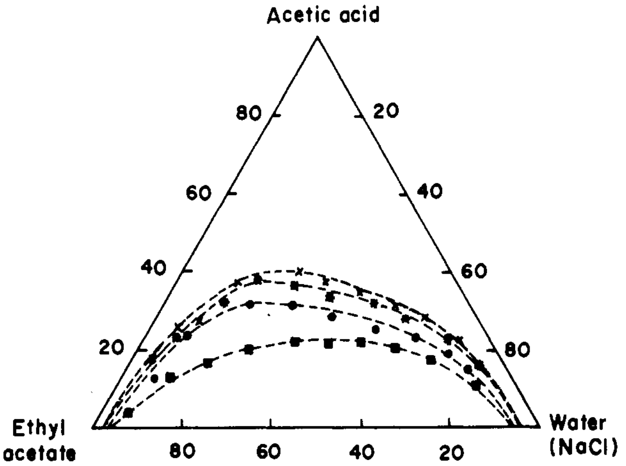

Figure 3. Binodal curves for the system ethyl acetate–acetic acid–water with and without NaCl salt—concentrations on salt-free basis: (■) no-salt binodal curve, (●) 5% NaCl binodal curve, (•) 10% NaCl binodal curve, (X) 15% NaCl binodal curve.

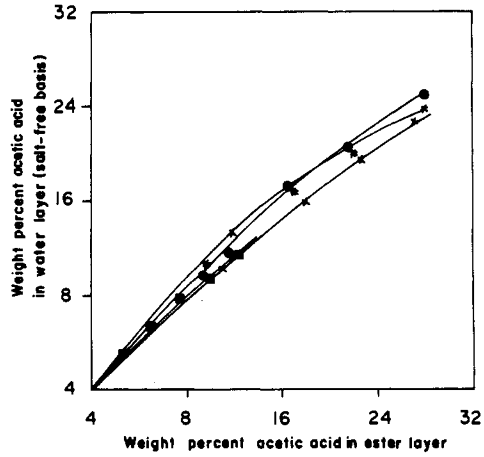

Figure 4. Distribution of acetic acid between ethyl acetate and water, 30 °C: (■) no salt present, (●) 5% KCl solution, (•) 10% KCl solution, (X) 15% KCl solution.

Table IV. Ethyl Acetate-Acetic Acid-5% Na_2SO_4 Solution

(a) Binodal Curve Data at 30 °C

concn, wt %			
ethyl acetate	acetic acid	water	Na_2SO_4
79.30	10.162	9.937	0.523
64.60	23.12	11.5710	0.609
55.93	28.27	15.0005	0.7895
52.30	30.45	16.3685	0.8615
50.20	30.89	17.955	0.945
42.27	35.43	21.166	1.114
33.63	36.80	28.0725	1.4775
31.43	37.50	29.507	1.553
24.45	27.19	45.885	2.415
20.80	24.20	52.155	2.745
18.80	23.35	54.9385	2.8915
16.55	22.35	58.026	3.054
14.09	20.90	61.7405	3.2495
12.65	20.62	63.3745	3.3355
11.30	18.90	66.253	3.487
8.30	15.08	72.7795	3.8305
6.20	10.966	78.565	4.135

(b) Tie-Line Data—Salt-Free Basis

ethyl acetate phase			water phase		
X_C	X_S	X_A	X_C	X_S	X_A
13.33	77	9.67	11.73	7.77	80.5
15.63	74.5	9.87	13.56	9.19	77.25
22.32	66.5	11.18	14.9	9.10	76
24.22	63	12.78	18.17	10.83	71
28.43	56.5	15.07	21.2	14.80	64

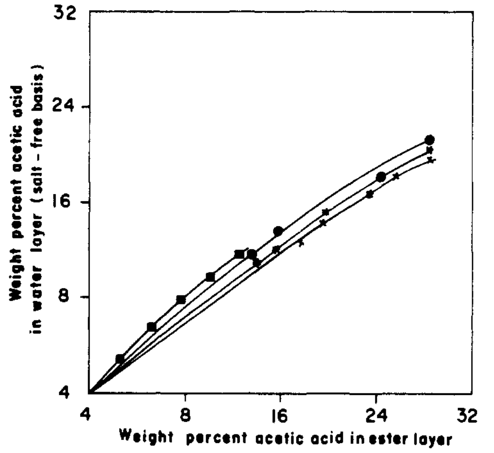

Figure 5. Distribution of acetic acid between ethyl acetate and water, 30 °C: (■) no salt present, (●) 5% Na_2SO_4 solution, (*) 10% Na_2SO_4 solution, (X) 15% Na_2SO_4 solution.

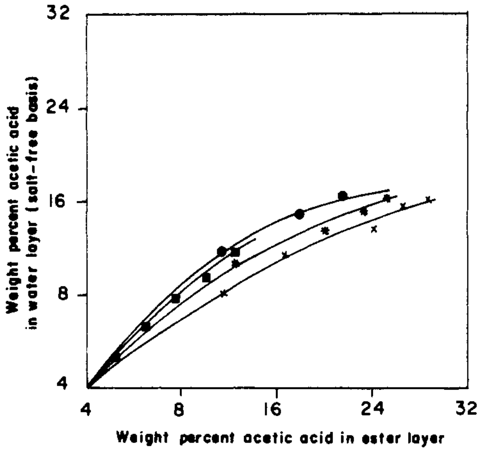

Figure 6. Distribution of acetic acid between ethyl acetate and water, 30 °C: (■) no salt present, (●) 5% NaCl solution, (*) 10% NaCl solution, (X) 15% NaCl solution.

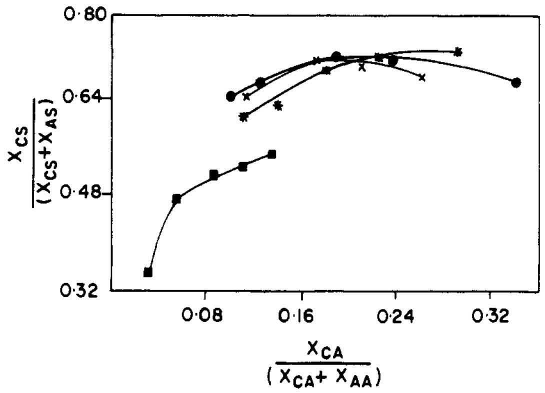

Figure 7. Selectivity diagram for the system ethyl acetate-acetic acid-water with and without KCl salt—concentrations on salt-free basis: (■) no salt present, (●) 5% KCl solution, (*) 10% KCl solution, (X) 15% KCl solution.

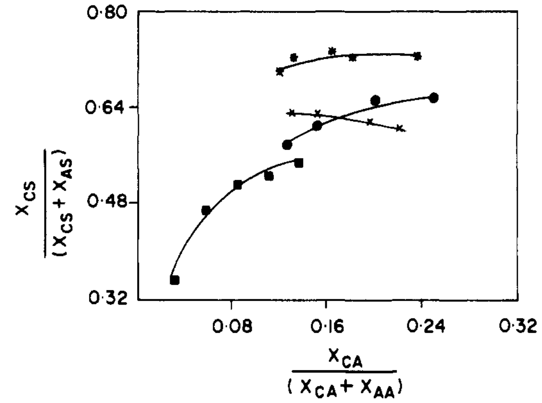

Figure 8. Selectivity diagram for the system ethyl acetate-acetic acid-water with and without Na_2SO_4 salt—concentrations on salt-free basis: (■) no salt present, (●) 5% Na_2SO_4 solution, (*) 10% Na_2SO_4 solution, (X) 15% Na_2SO_4 solution.

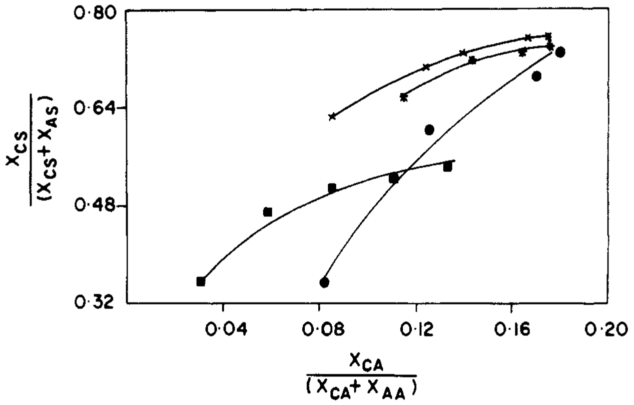

Figure 9. Selectivity diagram for the system ethyl acetate-acetic acid-water with and without NaCl salt—concentrations on salt-free basis: (■) no salt present, (●) 5% NaCl solution, (*) 10% NaCl solution, (X) 15% NaCl solution.

creases on adding these salts with the area (in general) increasing with an increase in salt concentration and in the case of 15% concentration of the sodium sulfate salt there is also a shift of the binodal curve to the right. Figures 4–6 show that salt addition (at these three concentrations) results in the preferential distribution of acetic acid in the ester layer. As has already been mentioned, this system tends to form a solutrope and the tie lines at no-salt condition are almost horizontal. The addition of any of the salts studied shifts the acetic acid distribution in favor of the ethyl acetate layer even at low concentration. Also, the tendency to form a solutrope ceases to exist.

Table V. Ethyl Acetate–Acetic Acid–10% Na_2SO_4 Solution

(a) Binodal Curve Data at 30 °C

concn, wt %			
ethyl acetate	acetic acid	water	Na_2SO_4
80.92	12.67	6.552	0.728
64.16	24.96	9.72	1.08
65.54	21.87	11.313	1.257
58.27	25.78	14.346	1.594
51.98	29.04	17.064	1.896
42.89	33.60	21.123	2.347
31.99	38.40	26.271	2.919
25.04	38.30	32.94	3.66
18.23	31.84	44.919	4.991
16.25	28.14	50.04	5.560
13.46	25.09	55.26	6.140
9.94	22.00	61.245	6.805
5.68	16.50	69.993	7.777

(b) Tie-Line Data—Salt-Free Basis

ethyl acetate phase			water phase		
X_C	X_S	X_A	X_C	X_S	X_A
13.81	80.25	5.94	11.2	5.8	83
15.63	78.4	5.97	12.1	6.0	81.9
19.58	73	7.42	15.36	5.89	78.75
23.34	67.5	9.16	16.63	6.12	77.25
28.42	60.5	11.08	21.5	8.75	69.75

Table VI. Ethyl Acetate–Acetic Acid–15% Na_2SO_4 Solution

(a) Binodal Curve Data at 30 °C

concn, wt %			
ethyl acetate	acetic acid	water	Na_2SO_4
83.50	8.50	6.8	1.2
72.41	15.00	10.7015	1.8885
58.78	22.84	15.623	2.757
43.01	31.57	21.607	3.813
33.16	35.52	26.486	4.674
20.05	37.35	36.193	6.387
14.43	34.46	43.435	7.665
12.24	29.94	49.130	8.67
10.84	27.76	52.1815	9.2085
9.29	24.89	55.930	9.870
5.32	19.23	64.1155	11.3145

(b) Tie-Line Data—Salt-Free Basis

ethyl acetate phase			water phase		
X_C	X_A	X_S	X_C	X_S	X_A
17.37	10.13	72.5	12.39	6.11	81.5
19.5	12.10	68.4	14.9	4.9	80.2
25.69	16.01	58.3	18.57	4.93	76.5
28.32	18.18	53.5	20.75	5.75	73.5

Table VII. 5% NaCl Solution–Acetic Acid–Ethyl Acetate

(a) Binodal Curve Data at 30 °C

concn, wt %			
ethyl acetate	acetic acid	water	NaCl
80.34	12.16	7.115	0.3745
67.25	23.96	8.341	0.439
55.08	30.526	13.6705	0.7195
48.17	30.84	19.9215	1.0485
38.89	30.61	28.767	1.513
31.80	27.86	38.8075	2.0425
23.53	25.213	48.683	2.5623
15.80	22.26	58.843	3.097
10.87	18.10	64.096	3.3735
8.41	14.68	73.055	3.845

(b) Tie-Line Data—Salt-Free Basis

ethyl acetate phase			water phase		
X_C	X_S	X_A	X_C	X_S	X_A
4.1	88.50	7.40	7.75	6.90	85.35
11.23	81.25	7.52	11.70	7.30	81.00
17.90	74.00	8.10	14.91	13.09	72.00
21.70	70.25	8.05	16.52	8.48	75.00
25.69	60.00	14.31	16.02	9.48	74.50

Table VIII. 10% NaCl Solution–Acetic Acid–Ethyl Acetate

(a) Binodal Curve Data at 30 °C

concn, wt %			
ethyl acetate	acetic acid	water	NaCl
68.12	22.68	8.271	0.919
61.34	26.83	10.638	1.182
54.54	30.37	13.239	1.471
43.26	37.27	17.505	1.945
35.63	35.514	25.956	2.884
28.65	32.60	34.785	3.865
21.63	29.71	43.776	4.864
14.70	25.57	53.703	5.967
8.82	19.72	64.3014	7.1446
5.87	14.78	71.397	7.933

(b) Tie-Line Data—Salt-Free Basis

ethyl acetate phase			water phase		
X_C	X_S	X_A	X_C	X_S	X_A
12.56	80.75	6.69	10.81	4.69	84.50
19.79	72.50	7.72	13.52	5.23	81.25
23.21	67.80	8.99	15.42	6.08	78.50
25.30	65.00	9.70	16.64	6.11	77.25

Table IX. 15% NaCl Solution–Acetic Acid–Ethyl Acetate

(a) Binodal Curve Data at 30 °C

concn, wt %			
ethyl acetate	acetic acid	water	NaCl
75.91	16.54	6.409	1.131
62.50	25.04	10.565	1.8645
47.38	36.13	14.013	2.4730
31.85	38.57	25.12855	4.434
27.40	34.45	32.4173	5.1380
21.95	32.20	38.5475	6.8025
16.90	28.20	46.656	8.2335
11.30	25.70	53.482	9.438
7.43	20.15	61.54	10.86

(b) Tie-Line Data—Salt-Free Basis

ethyl acetate phase			water phase		
X_C	X_S	X_A	X_C	X_S	X_A
11.50	81.50	7.00	7.99	5.51	86.50
16.13	76.90	6.97	11.70	5.30	83.00
23.86	66.90	9.24	13.54	5.46	81.00
26.47	64.50	9.03	15.79	5.71	78.50
28.88	61.50	9.62	16.515	5.985	77.50

The selectivity values (which vary with solute concentrations) have also been calculated for all these situations to ascertain their variation on adding a salt. It is found that the presence of dissolved salt has a pronounced effect on selectivity and this could be observed from Figures 7–9, which have $X_{CS}/(X_{CS} + X_{AS})$ on the ordinate and $X_{CA}/(X_{CA} + X_{AA})$ on the abscissa with the concentration of the salt in question as a parameter.

The reliability of the tie-line data obtained in this investigation has been checked by making the Othmer and Tobias (*9*) and Hand (*10*) plots. The data could be correlated satisfactorily, indicating their consistency according to these graphical methods. The tie-line data have also been correlated by the Eisen–Joffe equation (*3*, *4*)

$$\log \frac{X_{CS}}{X_{SS}} = (a + bX_S{}^1) + (c + dX_S{}^1) \log \frac{X_{CA}}{X_{AA}}$$

in which a, b, c, and d are constants whose magnitude depends on the nature of the system components, salt used, and temperature but are independent of salt concentration. The results of this data fitting are recorded in Tables X–XII, which include also the constants a, b, c, and d for the salts studied in this work. These constants were determined by using the

Table X. Eisen–Joffe Correlation for Ethyl Acetate–Acetic Acid–KCl Solution

(a) Correlation Constants

salt concn	*a*	*b*	*c*	*d*
no salt	0.041		1.068	
5% KCl	0.041 39	0.3102	1.068	−0.4126
10% KCl	0.041 39	0.2679	1.068	−0.421
15% KCl	0.041 39	0.3234	1.068	−0.338
		0.3005 ± 0.051 (av)		−0.4072 ± 0.088 (av)

(b) Tie-Line Data Correlation

exptl X_{CA}/X_{AA}	exptl X_{CS}/X_{SS}	calcd X_{CS}/X_{SS}
	5% KCl	
0.1122	0.1152	0.1156
0.1436	0.1472	0.14005
0.2337	0.2207	0.2263
0.3130	0.3103	0.3042
0.5250	0.4782	0.4975
	10% KCl	
0.1252	0.1213	0.126
0.1617	0.1506	0.1612
0.2212	0.2293	0.2243
0.2906	0.3210	0.2914
0.3970	0.4606	0.4036
	15% KCl	
0.1255	0.1295	0.1346
0.2076	0.2416	0.2276
0.2750	0.3315	0.2988
0.3491	0.4527	0.380

Table XI. Eisen–Joffe Correlation for Ethyl Acetate–Acetic Acid–Na_2SO_4 Solution

(a) Correlation Constants

salt concn	*a*	*b*	*c*	*d*
no salt	0.041		1.068	
5% Na_2SO_4	0.041	6.776	1.068	4.876
10% Na_2SO_4	0.041	6.307	1.068	5.153
15% Na_2SO_4	0.041	6.020	1.068	5.3437
		6.367 ± 0.699 (av)		5.124 ± 0.413 (av)

(b) Tie-Line Data Correlation

exptl X_{CA}/X_{AA}	exptl X_{CS}/X_{SS}	calcd X_{CS}/X_{SS}
	5% Na_2SO_4	
0.1457	0.1731	0.16358
0.1755	0.2098	0.2045
0.1960	0.3356	0.2403
0.2560	0.3840	0.3457
	10% Na_2SO_4	
0.1349	0.1721	0.1519
0.1477	0.1993	0.1788
0.1950	0.2682	0.2741
0.2152	0.3458	0.3176
0.3083	0.4697	0.5592
	15% Na_2SO_4	
0.1520	0.2396	0.2048
0.1858	0.2851	0.308
0.2427	0.4406	0.509
0.2823	0.5293	0.702

Table XII. Eisen–Joffe Correlation for Ethyl Acetate–Acetic Acid–NaCl Solution

(a) Correlation Constants

salt concn	*a*	*b*	*c*	*d*
no salt	0.0413		1.068	
5% NaCl	0.0413	5.192	1.068	2.96
10% NaCl	0.0413	5.0267	1.068	2.98
15% NaCl	0.0413	4.8135	1.068	2.73
		5.0107 ± 0.333 (av)		2.89 ± 0.244 (av)

(b) Tie-Line Data Correlation

exptl X_{CA}/X_{AA}	exptl X_{CS}/X_{SS}	calcd X_{CS}/X_{SS}
	5% NaCl	
0.0908	0.046	0.099
0.1444	0.1382	0.1757
0.2071	0.2419	0.2506
0.2203	0.3088	0.2942
0.2203	0.4281	0.2832
	10% NaCl	
0.1279	0.1555	0.1829
0.1664	0.2730	0.2628
0.1964	0.3423	0.3264
0.2154	0.3892	0.3752
	15% NaCl	
0.0923	0.1411	0.1340
0.1409	0.2097	0.2547
0.1672	0.3566	0.3273
0.2011	0.4104	0.4291
0.2131	0.4696	0.4685

tie-line data of this investigation along with literature data (*8*) for this system in the absence of salts and employing a graphical procedure. A plot of X_{CS}/X_{SS} vs. X_{CA}/X_{AA} of the literature data on log–log coordinates gives the constants *a* and *c* directly as at zero salt concentration, i.e., at $X_S{}^1 = 0$ the above equation reduces to $\log (X_{CS}/X_{SS}) = a + C \log (X_{CA}/X_{AA})$. Then by using the tie line obtained in this investigation at three salt concentrations and *a* and *c* already obtained, we determined the constants *b* and *d* by a similar graphical procedure. The 95% confidence limits for the constants *b* and *d*, respectively, calculated by the standard procedure are as follows: ethyl acetate–acetic acid–KCl solution, 0.3005 ± 0.051, −0.4072 ± 0.088; ethyl acetate–acetic acid–Na_2SO_4 solution, 6.367 ± 0.699, 5.124 ± 0.413; ethyl acetate–acetic acid–NaCl solution, 5.0107 ± 0.333, 2.89 ± 0.244.

As could be seen from Tables X–XII barring a few data points, the tie-line data in the presence of salts could be correlated with an accuracy of ±10%.

In conclusion, it may be mentioned that the effects of dissolved salts on the distribution of a solute between two immiscible solvents is a problem having potential engineering applications despite a few negative features like corrosion and recovery problems that are associated with such commercial applications.

Glossary

X_A	weight percent of water on a salt-free basis
X_C	weight percent of acetic acid on a salt-free basis
X_S	weight percent of ethyl acetate on a salt-free basis
X_{AA}	weight fraction of water in aqueous phase on a salt-free basis
X_{SS}	weight fraction of solvent (ethyl acetate) in solvent phase on a salt-free basis
X_{CA}	weight fraction of solute (acetic acid) in aqueous phase on a salt-free basis
X_{CS}	weight fraction of solute in solvent phase on a salt-free basis
$X_S{}^1$	salt concentration, g of salt/(100 g of salt and water)

Registry No. Na_2SO_4, 7757-82-6; NaCl, 7647-14-5; KCl, 7447-40-7; acetic acid, 64-19-7; ethyl acetate, 141-78-6.

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Received for review February 1, 1984. Accepted September 4, 1984.

Vapor–Liquid Equilibria for the System Cyclohexane–*tert*-Butyl Alcohol

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Isothermal vapor pressure data over the whole range of composition were obtained for the binary system cyclohexane–*tert*-butyl alcohol. Data were taken at temperatures of 328.2 and 343.3 K by using a vapor-recirculating equilibrium still. Data were correlated by the Wilson, NRTL, and modified UNIQUAC equations. The Wilson equation gives the best fit for the two-parameter models. The three-parameter NRTL equation gives the best fit for all the models considered in this work.

Introduction

The vapor–liquid equilibria for the system cyclohexane–*tert*-butyl alcohol have been previously investigated (*1–6*). Most of these studies have been carried out under isobaric conditions (*2–5*). Prigogine and Desmyter (*1*) have measured this system at 300 K for a range of composition up to 60% of the alcohol mole fraction. Buchowski and Bartel (*6*) have reported data at 303.15 K over the whole range of composition.

The aim of this work was to provide equilibrium data for the binary system cyclohexane–*tert*-butyl alcohol at 328.2 and 343.3 K. This paper reports the results of these measurements and their correlation by the Wilson, Renon–Prausnitz (NRTL), and modified Abrams–Prausnitz (UNIQUAC) equations.

Experimental Section

Chemicals. Cyclohexane and *tert*-butyl alcohol were Merck analytical-grade reagents used without any further purification (minimum purities of 99.5%). Some physical properties of the chemicals are listed in Table I along with literature values.

Vapor Pressure Measurements. Vapor pressures were measured at constant temperature as a function of composition by using a vapor-recirculating equilibrium still. The equilibrium still was a simplified version of the one described by Hipkin and Myers (*7*). Instead of the vapor jacket used in the original design, the contactor is self-lagged with its own vapor assuring adiabatic conditions. A schematic view of the apparatus is shown in Figure 1. The equilibrium still was connected through a cold trap to the regulating and measurement pressure devices. Pressures were measured by a mercury manometer. Mercury heights were determined with a cathetometer whose accuracy was ±0.2 mm. All observed pressures were corrected to give the equivalent height of a mercury column at 273.2 K and standard gravity. Temperatures were measured with a certified thermometer (Will Scientific 710-5) with a stated accuracy of ±0.1 K.

Table I. Physical Properties of Chemicals

	refractive index at 298.2 K		vapor press./kPa			
			328.2 K		343.3 K	
	exptl	lit.	exptl	lit.	exptl	lit.
cyclohexane	1.4235	1.423 54[a]	43.72	43.68[c]	72.44	72.58[c]
tert-butyl alcohol	1.3860	1.385 2[b]	30.43	30.73[c]	60.98	60.82[c]

[a] Reference *16*. [b] Reference *17*. [c] Reference *18*.

Table II. Vapor–Liquid Equilibrium Data for the Binary System Cyclohexane (1)–*tert*-Butyl Alcohol (2) at 328.2 K

	P/kPa	x_1	y_1
1	30.43	0.000	0.000
2	35.32	0.034	0.166
3	38.15	0.069	0.253
4	41.56	0.128	0.334
5	44.00	0.156	0.393
6	48.00	0.231	0.474
7	50.37	0.315	0.531
8	51.96	0.391	0.567
9	53.26	0.471	0.609
10	54.04	0.536	0.628
11	54.26	0.601	0.657
12	54.44	0.679	0.683
13	54.42	0.736	0.705
14	54.13	0.802	0.729
15	53.82	0.835	0.738
16	51.08	0.948	0.821
17	43.72	1.000	1.000

Table III. Vapor–Liquid Equilibrium Data for the Binary System Cyclohexane (1)–*tert*-Butyl Alcohol (2) at 343.3 K

	P/kPa	x_1	y_1
1	60.98	0.000	0.000
2	65.33	0.018	0.073
3	69.61	0.073	0.187
4	74.40	0.111	0.264
5	79.26	0.144	0.329
6	83.64	0.202	0.391
7	90.89	0.342	0.496
8	93.57	0.444	0.523
9	93.94	0.489	0.575
10	94.40	0.504	0.587
11	95.10	0.599	0.628
12	94.81	0.618	0.623
13	94.96	0.643	0.643
14	94.93	0.655	0.630
15	93.41	0.783	0.695
16	87.76	0.941	0.790
17	77.85	0.994	0.924
18	72.44	1.000	1.000

Compositions of the liquid and condensed vapor were obtained from measurements of their refractive indices at 298.2

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0021-9568/85/1730-0171$01.50/0