

**Liquid Parahydrogen.** There are two sets of earlier measurements on liquid parahydrogen at saturation pressures. Powers, Mattox, and Johnston (5) obtained values ranging from 0.00118 at 16.83° K. to 0.00128 watt per cm. ° K. at 23.23° K. The other set of data is from unpublished (4) results of work carried out by McCall at the University of St. Andrews in Scotland; the values obtained there range from 0.00146 at 18.0° K. to 0.00166 at 25.6° K. The authors' mean value at saturation pressure is  $0.0030 \pm 0.0015$ ; it agrees with McCall's results within the authors' estimated experimental error, but is slightly larger than the measurements made by Johnston and his associates. Considering the necessity of having the walls of the cell relatively thick to withstand higher pressures, the agreement of the present results with those previously published for the liquid at saturation pressure are considered to be fairly good.

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## Salt Effect on Liquid-Liquid Equilibria in the Ethyl Acetate-Ethyl Alcohol-Water System

M. U. PAI and K. MADHUSUDANA RAO<sup>1</sup>  
National Chemical Laboratory, Poona, India

**Salt effect on the liquid-liquid equilibria of the ternary ethyl acetate-ethyl alcohol-water system has been investigated at 30° C. with potassium acetate and sodium acetate, respectively. Solubility and tie-line data of the two quaternaries have been determined at salt saturation in each case, as well as in the basic ternary in the absence of salt at that temperature. Salt effect is discussed. Certain features of the potassium acetate system indicate its advantage over sodium acetate. Data on the effect of some electrolytes on mutual solubilities of ethyl acetate and water at salt saturation at 30° C. also are presented here.**

**T**HE RECOVERY of anhydrous, technically pure ethyl acetate from its mixtures with ethyl alcohol generally involves an aqueous extraction step to remove the latter. The ternary system ethyl acetate-ethyl alcohol-water is, thus, of considerable industrial importance. Concurrent with separation of ethanol from the ester, lowering the mutual solubilities of the ester and water in presence of ethanol is important to minimize the loss of ester in the aqueous phase and to obtain a drier ester. The latter is particularly essential in certain organic processes requiring anhydrous conditions as in the production of ethyl acetate. Each part of water is accompanied by about 10 parts of ester in the ternary azeotrope on distillation (5); even more ester is removed per part of water when the ethyl acetate-water binary is fractionated (5).

Although the industrial use of potassium acetate solution has been reported (2) for this system, no phase data seem to be available in literature. Such data have been published only for a few systems until now, although salt effect on binary liquid systems seems to have been investigated more extensively. The present work deals mainly with the effect of potassium acetate and sodium acetate on this ternary at 30° C.

<sup>1</sup>Present address: Central Salt & Marine Chemical Research Institute, Bhavnagar, India.

#### EXPERIMENTAL

**Materials.** ETHYL ALCOHOL. Absolute ethyl alcohol was purified by the method recommended by Vogel (10) (B.P. at 710 mm. of Hg, 76° C.,  $d_4^{30}$  0.7810). ETHYL ACETATE. Technical grade ester was treated with potassium carbonate and then fractionated (B.P. at 710 mm. of Hg, 75.4° C.,  $d_4^{30}$  0.8877). WATER. Pure double-distilled. SALTS. Anhydrous potassium acetate and sodium acetate and other salts, all of C.P. grade were used.

**Procedure.** The binodal curve and the tie lines for the ternary system at 30° C. were determined by the method of Othmer, White, and Trueger (4). About 3 hours' settling time, after 30 minutes of vigorous shaking, was sufficient for complete phase separation in tie-line determinations. The tie-line data were checked by the addition-point method.

The binodal curve of the quaternary system ethyl acetate-ethyl alcohol-salt-water at complete salt saturation was determined essentially by the trial and error procedure adopted by Swabb and Mongan (8). Known mixtures of ethyl acetate and fine dry salt crystals were titrated carefully with water and ethanol in 125-ml. stoppered glass conical flasks maintained at 30° C. in a thermostat (30° + 0.1° C.). The titrations were so adjusted that the disappearance of the two liquid phases closely coincided with the dissolution of all but a couple of salt crystals. This then was

equilibrated for an hour with frequent shaking to ensure the end point as indicated by no perceptible change in solid salt content in the homogenous liquid phase. Quite good reproducibility could be obtained after some preliminary trials. All readings were checked by duplicate or more runs and any discordant values were discarded. While the entire potassium acetate system and the water-rich side of the sodium acetate system did not present any difficulties, the ester-rich curve of the latter required very careful manipulation to obtain the correct titration end-points since it is more sensitive to alcohol concentrations. The binodal curve points were calculated on weight basis with the help of accurate density values of the liquids.

Tie-line data were determined by the usual procedure in the presence of solid salt after vigorous contact for an hour followed by settling for about three hours at 30° C. In each liquid phase, ethyl acetate content was determined using 1*N* alcoholic KOH (7), water by Karl Fischer reagent (3), and salt by careful evaporation. All analysis was done until duplicates agreed closely. Blank readings for alcoholic KOH were taken. Water content in the aqueous phase was determined by admixing it in known proportions with water-free methanol to obtain a low-water mixture for analysis and, thus, finally by calculating the water content of the water phase samples. The blank reading for methanol also was taken. Special precautions were taken to avoid spurting during evaporation and in drying to the completely anhydrous state at about 150° C. in salt-content deter-

minations; sodium acetate presented greater difficulty than potassium acetate.

## RESULTS

The binodal curve and tie-line data for the ternary ethyl acetate-ethyl alcohol-water are given in Table I. Mutual solubilities of ethyl acetate and water at salt saturation are given in Table II. Tables III and IV give the solubility and tie-data for the four-component systems with potassium acetate and sodium acetate, respectively.

As the two four-component systems were studied at 30° C., solubility and equilibria without salt were also determined at 30° C. to observe the isothermal salt-effect by comparison. The latter data supplement the available experimental polythermal data, since tie-line data at 30° C. do not seem to have been reported yet.

The authors' latter data satisfied the Hand as well as Othmer-Tobias correlations. The Bachman coordinates, however, gave a curve.

Since the reliability criteria and correlation tests for four-component systems require elaborate procedure, the authors' data were plotted on conventional triangular plots on a salt-free basis. While complete representation of four-component systems in the interior of a tetrahedron would give a curved surface, it will not only require additional data but does not enable a ready comparison with the basic ternary data obtained in the absence of salt. The two "pseudo" (salt-free basis) solubility curves *B* and *C* with their respective tie-lines, are shown superimposed on the basic ternary curve *A* in Figure 1. These pseudo curves, incidentally, have a realistic significance since they repre-

Table I. Binodal Curve Data for Ethyl Acetate-Ethanol-Water System

Data in wt. %; temp., 30° C.

Ethylacetate	Ethanol	Water
96.51	0.00	3.49
87.52	6.03	6.45
77.97	10.51	11.52
53.72	18.20	28.08
41.51	19.30	39.19
30.96	19.43	49.61
23.23	18.78	57.99
18.48	17.67	63.85
17.56	17.17	65.27
9.93	10.19	79.88
8.71	5.86	85.43
8.42	4.88	86.70
7.25	0.00	92.75

Tie-Line Data

Ester Layer		
91.05	4.48	4.47
84.26	8.15	7.59
72.80	13.35	13.85
67.61	15.76	16.63

Aqueous Layer		
7.83	5.65	86.52
9.04	9.96	81.00
12.04	14.72	73.24
13.86	15.33	70.81

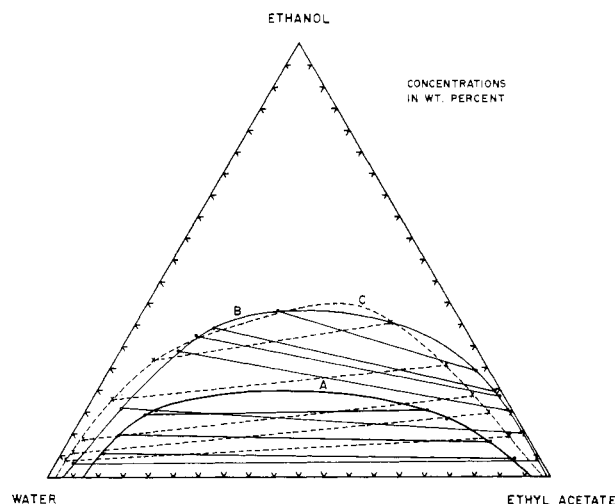


Figure 1. Ethyl acetate-ethanol-potassium/sodium acetate-water at 30° C.

Basic ternary in absence of salt(A), potassium acetate (B), and sodium acetate(C) pseudo (salt free) basis

Table II. Liquid-Phase Equilibrium Compositions in the Three-Phase Ethyl Acetate-Water-Solid Salt Systems

Data in wt. %; temp., 30° C.

Salt Used	Ester Layer			Aqueous Layer		
	Ethyl acetate	Water	Salt	Ethyl acetate	Water	Salt
No salt used	96.51	3.49	...	7.25	92.75	...
Potassium acetate	99.29	0.71	...	0.75	27.72	71.53
Sodium acetate	98.33	1.67	...	0.88	61.77	37.35
Potassium chloride	97.81	2.19	...	1.22	72.50	26.28
Sodium chloride	98.22	1.78	...	0.62	73.24	26.13
Potassium sulfate	97.20	2.80	...	3.17	87.87	8.96
Sodium sulfate	97.18	2.82	...	0.25	73.41	26.34

Table III. Binodal Curve Data for Ethyl Acetate–Ethanol–Water–Potassium Acetate System at Salt Saturation

Data in wt. %; temp., 30° C.

Ethyl Acetate	Ethanol	Water	Potassium Acetate
0.75	0.00	27.72	71.53
1.75	2.58	26.41	69.26
2.53	6.51	23.33	67.63
3.34	8.45	22.66	65.55
6.69	13.70	18.50	61.11
15.51	20.44	16.75	47.30
22.25	22.87	13.73	41.15
27.32	25.54	13.48	34.66
33.57	25.11	10.54	30.78
35.74	25.20	10.00	29.06
40.67	25.85	8.86	24.62
45.72	25.96	6.97	21.35
49.83	26.50	6.50	17.17
55.53	26.27	5.01	13.19
63.77	24.88	3.05	8.30
71.89	22.79	1.93	3.39
81.13	16.94	0.81	1.12
94.74	4.47	0.74	0.05
99.29	0.00	0.71	0.00

Tie-Line Data  
Ester Layer

95.54	3.72	0.71	0.03
88.96	10.01	0.76	0.27
83.57	14.96	0.77	0.70
79.52	18.16	1.06	1.26
77.96	19.12	1.23	1.69
69.39	22.90	2.43	5.28

Aqueous Layer

0.89	0.92	27.25	70.94
2.14	4.95	24.07	68.84
3.83	10.47	21.01	64.69
4.77	12.25	20.21	62.77
6.13	13.09	18.92	61.86
12.88	18.48	56.88	51.76

sent the compositions after complete separation from salt and, particularly, as they lie wholly outside the heterogeneous region in these systems. The reliability of the present four-component experimental data given in Tables III and IV is evident by the close concurrence of tie-line plots on the solubility curves in the pseudo diagrams. While the experimental determination of salt content and any one component of equilibrated liquid phases would have been sufficient to know their complete compositions with the help of the pseudo solubility curves, three components were actually determined as already mentioned in the procedure to enable close checks on the results.

Certain correlations, such as the Setschenow (6) and Butler (7) equations, derived from theoretical stand-point, are useful in the study of salting-out effect of electrolytes on nonelectrolytes in aqueous solutions. Swabb and Mongan (8) could satisfactorily extend the application of the former to their four-component system. Both of the present four-component systems, however, gave progressively decreasing values of constants of both the equations. This may be due to rather high salt concentrations in the aqueous phase, whereas the first equation is expected to hold up to 3M and the latter up to 2M salt concentrations per liter, thus limiting the utility of the equations for the authors' systems.

#### DISCUSSION

Although salt effect on the ethyl acetate–water binary has been reported in literature with some salts, most of the

Table IV. Binodal Curve Data for Ethyl Acetate–Ethanol–Water–Sodium Acetate System at Salt Saturation

Data in wt. %; temp., 30° C.

Ethyl Acetate	Ethanol	Water	Sodium Acetate
0.88	0.00	61.77	37.35
1.78	5.79	60.10	32.33
3.14	14.38	52.63	29.85
11.52	24.16	42.14	22.18
14.20	26.50	39.55	19.75
17.90	29.06	35.97	17.07
30.09	35.74	24.36	9.81
31.06	36.20	23.25	9.49
36.10	37.45	19.67	6.78
37.92	37.53	18.72	5.83
43.23	37.00	15.85	3.92
48.49	35.05	14.09	2.37
54.62	31.52	11.63	2.23
65.93	24.93	7.90	1.24
90.82	6.06	3.10	0.02
95.48	2.12	2.39	0.01
98.33	0.00	1.67	...

Tie-Line Data  
Ester Layer

87.42	9.08	3.47	0.03
80.52	14.42	4.98	0.08
74.88	18.35	6.58	0.19
66.21	25.25	7.99	0.55
48.96	35.03	13.66	2.35

Aqueous Layer

0.92	2.84	61.65	34.59
1.30	3.58	61.43	33.69
1.61	5.49	60.46	32.44
2.32	12.34	53.83	31.51
5.58	20.79	50.72	22.91

data seem to be below salt saturation. The effect of some common electrolytes on this binary, given in Table II, was studied to assess the change in the mutual solubilities of the ester and water at salt saturation. While potassium acetate gave the least water content in the ester layer and sodium acetate next-best, the ester uptake in the aqueous layer was the least with sodium sulfate specially when considered on salt-free basis.

Heterogeneous area is an important characteristic. In the present system, the areas of the pseudo-solubility curves (Figure 1) are nearly twice that of the basic ternary. This is in marked contrast to the slight effect of sodium sulfate on the isopropyl alcohol–acetic acid–water system at 20° C. (8).

Figure 2 shows the distribution curves. The ester phase in both quaternaries exhibits a greater affinity for ethyl alcohol, this being more with sodium acetate (curve 3) than with potassium acetate (curve 2). In the basic ternary, however, a slightly greater affinity for aqueous phase is exhibited. The pseudo-distribution curves differ from each other. While a marked affinity of ethyl alcohol for aqueous phase is seen in the potassium acetate system (curve 4), the reverse is seen in the sodium acetate system (curve 5). The factual distribution coefficient—ratio of weight fraction of ethyl alcohol in aqueous phase to that in the ester phase—in the present four-component systems are appreciably less than one. The pseudo-distribution coefficients, however, are distinctly higher with potassium acetate than with sodium acetate. Swabb and Mongan's (8) four-component as well as salt-free basis data on their system do not exhibit any greater affinity of acetic acid to water than in their basic system. A slight solutropic effect also is noted in the pseudo-distribution curve of the potassium acetate system at low alcohol concentration while a clear solutrope

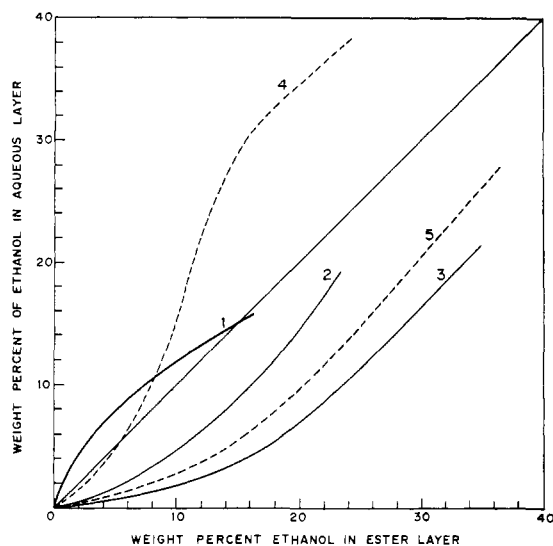


Figure 2. Distribution of ethanol between water and ethyl acetate at 30° C.

Basic ternary in absence of salt (1), potassium acetate (2) and sodium acetate (3) quaternary distribution, potassium acetate (4) and sodium acetate (5) pseudo (salt free) basis

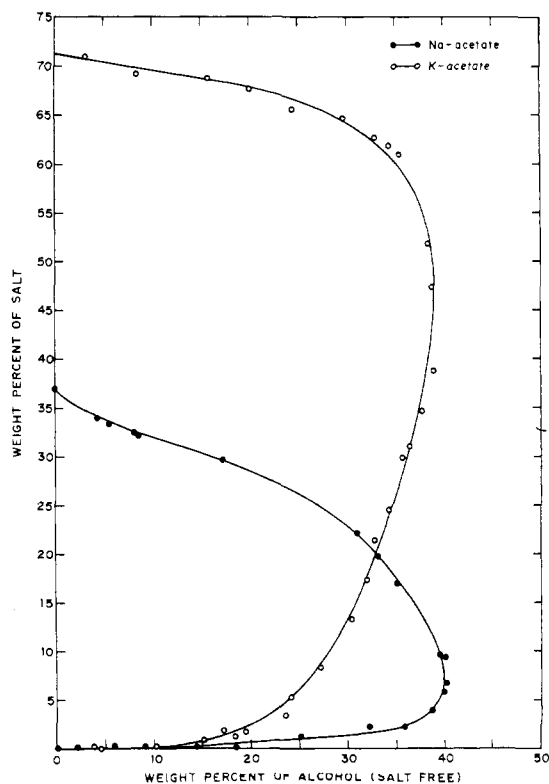


Figure 3. Salt concentration in the systems ethyl acetate-ethanol-potassium/sodium acetate-water at 30° C.

is indicated in the basic ternary (curve 1) at 15.2% ethyl alcohol concentration.

The quaternary selectivity (9) of water, with ethanol and salt as solutes, is quite low in both the systems—evidently due to the high solubility of salts in water. The pseudo-ternary selectivities, on salt-free basis, are much higher than in the basic ternary. Sodium acetate gives slightly higher values than potassium acetate.

Both sets of four-component data indicate salting-out of alcohol from the aqueous phase. However, considering the data on salt-free basis, the pseudo-distribution coefficients for the potassium acetate system, show salting-out from the ester phase leading to salting in to the aqueous phase. This helps to separate ethanol from the ester.

Potassium acetate also gives a dryer ester. Sodium acetate, on the other hand, depresses the solubility of ester in the aqueous phase. Since pseudo-distribution coefficients are higher with potassium acetate than with sodium acetate, the pseudo-selectivities in both cases being nearly of the same order, the former salt appears to be better. Potassium acetate, however, has the disadvantage of its higher solubility (Figure 3) and the consequent larger process inventory. The upper portion of each curve in Figure 3 corresponds to the aqueous phase, and the lower portion to the ester phase.

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