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SALT EFFECT IN LIQUID-LIQUID EQUILIBRIA OF ACETIC ACID-WATER-BENZENE SYSTEM

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The effect of sodium sulphate, potassium-sulphate and potassium chloride on the distribution of acetic acid between benzene and water at 35°C is reported. Distribution data of the three quaternaries have been determined at salt saturation and unsaturation in each case, as well as the basic ternary in the absence of salt at that temperature. The simple method of Setschenov is used to correlate the distribution data for the salt effect. All the three salts studied are found to have salting out effect for acetic acid in varying degrees.

KEYWORDS Salt effect Liquid-liquid equilibria Acid-water-benzene.

INTRODUCTION

The presence of a salt can either raise or lower the distribution coefficient of a solute in liquid-liquid equilibria. The distribution coefficient of solute is defined as the ratio of the composition of solute in solvent rich phase to the composition of solute in diluent (water) rich phase. These phenomena are known as salting out or salting in, respectively. Some data on salt effects in both aqueous and nonaqueous ternary systems are available in literature¹⁻⁸ suggesting empirical correlations.¹⁻⁵

EXPERIMENTAL SECTION

Materials

Analytical grade acetic acid, benzene, succinic acid, sodium hydroxide, sodium sulphate, potassium sulphate and potassium chloride were used. Acetic acid and succinic acid were supplied by Sarabhai M Chemicals, sodium hydroxide by Smith Stances and Blackwood Hodge, the three salts by Oster Chemicals and Pharmaceutical Works. Benzene is supplied by E Merck (India). Distilled water was prepared in the laboratory. All the liquid reagents were tested by chromatograph and failed to show the presence of any significant impurities.

Analyses

The standard succinic acid solution was prepared by weighing solid succinic acid accurately and dissolving it in a known volume of distilled water. The sodium hydroxide solution was standardized by using standard succinic acid solution with phenolphthalein as indicator. Weight percent acetic acid in each layer was estimated by titrating a weighed amount of solution against standard sodium hydroxide solution with phenolphthalein as indicator. The amount of salt present in aqueous layer was determined by evaporation and the amount of salt in organic layer was calculated by material balance. The results were reproducible with a maximum error of 0.5 percent.

PROCEDURE

Accurately weighed amounts of acetic acid, water and benzene were mixed in different ratios to obtain various *X*-*Y* values without salt. The mixture was stirred by a flask shaker for at least four hours in a stoppered conical flask. The layers were settled and separated in a separating funnel. A sample of around 2 ml

TABLE I

Distribution data of acetic acid in acetic acid-water-benzene system with Na₂SO₄ at 35°C

<i>X</i>	<i>Y</i>	Wt. percent Na ₂ SO ₄ in solution (salt free basis)	<i>Y</i> without salt
7.3	1.02	16.38 (S)	0.20
11.96	1.41	12.91 (S)	0.55
18.4	2.5	11.54 (S)	1.20
19.06	3.50	10.77 (S)	1.30
19.28	4.28	13.47 (S)	1.35
24.1	4.01	9.31 (S)	2.20
29.04	5.54	9.65 (S)	3.10
32.05	6.62	8.27 (S)	3.85
39.76	7.97	5.78 (S)	6.55
39.96	8.95	6.88 (S)	6.60
48.5	12.07	3.79 (S)	10.10
52.5	14.89	2.58 (S)	12.20
53.6	15.15	2.22 (S)	12.80
60.13	22.48	0.508 (S)	16.90
61.1	20.10	0.86 (S)	17.50
65.53	26.93	0.533 (S)	20.70
68.42	30.57	0.564 (S)	23.40
4.4	0.18	5.8	0.05
7.71	0.44	4.48	0.15
10.1	0.584	6.34	0.40
19.2	1.97	4.52	1.30
23.15	2.55	4.27	2.05
31.2	4.04	5.19	3.65
34.01	5.30	4.76	4.45
59.17	19.88	0.76	16.30

(S) Saturated.

from each layer was weighed accurately in an electrical balance and then titrated with standard sodium hydroxide. For X - Y values at saturation of salt, a weighed amount of the salt was taken and from this small amounts were added at a time to the weighed, layers forming mixture of acetic acid-water-benzene. The mixture was stirred using a magnetic stirrer and the addition of salt was continued until no salt was seen at the bottom of the stoppered conical flask. This was continued upto 8 hours. The amount of salt added for saturation was the beginning salt minus the remaining salt. Acetic acid content was determined as above. For unsaturated values, the amount of salt to be added to the mixture was calculated from the knowledge of salt consumed at saturation.

RESULTS AND DISCUSSION

Table I to III contain the experimental distribution data of acetic acid in water-benzene-acetic acid system with the three salts at different salt concentrations. Table IV contains the experimental distribution data of acetic acid without salt. Table V contains the comparison of distribution data by Garner *et al.* and by the authors without salt. Addition of Na_2SO_4 , K_2SO_4 and KCl results in 'salting

TABLE II
Distribution data of acetic acid in acetic acid-water benzene system with K_2SO_4 at 35°C

X	Y	Wt. percent K_2SO_4 in solution (salt free basis)	Y without salt
7.41	0.98	13.82 (S)	0.20
15.52	2.63	10.1 (S)	0.95
21.23	5.04	6.79 (S)	1.60
32.95	8.45	3.51 (S)	4.05
41.86	14.32	2.32 (S)	7.50
49.17	16.79	1.58 (S)	10.40
52.5	19.20	1.13 (S)	12.20
54.0	21.70	0.83 (S)	13.10
57.8	23.20	0.675 (S)	15.50
59.5	25.40	0.525 (S)	16.50
59.8	26.60	0.354 (S)	16.55
61.63	28.16	0.39 (S)	17.90
3.97	0.302	3.48	0.10
6.02	0.513	6.95	0.15
7.1	0.542	10.43	0.18
12.6	1.031	2.54	0.60
13.88	1.762	5.07	0.80
15.53	2.091	7.60	0.95
19.42	3.00	2.27	1.30
21.56	3.51	4.54	1.70
30.06	6.23	1.17	3.40
31.91	6.96	2.34	3.80
40.47	11.13	1.17	6.90
47.32	14.43	0.79	9.60

TABLE III

Distribution data of acetic acid in acetic acid–water–benzene system with KCl at 35°C

<i>X</i>	<i>Y</i>	Wt. percent KCl in solution (salt free basis)	<i>Y</i> without salt
16.67	2.64	17.02 (S)	1.0
27.8	4.85	16.38 (S)	2.85
31.55	5.89	11.28 (S)	3.70
40.44	8.04	8.51 (S)	6.90
44.64	11.09	6.11 (S)	8.60
55.02	14.32	4.20 (S)	13.70
58.83	17.01	3.56 (S)	16.10
60.99	18.85	3.28 (S)	17.40
64.98	20.73	2.56 (S)	20.40
64.50	21.06	2.05 (S)	20.00
68.50	24.35	1.51 (S)	23.40
10.65	1.15	8.10	0.40
11.0	0.98	6.50	0.42
16.01	1.97	12.17	1.00
17.0	2.10	5.70	1.05
23.56	3.58	8.45	2.15
25.02	3.97	4.27	2.35
31.13	5.24	3.09	3.60
32.2	4.67	6.28	3.85
38.23	6.82	4.65	6.00
39.8	7.23	3.44	6.60
42.0	7.93	2.70	7.50

out' of acetic acid. A simple equation of the type

$$\ln\left(\frac{X_0}{X}\right) = K_s X_s$$

fits the data for the three salts studied in this system. Steschenov equation is normally used with molar units (moles solute per litre of aqueous phase). Since acetic acid and water do not differ much in specific gravities, so using weight

TABLE IV

Distribution data of acetic acid in acetic acid–water–benzene system without salt at 35°C

<i>X</i> ₀	<i>Y</i> ₀
4.939	0.0931
8.37	0.22
15.2	0.86
22.37	1.79
28.0	2.88
33.36	4.22
43.18	7.98
51.91	11.73
53.47	12.86
59.32	16.26
66.01	20.99
69.5	24.03
74.74	28.6

TABLE V

Comparison of distribution data of acetic acid-water-benzene system without salt

X	Y at 30°C by Garner <i>et al.</i>	Y by authors at 35°C	X	Y at 40°C by Garner <i>et al.</i>	Y by authors at 35°C
23.4	2.3	2.2	23.5	2.4	2.25
48.8	8.7	9.4	42.5	6.7	7.4
64.6	20.1	20.2	47.5	8.3	8.8
73.5	28.0	27.8	56.0	12.4	13.2
			64.0	22.0	20.0
			64.1	22.5	20.3

fractions instead of molar units, do not give much error for aqueous phase compositions ratios. K_s is the slope obtained by plotting $\ln(X_0/X)$ versus weight percent of salt in the mixture.

The maximum error at low concentrations of salt is around forty percent and at high concentrations is around ten percent. The reason for high error at low concentrations of salt may be that the solute favors one phase at low concentrations and the other phase at high concentrations. The low salt concentrations limits in weight percentages for Na_2SO_4 , K_2SO_4 and KCl are nearly 1, 2 and 3 respectively. The constants obtained are Na_2SO_4 , $K_s = 3.42$, K_2SO_4 , 8.7, and KCl , 2.44. The distribution data without salt are not far from those reported by Garner *et al.*⁹

NOMENCLATURE

- K_s salting out constant, gram of solution (salt free basis) per gram of salt.
 X weight percent of acetic acid in aqueous phase (salt free basis) in salt present system.
 X_0 weight percent of acetic acid in aqueous phase in salt absent system.
 X_s salt concentration, gram of salt per gram of solution (salt free basis).
 Y weight percent of acetic acid in organic phase (salt free basis) in salt present system.
 Y_0 weight percent of acetic acid in organic phase in salt absent system.

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