Liquid−Liquid Equilibria of the Benzene + Water + Acetic Acid Ternary System and Solubility of Benzene in Water: Effect of Calcium Chloride

Veera M. Boddu,[†] Abburi Krishnaiah,[‡] and Dabir S. Viswanath*

Particulate Systems Research Center, University of Missouri, Columbia, Missouri 65211

The aqueous solubility of benzene in the presence of calcium chloride at different concentrations was measured at 303.15 K. Also, experimental liquid−liquid equilibrium data were obtained at 303.15 K for the ternary system benzene + water + acetic acid as a function of calcium chloride concentration. The solubility of benzene in water is 1910 ppm at 303.15 K and decreases to 502 ppm with the addition of 20 mass % calcium chloride. The solubility data of benzene in calcium chloride solutions were correlated with the Setschenow equation, and the Setschenow constant, k_s, is 0.33 ± 0.002. From the liquid−liquid equilibrium studies it is observed that the amount of acetic acid extracted to the organic phase increases with the amount of added calcium chloride. It is suggested that the salt effect should be explored further to develop or improve processes to treat waste streams contaminated with organic compounds.

1. Introduction

The solubility of an organic solute in aqueous solutions can be altered by addition of inorganic salts such as KCl or NaCl. Since the solubility of a nonelectrolyte decreases by the addition of a salt, the phenomenon is called salting-out. Extensive studies have been conducted on the effect of various salts on the solubilities of nonelectrolytes in water.[1−5] The salting-out effect on liquid−liquid equilibria has been the topic of investigation,[6−10] as it has the potential for new applications in separations by preferential solvent extraction. The salt effect on vapor−liquid equilibria has also been found to be useful in dealing with azeotropic mixtures.[11,12] Though the salting-out effect has been observed for many years, it has not been explored particularly for practical applications in wastewater treatment. Sutton and Calder[13] studied the solubilities of some high molecular weight paraffins in distilled water and seawater. They concluded that the solubility of paraffins is less in seawater. They pointed out that the salt effect studies are important in the study of transport and fate of such organics. Dissolved salts may also effect the adsorption process due to electrostatic forces and ion-exchange processes because of the changes in solubility of the dissolved organics. Solvent extraction technologies for treatment of contaminated soils can be developed or improved by considering salt effects. One such example is the use of K_2SO_4 in the low energy extraction process (LEEP) where K_2SO_4 is used for preferential distribution of the pollutants between phases. Another example is the preconcentration method developed by Jenkins and Miyares[14] for the determination of nitroaromatics and nitroamines in water based on the salt effect. Addition of a salt decreases the concentration of the organic in the aqueous phase and thus facilitates the organic separation process.

The main objective of this paper is to present experimental data on the effect of a divalent salt, $CaCl_2$, on the solubility of benzene in water and on the distribution of acetic acid between benzene and water at (303.15 ± 0.5) K. There is a need for further research in this area to explore specific environmental applications. In the present study, benzene is considered, as it is one of the priority pollutants in water. Calcium chloride is considered because it is a divalent salt ubiquitous in natural waters. The acetic acid + benzene + water ternary system is considered for equilibrium studies because of industrial importance.

2. Theoretical Background

When a salt is added to a liquid−liquid system, the equilibrium distribution is affected by its interaction with liquid components. A decrease in the solubility of organic solvent in water by addition of a salt is due to the binding of a part of the water by some of the ions. The water bound by the ions is probably removed as a shell of oriented water dipoles around the ion. These water molecules become unavailable as solvent molecules. Thus, a net decrease in the solubility of the organic occurs. The amount of salting-out mainly depends on the ionic nature of the salt added. When the solubility of the organic increases due to the addition of a salt, the phenomenon is called salting-in (e.g. benzene is salted-in by methylammonium bromide $((CH_3)_4NBr)$. The salting-out or salting-in is a net result of the effect of anions and cations of the salt added. There are several theories such as the hydration theory, electrostatic theory, internal pressure theory, scaled particle theory, and Pitzer theory to predict solubilities of the solutes in the presence of salts.[2,15] These theoretical models predict the activity of the solute in the solution. In most cases the predicted solubilities are higher than the observed values.

Experimental salt effects are usually correlated with the Setschenow equation[15]

$$\log(f_i/f^o{}_i) = \log(S^o{}_i/S_i) = k_s c_s$$

* Corresponding author.
[†] Engineer Research and Development Center, USACERL, Champaign, IL 61826-9005.
[‡] Department of Chemistry, S. V. University, Tirupati 517502, India.

Table 1. Solubility of Benzene in Aqueous Calcium Chloride Solution at 303 K

mass % of $CaCl_2$	conc of benzene, ppm (mg/kg)	activity coefficient, S^0_i/S_i
0.0	1910.0	1.000
5.0	983.5	1.947
10.0	944.6	2.022
15.0	645.0	2.961
20.0	502.4	3.802

where f^0_i and f_i are the activities of the solute in water and in salt solution, and S^0_i and S_i are the equilibrium solubilities of the solute in water and salt solution. c_s is the molar concentration of the salt, and k_s is a constant. It is assumed that f^0_i is unity. The Setschenow equation fits the experimental data up to 2 to 3 M solutions, but it fails in the dilute solution regions. Lyman et al.[16] have mentioned that the value of k_s ranges from ∼0.04 to 0.4 for polynuclear aromatics.

3. Experimental Section

The chemicals, calcium chloride (Aldrich, 20 mesh, hygroscopic), benzene (Aldrich, HPLC grade), acetic acid (BDH, laboratory reagent, 99.5%), sodium hydroxide (BDH, laboratory reagent), and oxalic acid (BDH, Analar grade) were used as received without further purification. Distilled and deionized water was used in all measurements.

The equilibrium solubility measurements of benzene in water and calcium chloride solutions and the ternary liquid−liquid equilibrium experiments were conducted in an air-thermostat at a constant temperature of (303.15 ± 0.5) K. The $CaCl_2$ salt solutions of (5, 10, 15, and 20) ± 0.2% by mass were prepared in 1000 mL volumetric flasks. Cooling of the volumetric flasks was required because of the heat of dissolution of $CaCl_2$. The equilibrium solubility of benzene in water was obtained by adding excess (25 mL) benzene to water (100 mL) and salt solutions in 300 mL stoppered conical flasks. The conical flasks were allowed to equilibrate overnight in a shaker at 303 K. After equilibration, samples from the aqueous layer were analyzed for benzene concentration using a UV spectrophotometer (Spectronic 2000, Baush & Lomb) at 254 nm calibrated appropriately with salt solutions as the background. The solubility data are given in Table 1 along with the calculated activity coefficients.

The distribution of acetic acid between benzene and water in the absence and presence of $CaCl_2$ at different mass percents was obtained using volumetric analysis. Fresh NaOH solution was prepared and standardized using standard oxalic acid solution each time before the titrations were carried out. Equal volumes (50 mL) of benzene and water or $CaCl_2$ solutions were taken in stoppered conical flasks, and a known volume of acetic acid in the increments of 1 mL from 1 mL to 10 mL and in the increments of 10 mL from 10 mL onward was added. After equilibration, the aqueous and organic phases were separated and collected in stoppered conical flasks. A weighed amount of each phase was titrated for acid content using a standard NaOH solution with phenolphthalein indicator. The results are included in Table 2.

Ternary equilibrium experiments were conducted in three parts. In the first part, 50 mL of aqueous $CaCl_2$ solution was taken in a stoppered 250 mL conical flask and 10 mL of acetic acid was added. This mixture was titrated against benzene till a permanent turbidity (cloud point) was sustained after thorough shaking. The process was repeated with acetic acid up to 100 mL in steps of 10 mL.

Table 2. Distribution of Acetic Acid between Benzene (50 mL) and an Aqueous Calcium Chloride (50 mL) Solution at 303 K

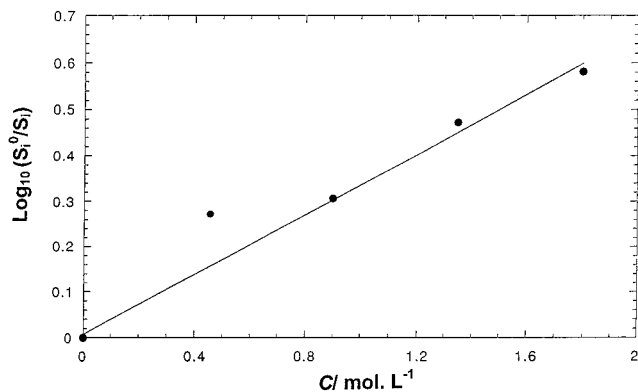| volume of acetic acid, mL	mass % of acetic acid in aq phase	mass % of acetic acid in org phase	volume of acetic acid, mL	mass % of acetic acid in aq phase	mass % of acetic acid in org phase
0 mass % $CaCl_2$			5 mass % $CaCl_2$		
1.0	2.00	0.09	1.0	1.90	0.05
2.0	3.72	0.10	2.0	3.65	0.06
3.0	5.74	0.21	3.0	5.32	0.25
4.0	7.42	0.37	4.0	7.03	0.44
5.0	9.01	0.51	5.0	8.55	0.59
6.0	9.82	0.67	6.0	10.05	0.83
7.0	12.86	0.75	7.0	11.64	1.04
8.0	14.98	0.94	8.0	12.99	1.22
9.0	15.66	1.04	9.0	14.29	1.41
10.0	16.87	1.32	10.0	15.74	1.69
20.0	27.98	3.43	20.0	26.37	4.06
30.0	35.98	5.08	30.0	34.55	6.54
40.0	43.70	7.03	40.0	41.08	8.28
50.0	49.37	8.72	50.0	49.40	11.08
10 mass % $CaCl_2$			20 mass % $CaCl_2$		
1.0	1.94	0.11	1.0	0.09	0.15
2.0	3.77	0.19	2.0	3.28	0.36
3.0	5.12	0.36	3.0	4.64	0.74
4.0	6.75	0.67	4.0	5.66	1.61
5.0	8.73	0.85	5.0	8.60	1.80
6.0	11.25	0.88	6.0	9.11	2.52
7.0	12.67	1.33	7.0	10.85	2.84
8.0	13.02	1.82	8.0	11.88	3.71
9.0	13.58	1.93	9.0	13.06	4.08
10.0	14.74	2.16	10.0	24.49	8.75
20.0	25.65	4.86	20.0	30.50	12.06
30.0	34.06	9.03	30.0	36.61	17.79
40.0	44.25	11.03	40.0	41.94	20.40
50.0	45.75	13.59			

In the second part, 50 mL of benzene was taken in a dried conical flask and 10 mL of acetic acid was added to it. The mixture was titrated against water or aqueous $CaCl_2$ solution to give the cloud point. The process was repeated as above for different amounts of acetic acid. In the third part, known volumes of benzene and aqueous $CaCl_2$ solutions were taken and titrated to the cloud point against acetic acid. The ternary data are presented in Table 3. The estimated reproducibility of the solubility data is about ±20 ppm.

4. Results and Discussion

Table 1 presents the values of salt concentrations, solubility of benzene, and activity coefficients of benzene in salt solutions. The solubility of benzene in water at 303 K is (1910 ± 20) ppm by mass, which is in agreement with the values of 1775 ppm reported by McDevit and Long[17] and 1794 ppm (2.3×10^{-2} mol dm^{-3}) reported by Valsaraj[18] at 298 K. The data are also shown in Figure 1. It can be seen that the Setschenow equation fits the data well above 5 mass % (≈0.5 M) $CaCl_2$. The Setschenow equation is generally valid for salt concentrations as high as 2 or 3 M, although it fails in dilute conditions.[6] The deviation can be explained in terms of the hydration theory.[15] According to this theory each salt ion in water binds with a constant number of water molecules as a shell of oriented water dipoles surrounding the ion. The salting out must largely be due to a preferential attraction between ions and water molecules. Each ion completely ties up a share of the water molecules and has no effect on the solvent properties of the rest of the water. This bound water is then unavailable as solvent for the nonelectrolyte. More water molecules are available to bind with the nonelectrolyte at

Table 3. Equilibrium Data for the Benzene−Water−Acetic Acid System in the Presence of Calcium Chloride at 303 K
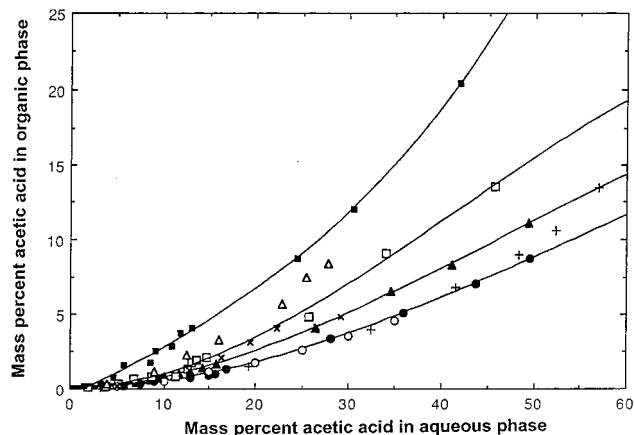
wt % of water	wt % of acetic acid	wt % of benzene	wt % of water	wt % of acetic acid	wt % of benzene
0 mass % CaCl$_2$			5 mass % CaCl$_2$		
82.50	17.21	0.29	82.43	16.45	1.12
70.26	29.31	0.44	70.06	27.97	1.97
61.11	38.23	0.65	60.58	36.28	3.14
31.19	58.53	10.28	53.24	42.51	4.25
29.38	60.11	10.51	43.33	51.89	4.78
11.52	62.56	25.90	38.47	54.00	7.53
10.47	61.32	28.21	35.34	56.44	8.22
9.42	57.60	30.89	31.21	59.83	8.96
6.68	55.20	38.11	24.23	50.18	25.59
4.82	52.04	43.12	23.59	41.30	35.11
3.13	47.59	49.27	22.70	35.29	42.00
2.72	40.86	56.40	19.31	23.52	57.17
2.18	31.85	65.96	17.89	6.25	75.86
10 mass % CaCl$_2$			20 mass % CaCl$_2$		
83.76	16.04	0.20	84.58	14.91	0.57
72.05	27.54	0.35	73.04	25.76	1.20
63.12	36.36	0.62	64.03	33.86	2.11
55.01	42.82	1.27	56.65	39.95	3.40
49.84	47.72	2.43	50.59	44.51	4.90
36.03	43.25	20.72	45.67	48.31	6.02
29.56	29.10	41.34	41.76	51.54	6.70
27.53	21.62	50.85	39.53	37.03	23.44
26.47	16.25	56.15	34.33	22.80	42.87
25.99	13.41	60.60	31.04	20.81	48.15
25.93	11.27	72.80	29.04	18.28	52.68
			28.52	15.25	56.23

Figure 2. Distribution of acetic acid between benzene and water in the presence of calcium chloride at 303 K. This work: ●, no salt present; ▲, 5% CaCl$_2$ solution; □, 10% CaCl$_2$ solution; ■, 20% CaCl$_2$ solution. Rao and Reddy (1978):[7] ○, no salt present; ×, 9.98% CaCl$_2$ solution; △, 20% CaCl$_2$ solution. Eisen and Hoffe (1966):[6] +, no salt present at 298.15 K.

Figure 1. Activity coefficients of benzene at 303 K as a function of calcium chloride concentration C.
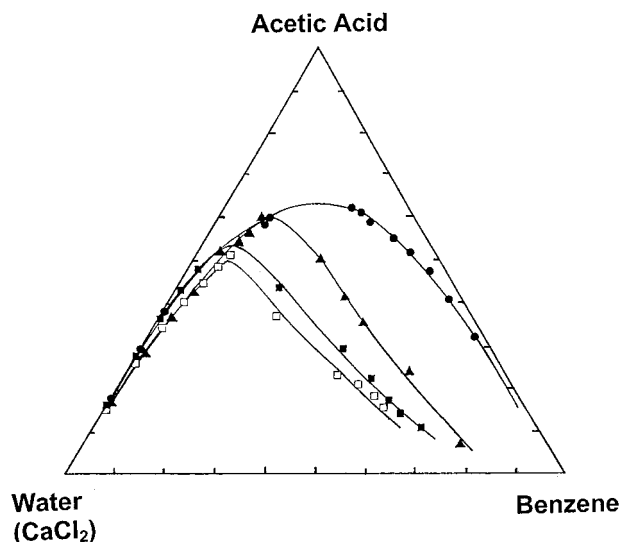
Figure 3. Ternary equilibrium data of benzene + acetic acid + water in the presence of calcium chloride at 303 K: ●, no salt present; ▲, 5% CaCl$_2$ solution; ■, 10% CaCl$_2$ solution; □, 20% CaCl$_2$ solution.

lower salt concentrations, hence giving a higher solubility of benzene.[6] There will be a certain minimum concentration above which the salting effect will be pronounced. The Setschenow equation is generally valid above this minimum salt concentration.

The salting-out parameter, k_s, for the benzene + water + CaCl$_2$ system is 0.33 ± 0.002, which is within the range of the values reported by Lyman et al.[16] May[19] reported a k_s value of 0.175 at 303.15 K for the system benzene + water + NaCl. This is in good agreement with the present value by considering concentration on a charge equivalent basis or by considering the changes brought about in the dielectric constant with the addition of a particular salt. In the present study, 48.5% of the benzene is salted out in 0.45 M CaCl$_2$ solution.

The distribution of acetic acid between aqueous and organic phases in the presence of different amounts of CaCl$_2$ is shown in Figure 2 along with the data reported by Rao and Reddy[7] and Eisen and Joffe.[6] The amount of acetic acid in the organic phase increases with the CaCl$_2$ concentration. The distribution data agree well for no salt and 10% salt concentration but deviate at 20% CaCl$_2$ concentration from the data of Rao and Reddy.[7] Information on the accuracy of their data is not reported. We believe our data are precise within the limits of maximum experimental error of ±0.006 in mass fraction. The ternary equilibrium data for the benzene−water−acetic acid system at different amounts of CaCl$_2$ are shown in Figure 3. We can see that addition of CaCl$_2$ improves acetic acid extraction, and therefore the extraction of acetic acid using benzene in the presence of CaCl$_2$ may be energy efficient compared to distillation.

In conclusion, we have reported the salting-out effect of CaCl$_2$ on the solubility of the benzene + water system at 303.15 K. The salt effect of CaCl$_2$ on the distribution of acetic acid between benzene and water indicates that the extent of extraction increases with increase of salt content. This study indicates that salt effects could potentially be utilized to reduce the concentration of organic pollutants in wastewater and to treat wastewater as well. The salting out effect can be combined with ion-exchange processes or with any other suitable process to treat organic pollutants.

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