Recovery of acetic acid from aqueous solutions using salting effect

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Abstract: The application of salting effect to isolate an organic acid, particularly Acetic acid, from aqueous solution is reported. In fact the presence of a salt can influence the solubility of a compound by either increasing it or decreasing it, leading to Salting-in and Salting-out, respectively. The addition of a salt in an aqueous solution introduces ionic forces which affect liquid-liquid equilibrium and which influence directly the distribution coefficient of the solute. The effect of NaCl and Na$_2$SO$_4$ on the liquid-liquid equilibrium data of the ternary system (Water+ Acetic Acid+ Dichloromethane) at a temperature of 293.15 K and an atmospheric pressure is studied experimentally in this work. The mass fractions of salt in the total mixture are 5%, 10% and 20%. It is noted that the equilibrium between phases is modified preferably to the extracted phase and the salting-out in the case of sodium sulfate is more significant than the effect of chloride.

1. Introduction

Acetic acid is one of the simplest and most widely used carboxylic acids having many important chemical and industrial applications. Total worldwide production of acetic acid is about 6.5 million tonnes per year; out of which about 5 million tonnes are produced by methanol carbonylation process and by bacterial fermentation and the remaining 1.5 million tonnes by recycling (Shin et al. 2009). The recovery of carboxylic acids from either fermentation broth or low titer wastewater presents a significant challenge. A great deal of effort has been made in developing feasible and economic method for recovery of carboxylic acids. For example, the precipitation with calcium hydroxide or calcium oxide, followed by filtration, acidification and crystallization, has been employed as the main recovery method, although it has great difficulty and low yield. The others acid recovery processes are available, including electrodialysis, esterification, chromatography, extractive fermentation and solvent extraction (Yang et al. 1991). Among them, Liquid-liquid extraction using aqueous two-phase systems (ATPS) has been demonstrated to be a highly efficient separation technique for small organic species (Fu et al. 2015).

The presence of inorganic salt changes the phase equilibrium behaviour of a mixture significantly. This phenomenon is often referred to as the salting in or salting-out effect (Singh et al. 2006). It can be used to optimize separation processes such as rectification to shift the azeotropic conditions, extraction to alter the miscibility gaps and also absorption and fractional crystallization to change the distribution coefficients. The salt effect is also important in biological processes such as purification of proteins, enzymes, nucleic acids, and others (Hasseine et al. 2009). During recent years, attempts have been made to generate the reliable as well as reproducible experimental data for systems containing salts. Typically, the salting-out effect on the (liquid + liquid) equilibria systems has been the topic of investigation in the separation processes using the preferential organic solvents (Aznar et al. 2000).

The study of efficiently separating and recovering Acetic acid from aqueous solutions is an important significance on industry and environmentally sustainable development. Many research groups in different countries are working in this field and some methods are proposed in the literature (Vakili-Nezhaad et al. 2004; Koga et al. 1978; Watanabe et al. 1985; Chand et al. 1994; Sano et al. 1995; Cockrem 1996; Baniel 1998 ; Saha et al. 2000; Demiral et al. 2003; Singh et al. 2006). Accordingly, the present research is aimed to recover acetic acid from aqueous solution using salting effect on the solvent extraction method.

In this work, effect of sodium chloride and sodium sulfate with different content (5%, 10% and 20%) on the liquid-liquid equilibrium data of (water+ acetic acid+ DCM) system is investigated. The experimental results were correlated based on the Othmer-Tobias correlation.

2. Experimental

2.1. Chemicals and apparatus

Acetic acid and Dichloromethane were obtained from Biochem (p.a.> 99.5%) and used without further purification. The sodium chloride and sodium sulfate was provided from Merck with purity 99%. Distilled water was prepared using GFL 2001/4 distillation unit.

The quaternary system was mixed with a magnetic stirrer (Nahita model 690 type), and heated at a constant temperature in the

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water bath (uncertainty is ± 0.1°C.). The masses were determined by an analytical balance (uncertainty is ± 0.001 g). Refractive index was measured by a refractometer (WYA Abbe refractometer 2WA-J).

2.2. Analytical methods

2.2.1. Binodal curve

The binodal curve values were determined by means of the cloud point method (Ghalami-Choobar et al. 2011). The measurements were made in a glass equilibrium thermostated cell equipped with a magnetic stirrer. The cell temperature was controlled with a temperature-controlled bath with an accuracy of ±0.01K. A known composition, homogeneous and transparent (acetic acid + salted water) was prepared in a glass equilibrium cell at constant temperature. The mixture was made by mass using an analytical balance. Then dichloromethane was progressively added to the mixture using a micro-burette. The cloud point was determined by observing the transition from a homogeneous to a heterogeneous mixture as indicated by the mixture turbidity.

2.2.1. Tie-lines

A weighed amount of aqueous solution containing a known quantity of solute was mixed with a known quantity of solvent in a stoppered funnel. Quantities of salt were added to make corresponding mixtures of different salt mass percentages of 5, 10 and 20. These mixtures were maintained at constant temperature of (293 ± 0.1) K in a thermostatic bath and agitated for an extended period of time until complete dissolution of the salt. The thermodynamic equilibrium was finally achieved by letting the mixture rest for 24 h. After the equilibrium two phases are separated and weighed. Refractive index measurements are carried out to determine the concentrations of the various compounds in each phase. Prior to these refractometer measurements, graphs giving the change of the refractive index with concentration of the solution have been plotted and used to read off the concentrations of the non-electrolytes and the salt in the organic phase. The concentrations in the aqueous phase solution are obtained by satisfaction of the material balance.

3. Results and Discussion

3.1. LLE measurements

The solubility and the equilibrium tie-line data were measured at 293.15 K and atmospheric pressure. The data determined for studied systems (water + acetic acid + DCM) and (water + acetic acid + DCM + salt) are reported in tables 1-2, in which W_i denotes the mass fraction of the i th component.

Table 1. Experimental solubility data for [water (1)+ acetic acid (2) +dichloromethane (3)] ternary system at T= 293.15 K

W_1	W_2	W_3
0.9460	0.0000	0.0540
0.8212	0.1292	0.0495
0.7399	0.1941	0.0658
0.6595	0.2768	0.0636
0.6028	0.3163	0.0807
0.5585	0.3516	0.0898
0.4843	0.4066	0.1090
0.4151	0.4357	0.1491
0.1347	0.3800	0.4852
0.1006	0.3464	0.5528
0.0871	0.3291	0.5837
0.0460	0.2684	0.6855
0.0372	0.2296	0.7331
0.0231	0.2022	0.7746
0.0164	0.1034	0.8801
0.0307	0.0537	0.9154
0.0489	0.0000	0.9540

Table 2. Experimental solubility data for [water (1)+ acetic acid (2) +dichloromethane (3) + NaCl (4) / Na₂SO₄ (4)] quaternary system at T= 293.15K.

	5%			10%			20%		
	W_1	W_2	W_3	W_1	W_2	W_3	W_1	W_2	W_3
NaCl	0.9178	0.0000	0.0822	0.923	0.0000	0.0770	0.9345	0.0000	0.0655
	0.7746	0.1554	0.0700	0.7809	0.1583	0.06081	0.7878	0.1613	0.0509
	0.6029	0.3090	0.0881	0.6148	0.3058	0.0794	0.6172	0.3234	0.0594
	0.4487	0.4290	0.1223	0.4588	0.4579	0.0833	0.4403	0.4463	0.1134
	0.2121	0.4775	0.3104	0.3521	0.4633	0.1846	0.2048	0.4667	0.3285
	0.1452	0.4278	0.4270	0.2213	0.4876	0.2911	0.1406	0.4675	0.3919
	0.0893	0.3505	0.5602	0.0868	0.4375	0.4757	0.1020	0.3698	0.5282
	0.0753	0.2836	0.6411	0.0741	0.3704	0.5555	0.0904	0.2490	0.6606
	0.0905	0.0915	0.8180	0.0745	0.1006	0.8249	0.0645	0.0965	0.8390
	0.1306	0.0000	0.8694	0.095	0.0000	0.9050	0.0535	0.0000	0.9465
Na₂SO₄	0.8904	0.0000	0.1096	0.9065	0.0000	0.0935	0.9230	0.0000	0.077
	0.8259	0.0915	0.0826	0.8371	0.0915	0.0714	0.8346	0.1246	0.0408
	0.6633	0.2772	0.0595	0.6922	0.2661	0.0417	0.6780	0.2901	0.0319
	0.4405	0.4353	0.1242	0.4493	0.4423	0.1084	0.4425	0.4743	0.0832
	0.3543	0.4610	0.1847	0.3397	0.4903	0.1700	0.3047	0.538	0.1573
	0.1286	0.4130	0.4584	0.2139	0.4689	0.3172	0.1053	0.4503	0.4444
	0.0845	0.3621	0.5534	0.0694	0.3647	0.5659	0.0371	0.3647	0.5982
	0.0304	0.2205	0.7491	0.0211	0.2400	0.7389	0.0073	0.2392	0.7535
	0.0191	0.1140	0.8669	0.0336	0.1220	0.8444	0.0108	0.1353	0.8539
	0.0512	0.0000	0.9488	0.0512	0.0000	0.9488	0.0327	0.0000	0.9673

Figures 1 and 2 show the binodal curves in the presence of sodium chloride and sodium sulfate, respectively. After salt addition, the experimental results (tie-lines) for various concentration of salt (0.05, 0.1 and 0.2) were evaluated and are presented in table 3.
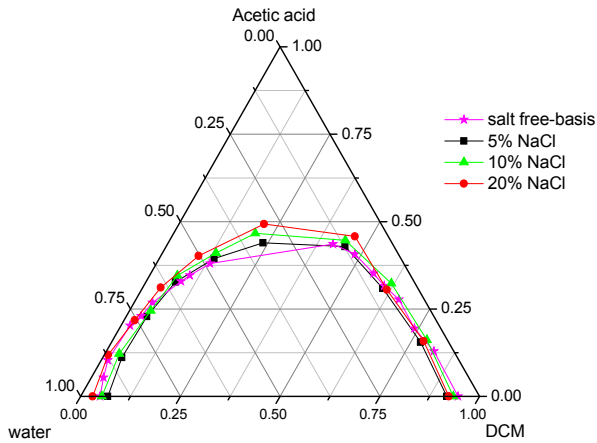

Fig. 1. Experimental solubility diagram for (water + acetic acid + dichloromethane +NaCl) quaternary system at 293.15 K
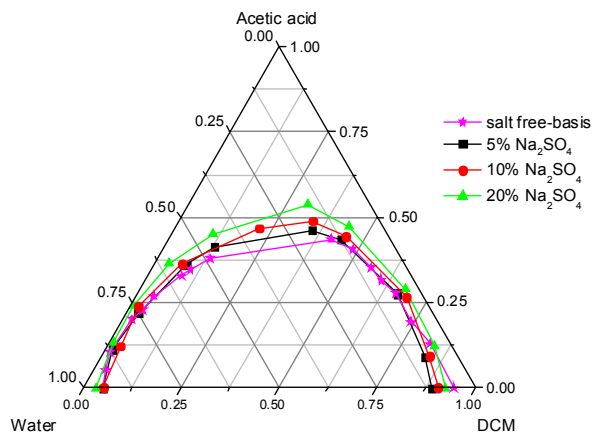

Fig. 2. Experimental solubility diagram for (water + acetic acid + dichloromethane +Na$_2$SO$_4$) quaternary system at 293.15 K

From figures 1 and 2, it can be seen that the heterogeneous zone of each sample system become larger with the increase in concentration of salt. The addition of salt to the system is beneficial for separation and enlarges the operation range of extraction. It can be seen from table 3 that at 20 % of salt mass we haven't data because at this concentration the salt precipitate and it forms a third phase.

Distribution coefficient, D_2, of acetic acid and separation factor, S, of the chosen solvent were calculated as follows (Mohsen-Nia et al. 2009):

$$D_2 = \frac{w_{23}}{w_{21}} \tag{1}$$

$$S = D_2 \frac{w_{11}}{w_{13}} \tag{2}$$

Where w_{23} and w_{21} are acetic acid mass fraction in solvent-rich and water-rich phases, respectively, and w_{13} and w_{11} are the water mass fractions in solvent-rich and water-rich phases, respectively. The distribution coefficient and separation factor for each aqueous solution containing sodium chloride and sodium sulfate are summarized in table 4.

Figure 3 shows the results for the system (water + acetic acid + DCM) in the presence of NaCl and Na$_2$SO$_4$. It can be seen how the slopes of the Distribution curves change with the addition of salt implying an increase of the activity coefficient of the solute, and hence causing salting-out of acetic acid. This can be explained by the fact that salt molecules compete with those of solute for water molecules, causing therefore a deficit in the solvatation shells around the organic solute which may become free to move and migrate into the organic phase. In this figure, a very similar influence of NaCl and Na$_2$SO$_4$ on the distribution of the solute is shown. However, salting-out is slightly more pronounced with Na$_2$SO$_4$ as shown by the position of the curves for each salt and at different concentrations used.

Table 3. Experimental tie-lines data of [water (1) + acetic acid (2) +dichloromethane (3) +NaCl(4) / Na$_2$SO$_4$ (4)] quaternary system at 293.15 K.

		5%				10%				20%			
		W1	W2	W3	W4	W1	W2	W3	W4	W1	W2	W3	W4
NaCl	Aqueous phase	0.6990	0.1948	0.0713	0.0349	0.6705	0.1873	0.0751	0.0671	0.6445	0.1733	0.0533	0.1289
		0.6481	0.2288	0.0907	0.0324	0.6478	0.208	0.0794	0.0648	0.6144	0.2061	0.0566	0.1229
		0.5943	0.2628	0.1132	0.0297	0.6229	0.2345	0.0803	0.0623	0.5832	0.2345	0.0657	0.1166
		0.5532	0.3002	0.1189	0.0277	0.5895	0.2675	0.0840	0.0590	0.5323	0.2551	0.1062	0.1065
	Organic phase	0.1202	0.0627	0.8111	0.0060	0.2021	0.0792	0.6985	0.0202	0.1495	0.0918	0.7288	0.0299
		0.1135	0.0880	0.7928	0.0057	0.1855	0.1147	0.6812	0.0186	0.2003	0.1387	0.6210	0.0400
		0.0921	0.1311	0.7722	0.0046	0.1599	0.1627	0.6614	0.0160	0.2203	0.1906	0.5450	0.0441
		0.0663	0.1818	0.7486	0.0033	0.1464	0.2184	0.6206	0.0146	0.2576	0.2311	0.4598	0.0515
Na$_2$SO$_4$	Aqueous phase	0.7077	0.1807	0.0762	0.0354	0.6999	0.1629	0.0672	0.0700				
		0.6987	0.2005	0.0659	0.0349	0.6640	0.1873	0.0823	0.0664				
		0.6776	0.2213	0.0672	0.0339	0.6324	0.2156	0.0888	0.0632				
		0.6197	0.2476	0.1017	0.0310	0.6228	0.2316	0.0833	0.0623				
	Organic phase	0.0817	0.0842	0.8300	0.0041	0.0246	0.1044	0.8685	0.0025				
		0.0816	0.1235	0.7908	0.0041	0.0625	0.1564	0.7748	0.0063				
		0.0473	0.1767	0.7736	0.0024	0.0687	0.2033	0.7211	0.0069				
		0.0497	0.2363	0.7115	0.0025	0.0735	0.2691	0.6500	0.0074				

Table 4. The values of ionic strength, distribution coefficients for acetic acid and separation factor in the presence of NaCl / Na$_2$SO$_4$ at T=293.15 K.

	5%		10%		20%	
	0.05 I/mol.l^{-1}		0.10 I/mol.l^{-1}		0.20 I/mol.l^{-1}	
	D$_2$	S	D$_2$	S	D$_2$	S
NaCl	0.3219	1.8718	0.4229	1.4029	0.5297	2.2836
	0.3846	2.1962	0.5514	1.9257	0.6730	2.0643
	0.4989	3.2190	0.6938	2.7028	0.8128	2.1517
	0.6056	5.0530	0.8164	3.2875	0.9059	1.8720
Ia$_2$SO$_4$	0.4659	4.0357	0.6408	18.2315		
	0.6159	5.2736	0.8350	8.8710		
	0.7984	11.4375	0.9429	8.6796		
	0.9543	11.8989	1.1620	9.8461		

It can be concluded that acetic acid concentration in the organic phase increases with increase of salt ionic strength. The effectiveness of extraction of acetic acid by solvent mixture is given by its separation factor presented in figure 4, which is an indication of the ability of solvent to separate acetic acid from water. This quantity is found to be greater than 1 for the systems reported here, which means that extraction of acetic acid by these solvent mixtures is possible. The separation factor for the acetic acid at T=293.15K gradually increases with the increase in concentration of NaCl and Na$_2$SO$_4$.
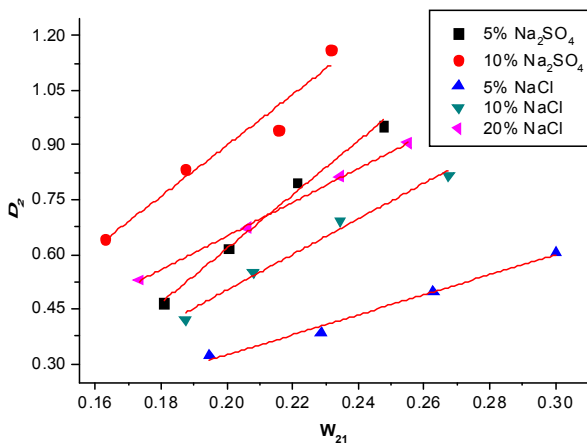
Table 5. Values of Othmer-Tobias parameters of the system [water + acetic acid +dichloromethane + salt] at T=293.15 K

Salt	Concentration	A	B	R^2
NaCl	5%	-0.9847	0.5721	0.9856
	10%	-0.1481	0.9931	0.9780
	20%	0.5436	2.4091	0.9387
Na$_2$SO$_4$	5%	-0.1350	1.5243	0.8734
	10%	1.0152	3.4033	0.9581

3.2. Othmer-Tobias correlation

The reliability of the measured LLE data was tested by Othmer-Tobias equation (Othmer et al. 1942):

$$ln \frac{1-w_{33}}{w_{33}} = A + B \ ln \ \frac{1-w_{11}}{w_{11}} \qquad (3)$$

where w_{11} is mass fraction of water in the aqueous phase; w_{33} is mass fraction of the solvent in organic phase; A and B are constant which depend on the degree of immiscibility of components in systems. The parameters of the equation and the correlation coefficient values R^2 are given in table 5. Figures 5 and 6 show the plot of ln[(1-w$_{33}$)/ w$_{33}$] versus ln[(1-w$_{11}$)/ w$_{11}$] with sodium chloride and sodium sulfate, respectively. The linearity of the plots indicates the consistency of experimental data. It indicates that Eq. (3) can be satisfactorily used to correlate the tie-lines data of the investigated system.

Fig. 3. Effect of salts on the Distribution coefficient of acetic acid, D_2, at T=293.15 K.

Fig. 5. Othmer-Tobias plots of quaternary system (water + acetic acid + dichloromethane + NaCl) at T=293.15 K.

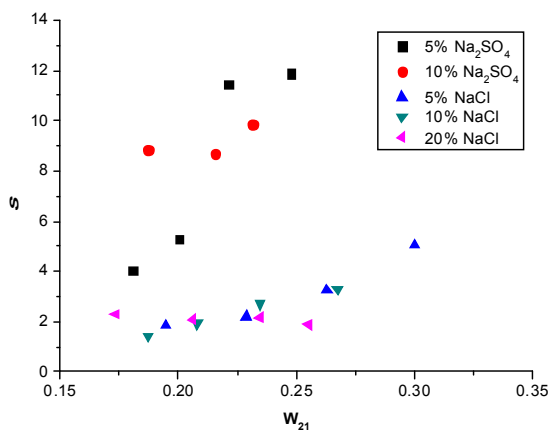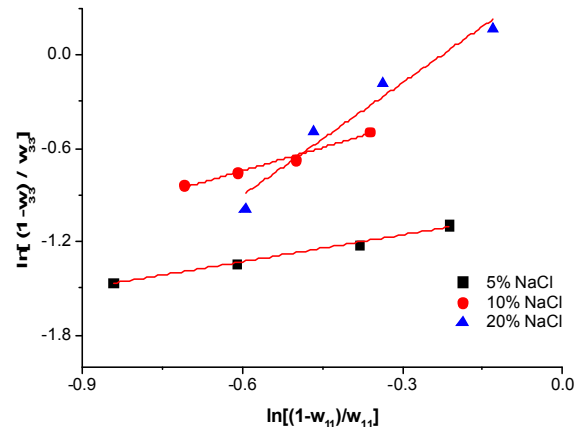**Fig. 4.** Separation factor plotted against the mass fraction of acetic acid in aqueous phase at T=293.15 K.
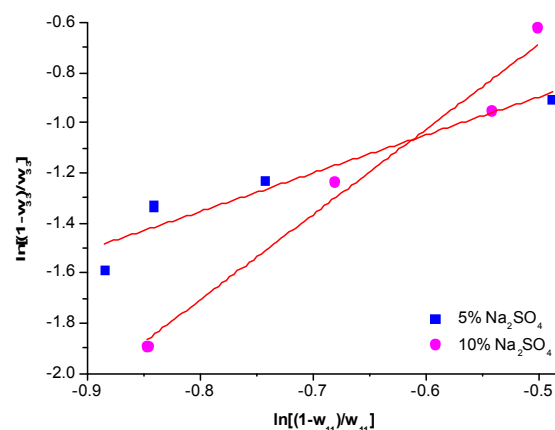

Fig. 6. Othmer-Tobias plots of quaternary system (water + acetic acid + dichloromethane + Na$_2$SO$_4$) at T=293.15 K.

4. Conclusion

In this paper, recovery of acetic acid from aqueous solution by dichloromethane as a solvent using the effect of sodium chloride and sodium sulfate was proven to be possible. The results show that the two-phase region of ternary system (water+ acetic acid + DCM) is relatively smaller without addition of salt, the enlargement of two-phase region and the decrease of solubility of acetic acid in aqueous phase occurred with an increase of salt concentration in initial aqueous solution. It can be concluded from the distribution coefficient and selectivity data that saline extraction was very helpful for separating acetic acid from aqueous solutions and the « *Salting-out* » effect of Na_2SO_4 is more significant than the effect of NaCl.

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