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Equilibrium for the Ternary System Water + Sodium Chloride + Ethyl Acetate at 30 °C

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Liquid–liquid–solid equilibrium for the ternary system water + sodium chloride + ethyl acetate has been measured at 30 °C.

Introduction

The decrease in solubility of a nonelectrolyte in the presence of inorganic salts (salting out) has potentially wide applications in solvent extraction for obtaining better recovery of organic liquids from aqueous solutions. A survey of the literature, however, indicates that only fragmentary work has been done on such systems (*1–9*), with a number of measurements (*1–3*) made using an experimental technique which is not considered accurate (*10*). For instance, in refs 2 and 3, the authors consider the system ethyl acetate + alcohol + (water + salt) as a pseudoternary system and the solution of salt in water as a single component. This concept is, at least in principle, not correct since the distribution of the salt between the aqueous and organic phases is different. Furthermore, it is incorrect to consider the system water + salt + ethyl acetate as a pseudobinary mixture.

In this work, solid–liquid–liquid equilibrium of the ternary system water + sodium chloride + ethyl acetate at 30 °C was measured. Results for this system have been determined previously (*2, 3*), but only solubility values were reported, and no experimental tie lines were presented. Our results differ considerably from those reported previously.

Experimental Section

Materials. All chemicals (Merck) were used as supplied. The contents of volatile impurities were determined by gas–liquid chromatographic analysis: all compounds contained negligible amounts of impurities (less than 0.2%). However, the content in water of the ethyl acetate might modify the correct experimental results. Consequently, it has been measured and considered in each sample of ethyl acetate used.

Experimental Methodology Proposed. A ternary system, water (W) + inorganic salt (S) + organic solvent (O), containing a partly miscible pair, water + organic solvent, is represented schematically in Figure 1 using an equilateral triangle. To characterize the equilibrium of the ternary system properly, initial mixtures must be selected covering the heterogeneous region and providing regular variations of composition in each region.

For the study on the ternary system selected, ten initial heterogeneous mixtures were prepared: six of the mixtures formed two liquid phases, three formed a liquid and a solid phase, and one formed three phases (two liquids and one solid). These compositions covered the phase diagram adequately.

Analytical Methods. Equilibrium measurements were made by preparing mixtures of known overall composition by mass, stirring intensively and allowing the mixtures to settle for 2 h at a constant temperature of 30.0 ± 0.1 °C. At the end of each experiment, samples were taken from liquid phases and analyzed.

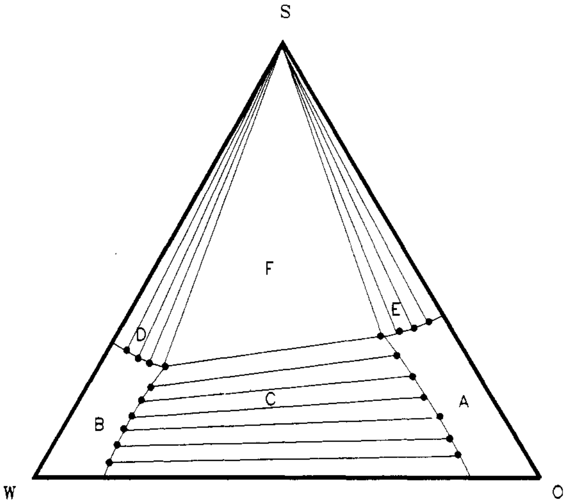

Figure 1. Equilateral representation of the ternary system water (W) + inorganic salt (S) + organic solvent (O) with the water + organic solvent partly miscible: (A) liquid A, (B) liquid B, (C) liquid A + liquid B, (D) liquid B + solid, (E) liquid A + solid, (F) liquid A + liquid B + solid.

Water in the organic phase was determined by gas chromatography using a 2-m × 3-mm column packed with Chromosorb 101 100/120. The column temperature was 150 °C, and detection was carried out by thermal conductivity. The helium flow rate was 30 cm^3 min^{-1}. To obtain quantitative results, an internal standard method was applied, 2-propanol being the standard compound used for this purpose. Furthermore, the addition of 2-propanol prevents separation effects.

Ethyl acetate in the aqueous phase was determined after dilution by a factor of 10 of the sample with water in order to decrease the problems and interferences produced by the high concentrations of sodium chloride. The analysis was carried out by gas chromatography using a flame ionization detector and the same conditions described above.

Sodium chloride in the aqueous phase was determined from the mass of the solid residue obtained by evaporation at 120 °C of a known mass of the sample.

For the determination of the sodium chloride in the organic phase an aliquot of the sample was treated with approximately the same amount of water. The concentration of salt extracted by water (which accounts for all the salt in the original organic phase since the distribution ratio of NaCl in the aqueous phase to the NaCl in the organic phase is very high and consequently the amount of sodium chloride remaining in the organic phase after extraction can be neglected) was measured by atomic absorption spectrometry. The sodium

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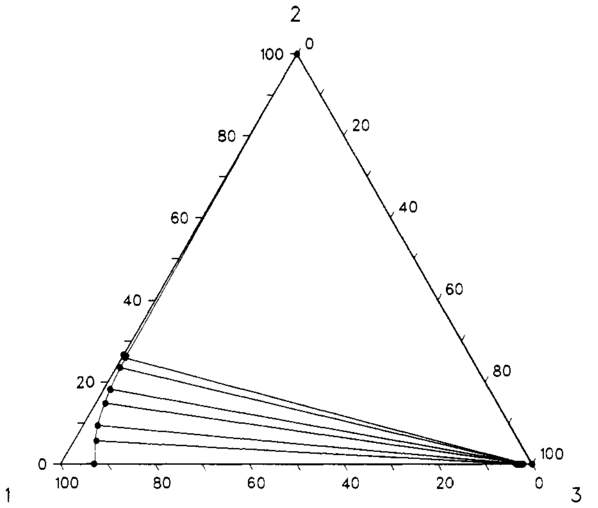

Figure 2. Representation of the equilibrium data (mass %) for the ternary system water (1) + sodium chloride (2) + ethyl acetate (3) at 30 °C.

Table I. Tie Line Data as Mass Fraction *w* for Water (1) + Sodium Chloride (2) + Ethyl Acetate (3) at 30 °C

aqueous phase			organic phase		
$100w_1$	$100w_2$	$100w_3$	$100w_1$	$100w_2$	$100w_3$
One Liquid Phase + One Solid Phase					
73.4	26.6				
73.0	26.3	0.71			
				<0.000 005	100
Two Liquid Phases					
92.9		7.10	3.40		96.6
89.6	5.7	4.69	3.20	0.000 028	96.8
87.5	9.4	3.12	2.90	0.000 059	97.1
83.1	14.8	2.09	2.68	0.000 081	97.3
80.4	18.2	1.43	2.34	0.000 127	97.7
75.7	23.5	0.81	2.10	0.000 180	97.9
Two Liquid Phases and One Solid Phase					
73.4	25.9	0.71	1.86	0.000 280	98.1

chloride aqueous standards used were saturated in ethyl acetate.

Results

The results obtained are given in Table I. The ternary equilibrium diagram is represented in Figure 2. The concentrations of sodium chloride in the organic phase are very small and can be neglected in the study of the salting out effect.

Figure 3 shows the results of the aqueous branch of the solubility curve which exhibits a continuous variation of the salt solubilities. In this figure the corresponding results from refs 2 and 3 have been plotted. These results show a considerable scatter and considerable discrepancy with our results, and even among themselves: results from ref 2 are inconsistent with those reported in ref 3. On the other hand, as early as in 1899, Euler (*11*) obtained some results for the solubilities of the system (also shown in Figure 3) in good agreement with our work.

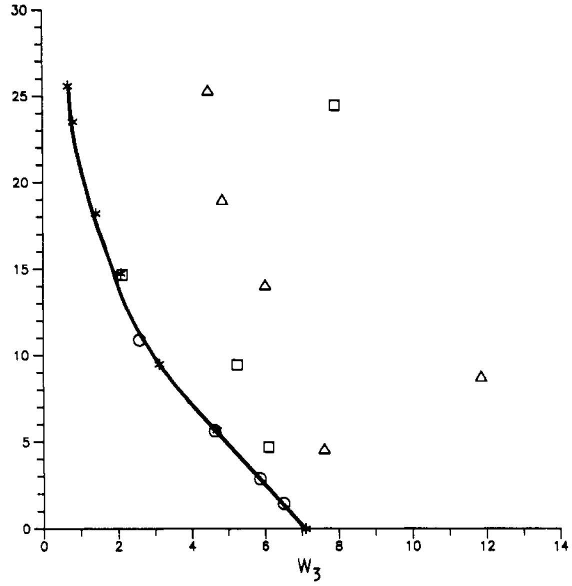

Figure 3. Solubility points of the aqueous branch of the ternary system water (1) + sodium chloride (2) + ethyl acetate (3): (*) this work; (○) ref 11, (△) ref 2, (□) ref 3.

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