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Liquid−Liquid and Solid−Liquid Equilibria of 2-Isopropoxyethanol−H_2O−NaCl Mixtures

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Liquid−liquid equilibria experiments demonstrated that mixtures of 2-isopropoxyethanol and water saturated with NaCl are partially miscible. The lower critical solution temperature was estimated to be 29.2 °C at a 2-isopropoxyethanol concentration of 0.399 ($m_{IPE}/(m_{IPE} + m_{H_2O})$). Solid−liquid equilibria experiments showed that the solubility of NaCl in water is reduced significantly by the presence of 2-isopropoxyethanol. As in pure water, the NaCl solubility in 2-isopropoxyethanol−H_2O mixtures increases weakly with temperature.

Introduction

In industry, soluble inorganic salts such as NaCl with a weak temperature dependence of the solubility are often separated from water by evaporative crystallization. The evaporation of water in these processes is energy consuming. To reduce energy costs in the production of such inorganic salts, drowning out crystallization by the addition of an organic antisolvent could be an interesting alternative. The addition of an antisolvent, however, introduces an additional separation step in which the antisolvent has to be recovered from the spent mother liquor. The antisolvent recovery must be carried out with little energy consumption in order to make the entire process economically attractive. Therefore, 2-isopropoxyethanol is a promising candidate for the crystallization of NaCl, since Chiavone-Filho and Rasmussen (1993) demonstrated that it reduces the KCl solubility in water and that the 2-isopropoxyethanol−H_2O−KCl system shows a double-liquid-phase area close to room temperature. This enables antisolvent recovery from the spent mother liquor after crystallization by a temperature-induced liquid−liquid phase split.

In this work the results of the experimentally determined liquid−liquid and solid−liquid equilibria of the 2-isopropoxyethanol−H_2O−NaCl system are presented.

Experimental Section

Chemicals. The chemicals were 2-isopropoxyethanol ($(CH_3)_2CHOCH_2CH_2OH$, Fluka Chemie AG, ≥99.7% (GC)) and pharmaceutically pure sodium chloride supplied by Akzo Nobel. Demineralized water with a conductivity of less than 4 $mS \cdot cm^{-1}$ was used in all experiments. In these experiments the 2-isopropoxyethanol concentration is expressed as a salt free weight fraction: $w_{IPE} = m_{IPE}/(m_{IPE} + m_{H_2O})$.

Apparatus and Procedures. All experiments were carried out in a jacketed 125 mL glass flask. A magnetic stirrer in combination with a stir bar provided agitation, and a Lauda RK-8-KP thermostat was used to control the temperature. The temperature of the vessel content was measured with an ASL precision thermometer (0.01 °C accuracy, 0.002 °C repeatability), and a small hole in the vessel cover ensured atmospheric pressure. Figure 1 shows a schematic drawing of the setup.

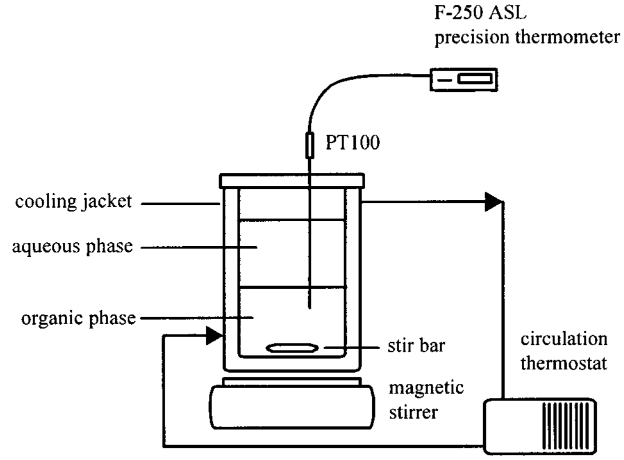

Figure 1. Experimental setup used for determining the liquid−liquid and solid−liquid equilibria.

The liquid−liquid equilibria experiments were carried out by filling the vessel with known amounts of antisolvent and water at room temperature. Subsequently, an excess of sodium chloride was added to ensure NaCl saturation during the experiments. Points on the liquid−liquid equilibrium line were determined in two different ways: either by visual observation of the mixing/demixing temperatures at a given overall 2-isopropoxyethanol-to-water ratio or by determining the compositions of both the organic and the aqueous phases at a fixed temperature in the two-liquid-phase area. In the second case, the samples were taken 30 min after the solution had reached the selected temperature. Previous experiments had shown that this period of time was sufficient to reach chemical equilibrium. When the compositions of both the organic phase and the aqueous phase vary strongly with temperature (the horizontal part of the L−L equilibrium line), points of the liquid−liquid equilibrium line are most reliably determined by using the first method (accuracy 0.05 °C). However, when the mixing/demixing temperature is a very steep function of the

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Table 1. Liquid−Liquid Equilibrium Data of 2-Isopropoxyethanol−H_2O Mixtures at NaCl Saturation

	aqueous-phase composition		organic-phase composition	
t/°C	[2-isopropoxyethanol] $100m_{IPE}/(m_{IPE}+m_{H_2O})$	[NaCl] $100m_{NaCl}/(m_{IPE}+m_{H_2O})$	[2-isopropoxyethanol] $100m_{IPE}/(m_{IPE}+m_{H_2O})$	[NaCl] $100m_{NaCl}/(m_{IPE}+m_{H_2O})$
49.88	9.88	32.00	80.30	3.87
59.55	8.26	33.37	83.09	3.46
79.97	6.31	35.24	85.82	2.26

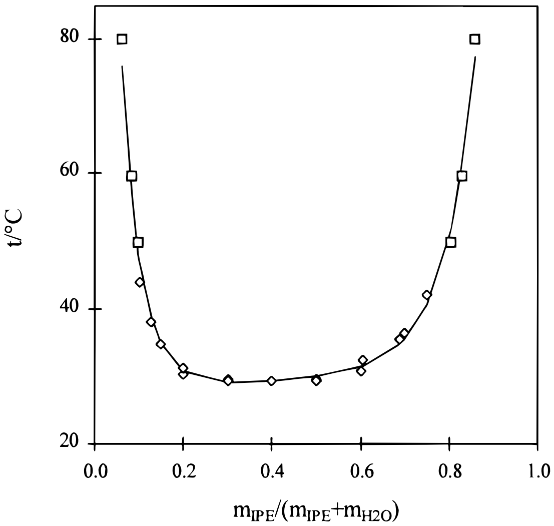

Figure 2. LLE data of 2-isopropoxyethanol−H_2O mixtures at NaCl saturation: (◇) collected by visual determination of the mixing/demixing temperature; (□) collected by analyzing samples of both phases.

Table 2. Demixing Temperatures of 2-Isopropoxyethanol−H_2O Mixtures at NaCl Saturation

[2-isopropoxyethanol] $100(m_{IPE}/(m_{IPE}+m_{H_2O}))$	t_{demix}/°C
10.12	44.00
12.67	38.05
14.96	34.65
19.98	30.70
29.99	29.40
30.20	29.30
39.92	29.20
39.96	29.35
49.84	29.35
49.98	29.40
59.98	30.65
60.68	32.30
68.92	35.30
69.94	36.45
74.96	42.15

2-isopropoxyethanol-to-water ratio in the mixture (the vertical sides of the L−L equilibrium line), the second method is favored for maximum reliability.

The sodium chloride solubilities were determined in the single-liquid-phase region as a function of the 2-isopropoxyethanol concentration at a temperature of 15 °C and as a function of temperature at 2-isopropoxyethanol concentrations of 0.25, 0.50, and 0.75 ($m_{IPE}/(m_{IPE}+m_{H_2O})$). The vessel was filled with known amounts of 2-isopropoxyethanol and water and an excess of sodium chloride. At the selected temperature the solution was stirred for 30 min and clear liquid samples of the mixture were taken for the determination of the sodium chloride concentration.

Analytical Methods. The 2-isopropoxyethanol concentration (in kg of 2-isopropoxyethanol/kg of mixed solvent) of the liquid samples was determined with a Chrompack CP 9002 gas chromatograph equipped with a CP-Sil-5 CB column. Sodium chloride concentrations (in kg of NaCl/kg of mixed solvent) were determined gravimetrically. Water concentrations were calculated from the measured 2-isopropoxyethanol and sodium chloride concentrations.

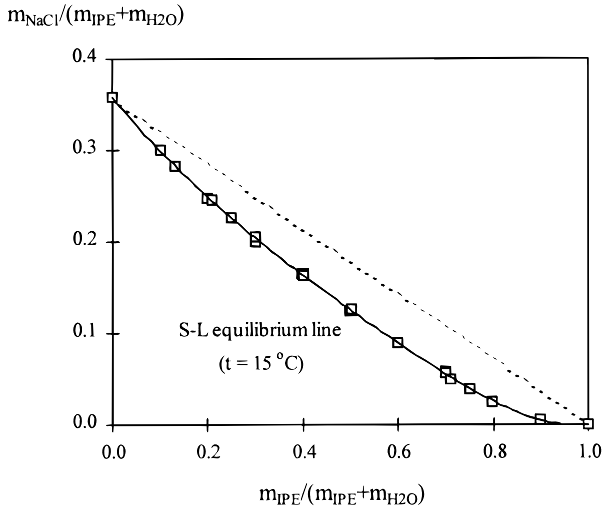

Figure 3. NaCl solubilities expressed as $m_{NaCl}/(m_{IPE}+m_{H_2O})$ in mixtures of 2-isopropoxyethanol and H_2O at 15 °C.

Results and Discussion

In Figure 2 and in Tables 1 and 2 the results of the liquid−liquid equilibria experiments are displayed. From these data it can be seen that 2-isopropoxyethanol, which is completely miscible with pure water, shows a two-liquid-phase area in the presence of NaCl. The lower critical solution temperature of the 2-isopropoxyethanol−H_2O system saturated with NaCl is approximately 29.2 °C at a 2-isopropoxyethanol concentration of 0.399. Similar observations were made by Chiavone-Filho and Rasmussen (1993), who demonstrated that water and 2-isopropoxyethanol are no longer completely miscible in the presence of KCl. In Figure 2 it can be seen that the mutual solubilities of water and 2-isopropoxyethanol in the two-liquid-phase region are still quite large. Therefore, recovery of 2-isopropoxyethanol by a temperature-induced liquid−liquid phase split can be used as a first separation step, but the remaining water phase will need further treatment.

In Figures 3 and 4 and in Table 3, NaCl solubilities in mixtures of 2-isopropoxyethanol and water at 15 °C as a function of the 2-isopropoxyethanol concentration are presented. In Figure 3 the NaCl concentrations are expressed as $m_{NaCl}/(m_{IPE}+m_{H_2O})$. The solid line represents the NaCl equilibrium concentrations, and the dotted line depicts the NaCl concentrations that would arise if a saturated sodium chloride solution is mixed instantaneously with pure 2-isopropoxyethanol in an arbitrary mixing ratio. Therefore, the difference between the dotted line and the solid line represents the total amount of NaCl that crystallizes as a result of this mixing. Figure 4 displays the NaCl solubility expressed as m_{NaCl}/m_{H_2O}. It shows the extent to which the antisolvent reduces the NaCl solubility in the water volume present in the mixture.

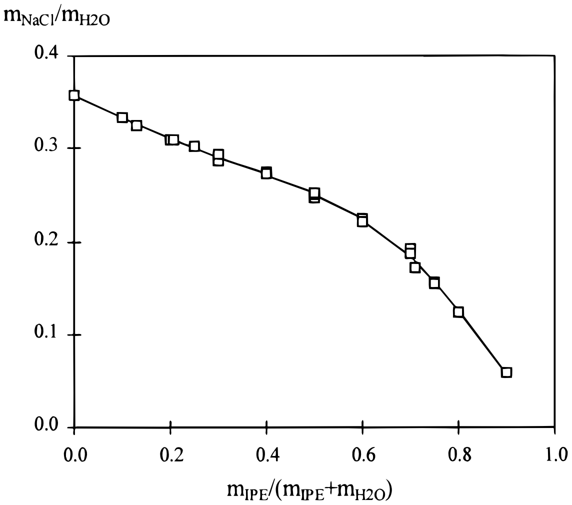

Figure 4. NaCl solubilities expressed as m_{NaCl}/m_{H_2O} in mixtures of 2-isopropoxyethanol and H_2O at 15 °C.

Table 3. NaCl Solubility in Mixtures of 2-Isopropoxyethanol and H_2O at 15 °C

[2-isopropoxyethanol] $100m_{IPE}/(m_{IPE} + m_{H_2O})$	$[NaCl]_{eq}$ $100m_{NaCl}/(m_{IPE} + m_{H_2O})$
0.00	35.76[a]
9.96	30.02
13.10	28.21
19.94	24.77
20.80	22.97
25.00	22.62
29.99	20.24
30.10	20.50
39.86	16.52
40.10	16.31
49.98	12.41
50.00	12.57
50.10	12.50
59.90	8.90
59.98	8.99
70.00	5.70
70.90	5.00
75.00	3.90
79.90	2.50
90.00	0.60
100.00	0.00[b]

[a] Mullin (1993). [b] Assumed zero.

In Figure 5 and Table 4 the NaCl solubilities in pure water (Mullin, 1993) and in 2-isopropoxyethanol−H_2O mixtures are displayed as a function of temperature. At all 2-isopropoxyethanol concentrations the solubility increases weakly with temperature. The NaCl solubility has the largest slope with temperature at the 2-isopropoxyethanol concentrations 0.25 and 0.50 ($\sim 5 \times 10^{-4}$ °C^{-1}) and is smaller in pure water ($\sim 1 \times 10^{-4}$ °C^{-1}) and in 0.75 2-isopropoxyethanol ($\sim 6 \times 10^{-5}$ °C^{-1}).

Conclusions

2-Isopropoxyethanol is a suitable antisolvent for the crystallization of NaCl, since it reduces the solubility of NaCl in water significantly and it shows a two-liquid-phase area close to room temperature with water saturated with NaCl. Because the mutual solubilities of water and 2-isopropoxyethanol in the two-liquid-phase region are still quite large, a temperature-induced liquid−liquid phase split can be used as a first separation step in the recovery of the 2-isopropoxyethanol, but the remaining aqueous phase will need further treatment.

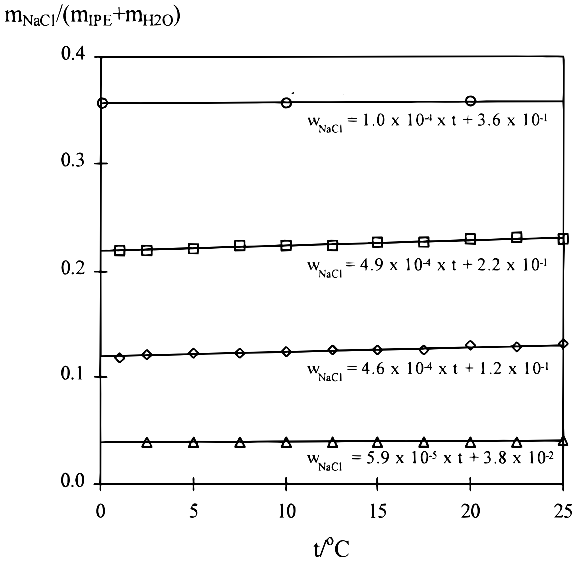

Figure 5. NaCl solid−liquid equilibrium lines in pure water and in mixtures of 2-isopropoxyethanol and H_2O as a function of temperature. 2-Isopropoxyethanol concentrations ($m_{IPE}/(m_{IPE} + m_{H_2O})$): (○) 0.00; (□) 0.25; (◇) 0.50; (△) 0.75.

Table 4. NaCl Solubility in Mixtures of 2-Isopropoxyethanol and H_2O as a Function of Temperature

	[NaCl] (100 $m_{NaCl}/(m_{IPE}+m_{H2O})$) at			
	[2-isopropoxyethanol] ($100m_{IPE}/(m_{IPE} + m_{H_2O})$) =			
t/°C	0.00	25.00	50.00	75.00
0.10	35.60[a]			
1.00		21.85	11.91	
2.50		21.94	12.12	3.83
5.00		22.07	12.23	3.83
7.50		22.26	12.28	3.90
10.00	35.70[a]	22.32	12.37	3.91
12.50		22.35	12.54	3.93
15.00		22.62	12.57	3.90
17.50		22.63	12.60	3.95
20.00	35.80[a]	22.89	12.99	3.95
22.50		23.00	12.92	3.95
25.00		22.96	13.31	3.97

[a] Mullin (1993).

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