Liquid–liquid–solid equilibria for the ternary systems water–lithium chloride–1-propanol or 2-propanol at 25 °C

Vicente Gomis ^{*}, Francisco Ruiz, Juan C. Asensi, Pilar Cayuela

Departamento de Ingeniería Química, Universidad de Alicante, Apdo. 99, Alicante, Spain

Received 3 July 1995; accepted 28 September 1995

Abstract

Liquid–liquid–solid equilibria for the ternary systems water–lithium chloride–1-propanol and water–lithium chloride–2-propanol at 25 °C have been measured experimentally. The equilibrium diagrams determined show differences between the two systems. In the system with 1-propanol, the solid phase of the liquid–liquid–solid region is monohydrated salt. However in the system with 2-propanol it is anhydrous salt.

Keywords: Experiments; Data; Solid–liquid; Liquid–liquid

1. Introduction

Liquid–liquid equilibria for ternary systems containing one salt and two solvents are of interest for many unit operations, for example for the recently developed unit operation called extractive crystallization (Weingaertner et al., 1991). The shape of the resultant ternary equilibrium diagrams water–salt–solvent can be very different depending on the salt and solvent involved. In a previous paper (Gomis et al., 1994) we showed the effect of two inorganic salts (NaCl and KCl) on the miscible systems water–1-propanol and water–2-propanol. This investigation presents the experimental observations on the effect of lithium chloride on the same water-propanol systems.

Unlike NaCl and KCl, which cannot be hydrated, LiCl can be present as either anhydrous salt or monohydrate. The shape of the equilibrium diagrams water–LiCl–solvent differs very much from those with water–NaCl or KCl–solvent because of the presence of two possible solid phases.

^{*} Corresponding author.

2. Experimental

1-Propanol and 2-propanol (Merck) were used as supplied. The contents of possible volatile impurities were examined by gas–liquid chromatography; all compounds contained negligible amounts of impurities (less than 0.3%). Merck anhydrous lithium chloride (min. purity 99.5%) served as salt.

Equilibrium measurements were made by preparing mixtures of known overall composition by mass, stirring intensely and settling at a constant temperature of 25.0 ± 0.1 °C. The mixing and settling procedure was repeated several times. The global duration of the processes of mixing and settling was longer than 50 h in order to ensure that equilibrium was reached, since dissolution and crystallization are slow processes. At the end of each experiment, samples were taken from both phases and analysed.

The concentrations of 1-propanol and 2-propanol in the aqueous phase were determined after dilution of the sample with water by a factor of 5 in order to prevent phase separation effects. The analysis was carried out by gas chromatography using a 2 m $\times$ 3 mm column packed with Porapak Q80/100. The column temperature was 180 °C, and detection was carried out by thermal conductivity. To obtain quantitative results, an internal standard method was used. 2-Propanol was the standard compound used in the determination of 1-propanol and 1-propanol was the standard in the determination of 2-propanol.

Fig. 1. Representation of the equilibrium data (% mass) for the ternary system water(W)–lithium chloride(LiCl)–1-propanol(1-P) at 25 °C.

The amount of water in the organic phase was determined by the Karl Fischer method using a Mettler DL18 Karl Fischer Titrator. The concentration of salt in the aqueous and organic phases was determined from the mass of the solid residue of a known mass of the sample, obtained by evaporation at 180 °C.

In order to ascertain whether the solid phase in equilibrium with certain samples was composed of either anhydrous LiCl or $\text{LiCl} \cdot \text{H}_2\text{O}$, two different methods were used: visual inspection of the crystals with a polariscope and thermogravimetric analysis. The polariscope was used in this study because it enables a quick and easy test to check whether the crystals belong to the cubic or tetragonal system (Anderson, 1971). Anhydrous LiCl crystals are cubic (therefore isotropic) and appear dark in all positions. Monohydrated crystals are tetragonal (anisotropic) and appear light and dark alternately.

For the thermogravimetric analysis a simultaneous TG.DTA Setaram 92-16.18 was used. The crystals were first washed with CCl_4 , since wetting of the crystal by the propanol–water mixture can change its composition during the heating and produce transformations in the structure of the salts. The experimental conditions were the following: the sample was heated in a He flow (60 ml min^{-1}) at 5 °C min^{-1} up to 80 °C, this temperature was held for 40 min, and the sample was then heated up to 200 °C at 1 °C min^{-1} . The anhydrous lithium chloride did not show any loss of weight above 120 °C, while the hydrate showed important loss at about 170 °C which corresponds to the boiling off the hydration water.

The methodology applied in selecting the points to be determined experimentally was as reported in a previous paper (Gomis et al., 1993). Duplicates of each heterogeneous mixture were prepared and

Table 1

Tie line data as mass fraction w for water(1) + lithium chloride(2) + 1-propanol(3) at 25 °C

Aqueous phase			Organic phase			Solid phase
$100w_1$	$100w_2$	$100w_3$	$100w_1$	$100w_2$	$100w_3$	
One liquid phase + one solid phase						
54.2	45.8			12.9	87.1	$\text{LiCl} \cdot \text{H}_2\text{O}$
			4.48	13.4	82.1	LiCl
			8.03	14.9	77.1	LiCl
			12.9	17.7	69.4	LiCl
			16.5	20.8	62.7	LiCl
Two solid phases + one liquid phase						
			20.1	23.9	56.0	$\text{LiCl} + \text{LiCl} \cdot \text{H}_2\text{O}$
Two liquid phases + one solid phase						
53.8	44.4	1.80	20.3	24.0	55.7	$\text{LiCl} \cdot \text{H}_2\text{O}$
Two liquid phases						
55.3	42.9	1.82	22.2	22.8	55.0	
58.9	38.2	2.92	26.2	20.3	53.5	
62.2	32.5	5.31	30.3	19.2	50.5	
62.5	26.3	11.2	44.6	19.0	36.4	

analysed. The results reported correspond to the mean value of the different analyses. The relative accuracy of the weight fraction measurements was approx. 1%.

3. Results

The results obtained are given in Tables 1 and 2. The ternary equilibrium diagrams are represented in Figs. 1 and 2.

In the same way as the systems water–NaCl–1-propanol, water–KCl–1-propanol and water–NaCl–2-propanol (Gomis et al., 1994), lithium chloride illustrates the salting out effect of a water miscible component as propanol. Nevertheless, the possible presence of two different solid phases changes the shape of the equilibrium diagrams. Now there are two regions with three phases instead of only one liquid–liquid–solid region as in the case of the systems with NaCl or KCl. The new three-phase region corresponds to equilibrium between one liquid and the two solid phases: anhydrous and monohydrate salt.

On the contrary, in spite of the similar characteristics of 1-propanol and 2-propanol, the equilibrium diagrams are quite different. In the water–LiCl–1-propanol system, the solid phase of the liquid–liquid–solid three phase region is the hydrate. However, in the system with 2-propanol it is the

Fig. 2. Representation of the equilibrium data (% mass) for the ternary system water(W)–lithium chloride(LiCl)–2-propanol(2-P) at 25 °C.

Table 2

Tie line data as mass fraction w for water(1)+lithium chloride(2)+2-propanol(3) at 25 °C

Aqueous phase			Organic phase			Solid phase
$100w_1$	$100w_2$	$100w_3$	$100w_1$	$100w_2$	$100w_3$	
One liquid phase + one solid phase						
54.2	45.8			11.4	88.6	$\text{LiCl} \cdot \text{H}_2\text{O}$
			3.02	11.5	85.5	LiCl
			8.51	12.4	79.1	LiCl
			14.4	16.8	68.8	LiCl
			20.5	20.9	58.6	LiCl
Two solid phases + one liquid phase						
52.6	44.2	3.21				$\text{LiCl} + \text{LiCl} \cdot \text{H}_2\text{O}$
Two liquid phases + one solid phase						
52.4	43.9	3.73	23.4	22.8	53.8	LiCl
Two liquid phases						
53.8	41.4	4.78	26.3	23.5	50.2	
54.0	38.9	7.09	30.7	23.9	45.4	
51.0	34.8	14.2	40.7	27.8	31.5	

anhydrous salt. Consequently, the other liquid–solid1–solid2 three phase region occupies a different relative position in each one of the diagrams.

Finally, with respect to the influence of the organic solvent, in the same way as with NaCl or KCl, the degree of salting out is lesser with 2-propanol than with 1-propanol: the heterogeneous region with two liquid phases is smaller for 2-propanol.

Acknowledgements

The authors wish to thank the DGICYT (Spain) for the financial aid of Projeet PB 93-0946.

References

- Anderson, B.W., 1971. Gem Testing, 8th edn., Butterworth.
- Gomis, V., Ruiz, F., Marcilla, A. and Pascual, M.C., 1993. Equilibrium for the ternary system water + sodium chloride + ethyl acetate at 30 °C. *J. Chem. Eng. Data*, 38: 589–590.
- Gomis, V., Ruiz, F., De Vera, G., López, E. and Saquete, M.D., 1994. Liquid–liquid–solid equilibria for the ternary systems water–sodium chloride or potassium chloride–1-propanol or 2-propanol. *Fluid Phase Equilibria*, 98: 141–147.
- Weingaertner, D.A., Lynn, S. and Hanson, D.N., 1991. Extractive crystallization of salts from concentrated aqueous solution. *Ind. & Eng. Chem. Res.*, 30: 490.