PHASE EQUILIBRIUM IN THE SYSTEM WATER–ACRYLONITRILE–ZINC CHLORIDE–CALCIUM CHLORIDE

J.Podnecká[a], H.Kohoutová[b], R.Holub[b] and J.Pick[b]

[a]*Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences, Prague 6,*
[b]*Department of Physical Chemistry, Institute of Chemical Technology, Prague 6*

Phase equilibrium in the four-component system water–acrylonitrile–zinc chloride–calcium chloride has been studied at a temperature of 20°C. Tie lines have been correlated by means of the Bachman equation. Solubility data in the region where salting-out effect prevails have been correlated by a modified Sečenov equation and for the other parts of the system by empirical equations proposed.

In the previous paper[1] liquid–liquid equilibrium data were given for the ternary systems water–acrylonitrile–zinc chloride and water–acrylonitrile–calcium chloride at 20, 30 and 40°C, with the aim to define the concentration region of complete miscibility of acrylonitrile in aqueous solutions of these salts. These data obtained have a considerable importance for the determination of conditions of a new method of acrylonitrile polymerization.

It was found in that measurement that the system water–acrylonitrile–zinc chloride showed a relatively large region of complete miscibility at all temperatures, while an increasing addition of calcium chloride caused a decrease in the mutual solubility of water and acrylonitrile. For this reason it is to be expected that an addition of calcium chloride into the system water–acrylonitrile–zinc chloride will give rise to a decrease of complete miscibility region of the components, until when, reaching a certain concentration, the salting-out effect of $CaCl_2$ prevails. For the quantitative determination of these dependences, the system water–acrylonitrile–zinc chloride–calcium chloride was measured and the results are given in this paper.

EXPERIMENTAL

Materials and analytical methods. Pure acrylonitrile, (Kaučuk, Kralupy) was used. Its values of refractive index and density compared with data from the literature[2] are as follows: n_D^{20} 1·3911 (ref. 1·3911), d_4^{20} 0·8068 (ref. 0·8060). Zinc chloride used was of analytical grade purity (Lachema, Brno). Calcium chloride, a reagent grade chemical, was dried[3] for about 15 minutes at 25°C. Zinc chloride as well as calcium chloride were determined as zinc and calcium by chelatometric titration method[4]. Its advantage consists in the determination of the content of both elements using only one weighed sample.

Procedure. The part of the solubility curve with higher content of water was determined by measuring the volumes in the Rifai and Durandet apparatus[5]. The part of the solubility curve with higher content of acrylonitrile could not be determined by this method and therefore it was determined by titration till the first turbidity appeared. The data obtained by means of this method were less accurate than those in the previous case. Besides the error of the method they are also subject to an inaccuracy when estimating the moment of turbidity appearance, for in the case when equilibrium liquid–liquid and liquid–solid curves were close to each other, these systems showed, when titrating, an opalescence close before originating the turbidity. To the greatest experimental error is apparently subject the system with weight ratio of salts $ZnCl_2 : CaCl_2$ 1·649 where both equilibrium curves approach each other very closely. In this case salts separated out instantaneously when determining the solubility curve of both liquids by titration up to the appearance of turbidity. And on the contrary when determining the solubility of the solid substances in a mixture of the liquids, two liquid phases appeared at the moment of dissolving the solid substances. The composition of conjugate phases was determined after the solubility curve had been measured, by analysing the content of salts after separating both phases. The acrylonitrile content was calculated from the solubility curve.
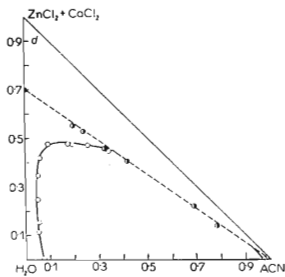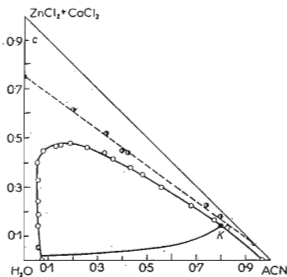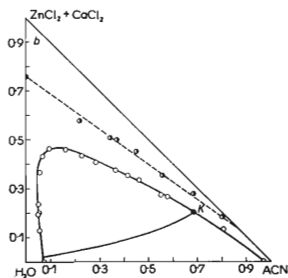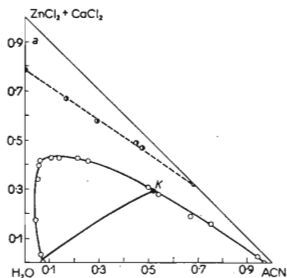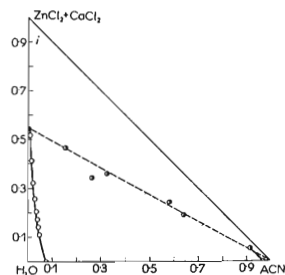
Fig. 1

Equilibrium in the System Water–Acrylo-nitrile–Zinc Chloride–Calcium Chloride with Various Weight Ratios of $ZnCl_2$: $CaCl_2$ at the Temperature 20°C

○ Equilibrium between liquid phases, ◑ equilibrium among liquid and solid phases. K represents plait point; weight ratio $ZnCl_2/CaCl_2$: *a* 9·246, *b* 3·562, *c* 2·427, *d* 1·649, *e* 1·082, *f* 0·7066, *g* 0·4985, *h* 0·2903, *i* 0·1474.

RESULTS AND DISCUSSION

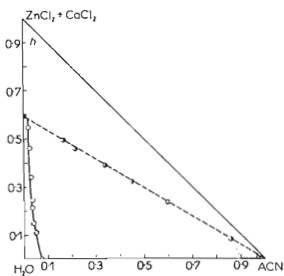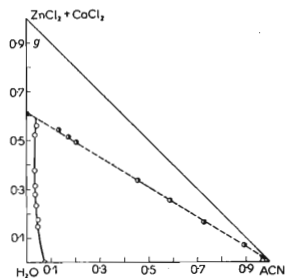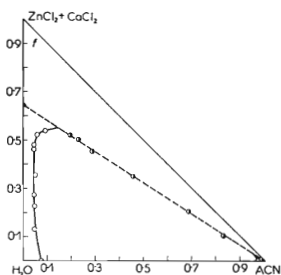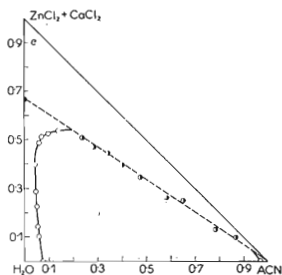Equilibrium data for the system water–acrylonitrile–$ZnCl_2$–$CaCl_2$ at 20°C are illustrated in Fig. 1. For the simplicity of representation this quaternary system was represented as a pseudoternary one in which the third component of the system was the mixture of $ZnCl_2$ and $CaCl_2$ with various mutual ratios ranging from 9·246 to 0·1474 of the weight ratio of $ZnCl_2$ in the mixture. Thus the triangular diagrams are plain sections of the rectangular triangular prism that represents the equilibrium in the quaternary system studied.

From Fig. 1 it is evident that with increasing $CaCl_2$ content in the mixture of salts increases gradually both the region of two liquid phases, and heterogeneous region of the liquid–solid equilibrium. The plait point shifts to lower concentrations of salts. This fact is due to a low solubility of $CaCl_2$ in acrylonitrile so that with increasing content of $CaCl_2$, saturated solutions with a lower content of salts are at equilibrium. In the range of weight ratio $ZnCl_2 : CaCl_2$ 2·247 to 1·649 the salting-out effect of $CaCl_2$ of $CaCl_2$ already begins to prevail, *i.e.* in our representation both equilibrium curves (liquid–liquid and liquid–solid) intersect. With further increase in $CaCl_2$ content the homogeneous area decreases very quickly till at the content about nine times higher than the $ZnCl_2$ concentration the area of the complete miscibility is practically quite inappreciable. Intense increase in the acrylonitrile solubility from a certain concentration of the salts is explained by the formation of complex compounds of $ZnCl_2$ with acrylonitrile. These complex compounds enable to make up one phase[1].

In the region where the salting-out effect of $CaCl_2$ is not operative, tie lines were correlated by the Othmer–Tobias[6] and Bachman[7] method. The Othmer–Tobias equation

$$(1 - w_{22})/w_{22} = k[(1 - w_{11})/w_{11}]^r, \qquad (1)$$

(w_{22}, w_{11} are weight fractions of acrylonitrile in the acrylonitrile-rich phase and water in the water-rich phase, respectively, and k, r are constants) was linearised by transferring into the logarithmic dependence. Eq. (1) did not express satisfactorily the measured data, whereas the linear Bachman equation

$$w_{22} = a(w_{22}/w_{11}) + b, \qquad (2)$$

(where a and b are constants) was applicable in all cases.

For correlating the tie lines it was necessary to know besides the content of salts in both conjugate phases yet the concentration of a further equilibrium component. Therefore the solubility curve was correlated first and from it the concentrations of acrylonitrile were interpolated for the measured concentrations of salts in both phases.

Correlating the solubility curve was carried out so that the curve was divided into four parts and each of them was correlated by an empirical equation. These

TABLE I
Constants of Correlation Equations of Solubility Curves for the System H_2O–Acrylonitrile–$CaCl_2$–$ZnCl_2$ with Various Ratios of Both Salts at 20°C

Weight ratio $ZnCl_2$: $CaCl_2$	Interval of $w_{(3)}$	Interval of $w_{(2)}$	Constants						Correlation equation
			Q_1	Q_2	Q_3	Q_4	Q_5	Q	
9·246	0·0000—0·1751	—	-0·0274	—	—	—	—	—	(3)
	0·1751—0·3392	—	—	—	—	—	—	—	(4)
	—	0·0497—0·2138	—	1·424	-4·293	0·1801	0·0619	—	(5)
	—	0·2138—0·9690	—	—	—	—	—	—	(6)
3·562	0·0000—0·1946	—	-0·0205	—	—	—	—	—	(3)
	0·1946—0·3637	—	—	—	—	—	—	—	(4)
	—	0·0551—0·2264	—	0·9054	-2·353	0·1302	0·4945	—	(5)
	—	0·2264—0·9690	—	—	—	—	—	—	(6)
2·427	0·0000—0·1421	—	-0·0207	—	—	—	—	—	(3)
	0·1421—0·4021	—	—	—	—	—	—	—	(4)
	—	0·0550—0·3583	—	0·4949	-0·9372	0·1002	0·5011	—	(5)
	—	0·3583—0·9690	—	—	—	—	—	—	(6)
1·649	—	—	-1·073	10·32	—	—	—	—	(8)
1·082	—	—	-1·054	10·80	—	—	—	—	(8)
0·7066	—	—	-1·136	8·40	—	—	—	—	(8)
0·4985	—	—	-1·467	10·77	—	—	—	—	(8)
0·2903	—	—	—	—	—	—	—	2·5108	(7)
0·1474	—	—	—	—	—	—	—	4·0074	(7)

functions were fixed at the end points of the intervals in order that the continuity of the course might be warranted. Functional dependences were chosen in accordance with the form of the curves in the single intervals. In all following equations w_2 denotes the weight fraction of acrylonitrile, w_3 the weight fraction of the mixture of salts, the superscript in parentheses the number of the fixed point, and Q_i are constants.

The part of the solubility curve in the region of higher concentration of water and low concentrations of salts was correlated by the relation

$$w_2 = w_2^{(0)} + \left(w_2^{(1)} - w_2^{(0)}\right)\overline{w}_3 + Q_1\overline{w}_3(1 - \overline{w}_3), \qquad (3)$$

where $\overline{w}_3 = w_3/w_3^{(1)}$, which holds for $w_3 \in \left(w_3^{(0)}, w_3^{(1)}\right)$ and $w_2^{(0)}$ is weight fraction of acrylonitrile dissolved in water containing no salts. For correlating the straight-line region of the solubility curve, the equation was used

$$w_2 = w_2^{(1)} + \left(w_2^{(2)} - w_2^{(1)}\right)\overline{w}_3, \qquad (4)$$

where $\overline{w}_3 = \left(w_3 - w_3^{(1)}\right)/\left(w_3^{(2)} - w_3^{(1)}\right)$, which holds for $w_3 \in \left(w_3^{(1)}, w_3^{(2)}\right)$. The region in the vicinity of the maximum of the solubility curve was correlated by the equation

$$w_3 = w_3^{(2)} + \left(w_3^{(3)} - w_3^{(2)}\right)\overline{w}_2 + Q_2\overline{w}_2(1 - \overline{w}_2)\exp\left(Q_3\overline{w}_2\right), \qquad (5)$$

where $\overline{w}_2 = \left(w_2 - w_2^{(2)}\right)/\left(w_2^{(3)} - w_2^{(2)}\right)$, which holds for $w_2 \in \left(w_2^{(2)}, w_2^{(3)}\right)$. For the acrylonitrile-rich region the relation was used

$$w_3 = w_3^{(3)} + \left(w_3^{(4)} - w_3^{(3)}\right)\overline{w}_2 + Q_4\overline{w}_2(1 - \overline{w}_2)\exp\left(Q_5\overline{w}_2\right), \qquad (6)$$

where $\overline{w}_2 = \left(w_2 - w_2^{(3)}\right)/\left(w_2^{(4)} - w_2^{(3)}\right)$, which holds for $w_2 \in \left(w_2^{(3)}, w_2^{(4)}\right)$. Eqs (3) −(6) reproduce the measured data with a mean deviation of ± 0.0035 in the weight fraction of corresponding component.

In concentration regions with prevailing salting-out effect of $CaCl_2$, the solubility curves were correlated by only one equation. In case of the weight ratios $ZnCl_2 : CaCl_2$ 0·2903 and 0·1474 where the solubility of acrylonitrile decreased with increasing concentration of salts, the Sečenov equation[8] was used, but instead of molar concentrations weight fractions were used for calculating

$$\log w_2 = -Qw_3 - 1.141575. \qquad (7)$$

Eq. (7) fits the measured data with a mean deviation of ± 0.0024 in weight fraction of corresponding component.

The curves in the region where the effect of $ZnCl_2$ is still relatively strong but the salting-out effect of $CaCl_2$ already becomes prevalent (the systems in the figures $1d-g$) were correlated by an empirical two-constant relation fixed at the first and last point. The first term of this relation is the Sečenov equation which accords well with a decrease in solubility at low concentrations of salts and the second one is the power function which can express a strong increase in solubility of acrylonitrile at higher concentrations of salts

$$w_2 = w_2^{(0)} \exp\left(Q_1 \bar{w}_3\right) + \left(w_2^{(1)} - w_2^{(0)} \exp Q_1\right) \bar{w}_3^{Q_2}, \qquad (8)$$

where $\bar{w}_3 = w_3/w_3^{(1)}$.

The mean of absolute values of deviations of the measured and calculated weight fractions according to Eq. (8) is ± 0.0072. The constants of Eqs $(3)-(8)$ and intervals used are given in Table I. The tie lines of conjugate liquid phases are not shown in Figs $1a-c$. By a solid line just the auxiliary curve is marked which is formed by points of intersection of parallels drawn along the legs of triangle through the points representing conjugate phases. The constants of equations of tie lines and the compositions of plait points calculated from Eq. (2) for corresponding ratios of salts are given in Table II. Thus, Eqs (1) and (2) are to be used even in the given pseudoternary systems, in spite of their assigning for correlating the ternary systems. Equilibrium curves for the mixtures of solid salts of a certain ratio and their saturated solutions with acrylonitrile in water are represented in Figs $1a-i$ by broken lines.

TABLE II

Constants of Eq. (2) for Tie Lines and Composition of Plait Point at the Temperature 20°C

Weight ratio $ZnCl_2 : CaCl_2$	a	b	$w_2^{(k)}$	$w_3^{(k)}$
9·246	−0·4349	1·747	0·5184	0·2981
3·562	−0·0507	1·040	0·6968	0·2003
2·427	−0·0118	0·9823	0·8077	0·1377

In order that the measured data may be used in technologic practice it will be expedient to carry out, after defining a closer concentration region, the measurement of solubility data for this quaternary system in their dependence on temperature. This measurement will be a subject of next paper.

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