PHASE EQUILIBRIUM OF THE TERNARY CONDENSED SYSTEM WATER–$NH_4SCN(BaCl_2\ CaCl_2)$–POLY(ETHYLENE GLYCOL)-6000 AT 25°C

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Experimental data are correlated with empirical relations or plotted in the isothermal concentration diagram. The sulphocyanide causes the changes in the phase behaviour of the system, when observed in the whole concentration range and its effect can be compared with KSCN in this system. The action of $BaCl_2$ does not differ from that of alkali metal chlorides, that means, the salt is salted out from the mixed solvent. On the other hand, $CaCl_2$ salts out the nonelectrolyte in the whole concentration range.

In our previous work[1–3], the equilibria of the ternary systems: water, poly(ethylene glycol) (PEG) of various molecular weight and an inorganic salt with common potassium cation and a serie of anions have been studied. A conclusion can be drawn from experimental data obtained: while the salts K_2SO_4, KCl, KBr in all studied systems are salted out from the mixed solvent water–poly(ethylene glycol) and KI in the systems with PEG of the molecular weight up to 1 500, the salts with SCN' and CO_3'' anion in the systems with PEG over the molecular weight 1 000 and KI in the system with PEG over 1 500 cause more complicated phase behaviour with salting out or salting in effects towards the PEG and with the formation of two coexisting liquid phases in certain concentration regions.

In the present work the effect of some cations was studied by determination of the isothermal phase diagrams of the systems water–PEG-6000- salts: NH_4SCN, $BaCl_2$, $CaCl_2$.

EXPERIMENTAL

The analytical method has been used for the determination of the equilibrium concentrations of the saturated or coexisting liquid phases in the samples permanently stirred 72 hours in the sealed ampules at the bath temperature 25 ± 0·05°C. The water content was determined by Fischer's method with electrometric titration, chlorides by Mohre's and sulphocyanide by Volhard's volumetric determination in the liquids formed from a certain mixture or in residual solids in equilibrium.

As for the solutions saturated with PEG we had to proceed so, that to an unsaturated solution of known composition stepwise small weighed amounts of PEG were added until the first cloudiness apeared. This procedure was needed because of amorphous dispersed solid PEG, which could not be separated from the saturated solution to be analysed.

The poly(ethylene glycol)-6000 was the product of Chemické závody W. Piecka, Nováky, ČSSR with the water content 0·58 weight per cent and with melting point range 52–65°C. The designation 6000 indicates the mean molecular weight. Other chemicals were of analytical reagent grade.

RESULTS AND DISCUSSION

The isothermal concentration diagram (Fig. 1) of the system H_2O–NH_4SCN–PEG-6000 is rather complicated with homogeneous region (*I*), two liquid phases region (*II*), saturated solution-solid phase regions (*IV*, *V*) and three phases region (*III*). The experimental data are summarised in Table I with the composition of two coexisting liquids, where W_{AA}, W_{CA} are the weight fractions of water and electrolyte in water rich phase, resp., W_{AB}, W_{CB} are the weight fractions of water and electrolyte in nonelectrolyte rich phase, resp., W_{BB} is the weight fraction of nonelectrolyte in the nonelectrolyte rich phase.

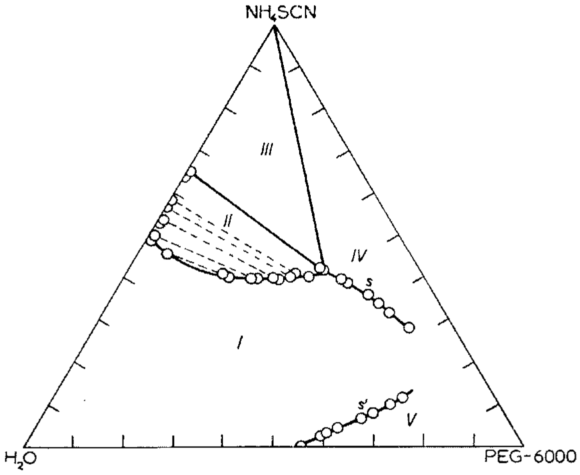

FIG. 1

Isothermal Concentration Phase Diagram of the System H_2O–NH_4SCN–PEG-6000

From the series of suggested empirical relations for correlation of the conjugated lines in two liquid phases equilibrium the Bachman's[4] (here relation (*1*)) and Othmer-Tobias's[5] relation (*2*) were used in the form

$$W_{AA} = a\left(\frac{W_{AA}}{W_{BB}}\right) + b\,, \qquad (1)$$

$$\frac{(1 - W_{AA})}{W_{AA}} = k\left(\frac{1 - W_{BB}}{W_{BB}}\right)^r . \qquad (2)$$

The calculated constants are: $a = 0{\cdot}0897$, $b = 0{\cdot}296$, $k = 0{\cdot}222$, $r = -0{\cdot}626$. The Othmer–Tobias's equation fits in the experimental data with mean relative deviation of calculated values from measured ones 4·9%, that means, better than that of Bachman with mean rel. dev. 7·3%. The experimental data of the composition of solutions saturated with NH_4SCN (the curve s in Fig. 1) and with PEG-6000 (the curve s') are tabulated in Table II, where W_A, W'_A and W_C, W'_C are the weight fractions of water and salt, respectively.

The system H_2O–$BaCl_2$–PEG-6000/is similar to that with KCl, (NH_4Cl, NaCl) in its phase behaviour, that means, the solubility of the salt is lower in the mixed solvent than in pure water. The experimental solubility data of the salt are summarised in Table III and were correlated with the polynomial second-order equation (*3*) written with calculated empirical constants

$$W_A = 0{\cdot}2888 - 0{\cdot}3878W_C + 0{\cdot}4253W_C^2 \qquad (3)$$

and the mean relative deviation ±1·18%.

In the system H_2O–$CaCl_2$–PEG-6000 the nonelectrolyte is salted out from the solution, so that the solid PEG-6000 is in equilibrium with the saturated solution.

TABLE I

The Composition of Coexisting Liquid Phases in the System H_2O–NH_4SCN–PEG-6000

W_{AA}	W_{CA}	W_{AB}	W_{BB}
0·3392	0·6491	0·1955	0·4179
0·3540	0·6420	0·1917	0·4293
0·3548	0·6344	0·2018	0·4218
0·3889	0·6190	0·2520	0·4216
0·4150	0·5882	0·2560	0·4111
0·4294	0·5730	0·2323	0·4000
0·4366	0·5699	0·2675	0·4029
0·4515	0·5299	0·2965	0·3946
0·4630	0·5360	0·3068	0·3962
0·4863	0·4583	0·4000	0·3905
0·4863	0·4569	0·4106	0·3989
0·4868	0·5080	0·3463	0·3955
0·4891	0·5078	0·3427	0·3912
0·5046	0·4810	0·3991	0·4009

TABLE II

The Experimental Data for Saturated Solutions (s, s′) in the System H_2O–NH_4SCN–PEG-6000

s		s′	
W_A	W_C	W'_A	W'_C
0·1710	0·3918	0·5809	0·0266
0·1600	0·3860	0·5918	0·0318
0·1337	0·3586	0·6073	0·0477
0·1220	0·3389	0·6434	0·0641
0·1102	0·3181	0·6622	0·0781
0·0903	0·2782	0·6818	0·1011
		0·6939	0·1190

TABLE III

The Solubility Data

W_A	W_C	W_B	W_A	W_C	W_B
H_2O–$BaCl_2$–PEG-6000			H_2O–$CaCl_2$–PEG-6000		
0·2460	0·1298	0·6242	0·1543	0·3937	0·4520
0·2717	0·0656	0·6627	0·1493	0·4012	0·4495
0·2320	0·2100	0·5580	0·1700	0·3680	0·4620
0·2514	0·0947	0·6539	0·2502	0·1231	0·6267
0·2240	0·2080	0·5680	0·2160	0·2379	0·5461
0·2130	0·2649	0·5221	0·1907	0·2970	0·5123
0·2045	0·3655	0·4300	0·2490	0·0987	0·6523
0·2036	0·3708	0·4256	0·2210	0·2131	0·5659
0·2655	0·0538	0·6807	0·2167	0·2208	0·5625
0·2340	0·1840	0·5820	0·2390	0·1490	0·6120
0·2220	0·2199	0·5581	0·2603	0·0842	0·6555
			0·2715	0·0519	0·6766
			0·1242	0·4438	0·4320
			0·4235	0	0·5765
			0·4247	0	0·5753

The experimental solubility data tabulated in Table III were correlated and the correlation equation *(4)* with calculated constants and the mean relative deviation is as follows

$$W_A = 0{\cdot}2789 - 0{\cdot}2076 W_C - 0{\cdot}2976 W_C^2 [\pm 1{\cdot}20\%] . \tag{4}$$

It can concluded, that the anion of the inorganic salt used in the ternary system with water and PEG-6000 is the main factor determining the type of the phase equilibrium. The similar isothermal concentration phase diagrams wih KSCN and NH_4SCN or with KCl, NH_4Cl, $BaCl_2$ are the examples. Among the examined salts the calcium chloride differs in its effect on the considered three component system. In the whole concentration range it salts out the nonelectrolyte, which fact can not be explained only in terms of the valency of the cation when compared with $BaCl_2$, but it is rather due to the strong hydration of Ca^{2+} ion.

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