

4. Ramalho R. S., Delmas J.: *J. Chem. Eng. Data* 13, 161 (1968).
5. Smirnova N. A., Kurtykina L. M.: *Ž. Fiz. Chim.* 43, 1883 (1969).
6. Sedláček Z., Hynek V., Svoboda V., Pick J.: *Chem. listy*, in press.
7. Hála E., Pick J., Fried V., Vilím O.: *Vapour-Liquid Equilibrium*; 2nd Ed. Pergamon, Press, London 1968.
8. Orye R. V., Prausnitz J. M.: *Ind. Eng. Chem.* 57 (5), 18 (1965).
9. Timmermans J.: *Physico-Chemical Constants of Pure Organic Compounds*. Elsevier, Amsterdam 1950.
10. Timmermans J.: *Physico-Chemical Constants of Pure Organic Compounds*, Vol. 2. Elsevier, Amsterdam 1965.
11. Hajjar R. F., Kay W. B., Leverett G. F.: *J. Chem. Eng. Data* 14, 377 (1969).
12. Pitzer K. S., Curl R. F.: *J. Am. Chem. Soc.* 79, 2369 (1957).
13. Jefremov V.: *Ž. Fiz. Chim.* 40, 1240 (1969).
14. Cruickshank A. J. B., Cutler A. J. B.: *J. Chem. Eng. Data* 12, 326 (1967).
15. Rose A., Supina W. R.: *J. Chem. Eng. Data* 6, 173 (1961).
16. Brown I., Fock W., Smith F.: *Australian J. Chem.* 17, 1106 (1964).

Translated by J. Linek.

SOLUBILITY OF KCl, KBr, KI AND KSCN IN THE TERNARY SYSTEM WATER-ELECTROLYTE-POLY(ETHYLENE GLYCOL) (200, 1000)

Z. ADAMCOVÁ

*Department of Physical Chemistry,
Institute of Chemical Technology, Prague 6*

Received August 10th, 1970

The present work is a continuation of an earlier publication¹. Solubilities of 1 : 1 electrolytes KCl, KBr, KI and KSCN in mixed solvents water-poly(ethylene glycol) (PEG) 200 and water-poly(ethylene glycol) 1000 are investigated. Homogeneous regions are delimited and empirical equations are proposed to describe solution isotherms. The mentioned solvent systems have not yet been studied.

EXPERIMENTAL

The chemicals used, KCl, KBr, KI and KSCN, of analytical reagent grade, were recrystallised from distilled water and dried to constant weight at 150°C. PEG-200 and PEG-1000 were commercial products (Chemische Werke Hüls A. G.); their mean molecular weights, as determined osmometrically in the vapour phase (with an error $\pm 5\%$) were 182 and 769, respectively. Composition of homogeneous mixture, in equilibrium with salt crystals or with the second liquid phase was established by determining two components, salt and water, whereas the third one was

calculated. Potassium chloride and bromide were determined volumetrically according to Mohr, potassium iodide and sulphocyanide using the method of Volhard. Water content was determined according to Fischer², with electrometric titration.

To a mixture of definite water: PEG ratio salt was added either in excess, when determining the solution isotherm, or in the calculated amount, when the salting out diagram was studied. The system was equilibrated in ampoules sealed in a thermostat, maintained at constant temperature $25 \pm 0.05^\circ\text{C}$. Samples were stirred for 72 hours. After the crystals had sedimented and the liquid phases had separated, the samples were taken through a cotton filter. In the case of two liquid phases the lower layer was sucked by means of a syringe.

RESULTS AND DISCUSSION

As can be seen from Figs 1 and 2, solution isotherms have the character of monotonous curves, if expressed in terms of weight per cent. Their course can be described by analytic second-order equation, defining the solubility of salt, S , in g/100 g of the mixed solvent. Constants of the general equation

$$S = A + Bx + Cx^2 \quad (1)$$

TABLE I

Coefficients of Empirical Equation, Describing the Solubility of Salt in a Mixed Solvent and the Relative Deviation of Calculated Values from the Measured Ones

Nonelectrolyte	Electrolyte	A	$-B$	$C \cdot 10^3$	Dev., %
PEG-200	KCl	35.3	0.581	2.79	1.63
	KBr	69.2	0.834	3.28	1.57
	KI	147.7	1.643	7.02	1.29
	KSCN	246.7	3.200	11.56	1.67
PEG-1 000	KCl	36.1	0.545	2.02	2.45
	KBr	69.4	0.887	3.52	2.13
	KI	147.9	1.600	5.71	0.85
Monoethylene glycol	KCl	35.8	0.505	2.00	0.80
	KI	148.8	1.447	4.69	0.45
	KSCN	252.4	1.815	-1.12	2.00
Diethylene glycol	KCl	35.8	0.560	2.40	1.22
	KI	146.9	1.476	5.13	1.36
	KSCN	251.6	2.748	7.42	1.62
Triethylene glycol	KCl	35.8	0.569	2.59	0.71
	KI	149.0	1.507	5.51	0.42
	KSCN	250.2	2.955	9.25	0.88

are summarized in Table I. x denotes the weight of PEG (in g) in 100 g of solvent. Using the least squares method also the coefficients of the empirical equation were determined for the system, studied in the previous paper¹.

Solubility of electrolytes in these systems is described by a second-order polynomial with the average deviation of experimental values from the calculated ones 0.42–2.45% (per cent of absolute value). With respect to the fact that the reproducibility of water content determination according to Fischer lay within $\pm 1\%$, the deviations can mostly be accounted for the experiments and the second order polynomial can therefore be taken as suitable for the description of solubility in the systems mentioned.

The authors who investigated the solubility of solid substances in a mixed solvent employed different empirical equations to evaluate the dependence of solubility on composition of the mixed solvent. According to Milicevic and Ivekovic³, these equations can be transformed into a single general equation

$$d \ln N_s = KN_x^n dN_x, \quad (2)$$

where N_s is the mole fraction of solute and N_x the mole fraction of one of the components of the mixed solvent; K and n are constants for the given system.

The dependence of $\ln N_s$ on N_x in our systems shows extrema, indicating that quantities K and n in Eq. (2) are not constant over the whole concentration range and, as far as they describe a certain kind of interaction in the system, the character of this interaction changes in the extremum points of the curves. This assumption is also supported by the course of solution isotherms, expressed in terms of the dependence of number of mol of electrolyte on the number of mol of nonelectrolyte in 100 mol of solution. Isotherms show minima in the vicinity of 10 mol % PEG in the mixed solvent.

In the system KSCN–water–PEG 1000 the nonelectrolyte is either salted out or salted in. The diagram of this system is shown in Fig. 3. The system was measured in the points on secants

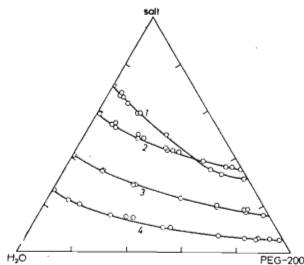


FIG. 1
Solution Isotherms of Salts in the System
Water-PEG-200
1 KSCN, 2 KI, 3 KBr, 4 KCl.

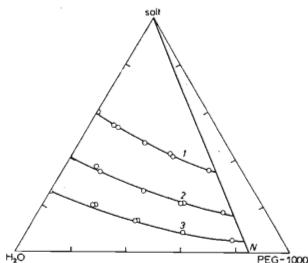


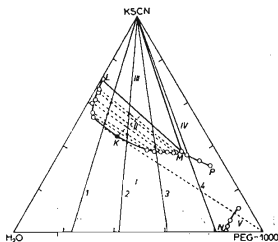
FIG. 2
Solution Isotherms of Salts in the System
Water-PEG-1000
1 KI, 2 KBr, 3 KCl.

1-4 having constant water: PEG 1000 ratio. Region I is homogeneous, containing one phase. Region II, delimited by binodal curve and the line, connecting points L and M is the region of co-existence of two liquid phases with nodes whose direction is given by experimental points on the binodal curve and which are controlled by the point of the initial mixture composition. Plait point K satisfies the definition given by Merclin^{4,5}, i.e. it is the point on the tangent to binodal curve that lies on the averted side from the prevailing pair of components. The tangent is directed to the top of the third component. Consequently, the prevailing pair in this system is water-KSCN. The predominance of the interaction of the pair H₂O-KSCN is also demonstrated

FIG. 3

Diagram of the System Water-PEG-100-KSCN

○ Experimental points, x points of initial composition, ● plait point.



by the direction of nodes, diverging towards the H₂O-KSCN axis. Point K is simultaneously extrapolated intersection of binodal curve with the line connecting the midpoints of nodes⁶ which in fact expresses the Cailletet-Mathias rule of linear average⁷, as applied to the determination of critical quantities. Region III is the zone of three phases: two liquid ones, of the composition corresponding to points L and M and one solid phase (salt crystals). IV is a two-phase region, the liquid phase having the composition defined by line MP and the solid phase being salt crystals. Region V is a two-phase one with one liquid phase and a solid one which is PEG-1000. Point N denotes mutual solubility of the components water and PEG-1000. KSCN acts as a salting agent for the nonelectrolyte by a high PEG-1000 content and in this manner makes the homogeneous region of this three-component system more expanded.

REFERENCES

1. Adamcová Z.: This Journal 34, 3149 (1969).
2. Fischer K.: Angew. Chem. 48, 394 (1935).
3. Milicevic B., Ivekovic H.: Croat. Chem. Acta 31, 91 (1959).
4. Merclin R. V., Nikurašina N. Y.: Ž. Fiz. Chim. 35, 2616 (1961).
5. Merclin R. V., Nikurašina N. Y., Ostapenko G. M.: Ž. Fiz. Chim. 43, 316 (1969).
6. Renard J. A., Heichelheim H. R.: J. Chem. Eng. Data 12, 33 (1967).
7. Cailletet J., Mathias E.: Compt. Rend. 102, 1202 (1886).

Translated by V. Čermáková.