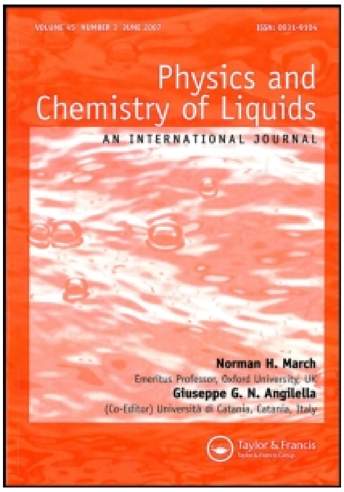

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Solubilities of Sodium and Potassium Iodides in Water-*n*-Propyl Alcohol Mixtures at 25°C

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SOLUBILITIES OF SODIUM AND POTASSIUM IODIDES IN WATER-*n*-PROPYL ALCOHOL MIXTURES AT 25°C

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The solubilities of NaI and KI and solid phase composition existing in equilibrium with saturated salt solution in water-*n*-propyl alcohol system at 25°C have been determined. It was found that the solubility curve of NaI as a function of alcohol content is divided into two areas oppositely to KI, where the observed dependence is monotonic. The changes of the plot of the solubility curves reflect the changes in the solid phase compositions. It was concluded that NaI was preferentially hydrated in almost the whole range of water-*n*-propyl alcohol mixture.

The dependencies of the logarithm of solubility on the reciprocal of electric permittivity of mixed solvent exhibit two linear sections with intersection points ca. 60–65 mol% of alcohol. The influence of the electric permittivity on solubility is more distinct in the case of KI.

The precipitating constant of *n*-propyl alcohol is for KI ten times higher than for NaI. So, *n*-propyl alcohol is a good precipitator for KI and worse for NaI in water-*n*-propyl alcohol mixture.

KEY WORDS: Solubility of NaI, solubility of KI, Water-*n*-Propyl alcohol mixture.

Previously, many properties of alkali halides in water-alcohol systems has been studied in our laboratory[1–8]. Now, I decided to undertake the solubility investigations of these systems, because the literature data for these systems are only fragmentary[9–12].

It is known that the solubility of sparingly soluble electrolytes in different solvents are related to the electric permittivity of these solvents. According to the Born's equation[13,14]:

$$\lg \frac{S_1}{S_2} = 0.4343 \frac{Ne^2}{RT} (r^+ + r^-)^{-1}(\varepsilon_1^{-1} - \varepsilon_2^{-1}) \tag{1}$$

or its modification[15,16] which correlates the solubilities of a salt in two solvents 1 and 2 with the reciprocal of the electric permittivities of the solvents, one can predict solubility of the salt in different solvent knowing the solubility in one of them and the electric permittivities of both of the solvents.

The solubility investigations especially in water-alcohol mixtures showed the deviations[9,17] from the above rule. Thus, the solubilities of salt in water-alcohol mixtures cannot be predicted from other solubility data and have to be studied experimentally.

I began my investigations from the solubility measurements of NaI and KI in water-*n*-propyl alcohol system at 25°C.

EXPERIMENTAL

Sodium iodide (Merck, analytical grade) was dried under vacuum at 70°C. Potassium iodide (Merck, suprapur grade) was dried at 105°C. *n*-Propyl alcohol (puriss grade, produced by POCh Gliwice, Poland) was purified by standard methods.[18]

The solubility measurements were performed in the glass vessels with capacity of ca. 100 cm^{-3}. The vessels with thermostatic jackets were embedded in the thermostatic covers of the cells and then placed in the cells of a large thermostat which temperature was kept within ±0.01°. The vessels were covered by glass-stoppers with glass stirrers and two glass tubes in them. The first one served for introducing the salt and the second for venting. There were the stopcocks above the bottom (ca. 2 cm) of the vessel to collect the samples of the saturated solutions.

The mixed solvent and the salt were placed in vessels and closed with tight glass-stoppers. The solution was continuously stirred. The salt was added by glass tubes when necessary. At least 24 hours were left for equilibration. Then the solution was filtered off (and the samples were taken out). The amount of solute in the saturated solution was determined in two ways: by potentiometric titration and evaporating to dryness.

During the potentiometric titration, the excess of $AgNO_3$ solutions of known concentrations was added to weighed and diluted with water samples of iodides and then potentiometrically titrated with NaCl solution of known concentration. The results of solubility were the average values of three independent determinations.

The samples with volume of ca. 5 cm^3 were evaporated to dryness at about 30°C under vacuum and then dried to their constant weight at 60°C.

The results of solubility were the average values of the data obtained from both the methods. All solubility measurements were performed twice.

The thermogravimetric method was applied to determine the composition of solid NaI and KI existing in equilibrium with saturated salt solutions in water-*n*-propyl alcohol mixtures at 25°C. The saturated salt solutions in the investigated mixed solvent were prepared by weight in order to obtain ca. 0.5 g of NaI and KI in solid phase. The solutions were kept in darkness in thermostat cell at constant temperature for about four days in order to reach the equilibrium between solid and liquid phases. Then they were filtered off under vacuum and the precipitates were analyzed immediately without drying in order to avoid the changes of the composition of salt. The measurements were made with a 102/1500 derivatograph (MOM, Hungary) recording TG, DTA and DTG curves. Samples of 250 mg were heated in static air in ceramic crucibles, Al_2O_3 was a reference material, at a heating rate -2.5 deg min^{-1} and with sensitivities TG -200 mg, DTG $-$ 1/10 and DTA $-$ 1/5. The samples were heated to 300°C only, because the earlier measurements showed that above 250°C

Table 1 Solubility and solid phase compositions of NaI in water-*n*-propyl alcohol mixtures at 25°C. Electric permittivity data from Ref. (19).

x_a	*S* *g/100 g solvent*	ρ *g cm*$^{-3}$	c_s *mol dm*$^{-3}$	*ln* c_s	$1/\varepsilon_x$	*Solid phase composition*
0.0	65.0	1.925	8.34	2.12	0.0127	$NaI*2H_2O$
0.10	57.5	1.660	6.37	1.85	0.0168	$NaI*2H_2O$
0.20	51.7	1.469	5.07	1.62	0.0216	$NaI*2H_2O$
0.30	45.3	1.350	4.08	1.41	0.0259	$NaI*2H_2O$
0.40	39.2	1.239	3.24	1.18	0.0321	$NaI*2H_2O$
0.50	34.5	1.162	2.68	0.984	0.0356**	$NaI*2H_2O$
0.55	32.1	1.125	2.41			$NaI*2H_2O$
0.60	30.7	1.104	2.26	0.817	0.0400	$NaI*2H_2O$
0.70	28.0	1.058	1.97	0.680	0.0427**	$NaI*2H_2O$
0.80	27.3	1.028	1.88	0.629	0.0455*	$NaI*H_2O$
0.90	26.0	0.998**	1.73**	0.548**	0.0472*	NaI
0.95	24.0	0.987	1.58	0.457	0.0483*	NaI
1.00	22.0				0.0492*	NaI

* Data from Ref. (20).
** Interpolated data.

there was only pure NaI in the sample and it decomposed at ca. 630°C. The products of decomposition were calculated on the basis of TG curves weight losses.

RESULTS AND DISCUSSION

The solubilities of NaI and KI in water *n*-propyl alcohol mixtures and the solid phase composition at 25°C are collected in Tables 1 and 2, respectively. The dependencies of solubility on mixed solvent composition for both systems are shown in Figure 1.

Table 2 Solubility and solid phase composition of KI in water-*n*-propyl alcohol mixtures at 25°C. Electric permittivity data from Ref. (19).

x_a	*S* *g/100 g solvent*	ρ *g cm*$^{-3}$	c_s *mol dm*$^{-3}$	*ln* c_s	$1/\varepsilon_x$	*Solid phase composition*
0.0	59.9	1.722	6.21	1.83	0.0127	KI
0.10	49.4	1.466	4.37	1.47	0.0168	KI
0.20	40.7	1.295	3.17	1.15	0.0216	KI
0.30	32.6	1.162	2.28	0.830	0.0259**	KI
0.40	25.3	1.061	1.62	0.480	0.0321	KI
0.50	19.0	0.989	1.13	1.126	0.0356**	KI
0.60	13.1	0.928	0.733	−0.311	0.0400	KI
0.70	7.83	0.877	0.414	−0.882	0.0427**	KI
0.80	3.67	0.839	0.185	−1.69	0.0455*	KI
0.90	1.38	0.815	0.068	−2.69	0.0472*	KI
1.00	0.456	0.801	0.022	−3.82	0.0492*	KI

* Data from Ref. (20).
** Interpolated data.

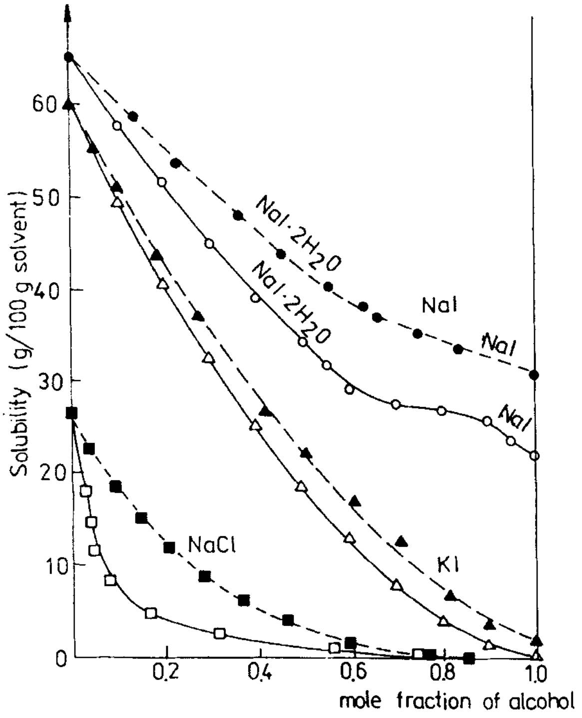

Figure 1 Solubilities for NaI, KI and NaCl in the mixtures of water with ethyl and *n*-propyl alcohols at 25°C; data for NaI and KI in water-ethyl alcohol from Ref. (9); data for NaCl in water-ethyl and *n*-propyl alcohol from Ref. (10).

The slopes of both curves are very similar in the water-rich region up to 70 mol% *n*-propyl alcohol. In the range of compositions of 70–85 mol% alcohol the solubility of NaI changes very slightly and have an inflection point about 80 mol%. Then, above ca. 85 mol% alcohol the changes of NaI solubility are significant. The curves for NaI can be divided into two sections. The first one i.e. water-rich region and up to $x_a < 0.8$ and the second in the alcohol rich region for $x_a > 0.8$. It was found that the changes on the solubility curves reflected the changes in the compositions of solid NaI existing in equilibrium with saturated salt solutions (see Table 1). In the composition range $0 < x_a < 0.8$ NaI is solvated by two molecules of water, then in the alcohol-rich region pure NaI was found in solid phase. So, it can be concluded that NaI is preferentially hydrated in almost the whole range of water-*n*-propyl alcohol mixture.

In the case of KI the solubility changes were monotonic with alcohol content in the whole range of the mixed solvent composition and in the solid phase only pure KI was found. So, it points out that KI is not solvated in the solid phase.

In Figure 1, I compared the above presented data and available in literature data on NaI, KI and NaCl solubilities in the mixtures of water with ethanol.[9,10] The solubilities for all salts, except for NaI, in water-alcohol systems have a monotonic course with increase of alcohol content in the mixtures. These observed differences are connected with the changes of composition in the solid phase. As it is known,[9] the saturated solutions of NaI in water-ethyl alcohol system exist in equilibrium with $NaI*2H_2O$ in water-rich region up to ca. 60 mol% alcohol and above 60 mol% alcohol with anhydrous NaI contrary to KI for which the solid phase was found to be unhydrous KI in the whole range of the mixed solvent composition. So, it confirmed my earlier conclusion that the changes of the plot of the solubility curves are closely connected with the changes of the solid phase composition.

The dependencies of the logarithm of solubility (in moles of salt per dm^3 of solution) for NaI and KI on the reciprocal of the electric permittivities of the mixtures of water with ethyl and *n*-propyl alcohol are shown in Figure 2. Unfortunately, a comparison with NaCl is impossible because of the lack of density data of saturated solutions.

For all systems, as it can be expected, the functions $\ln c_s$ vs. $1/\varepsilon_x$ are divided into two straight sections[9] with different slopes in water- and alcohol-rich regions, respectively. But there are evident differences in behavior of NaI and KI. In the case of KI, the slopes in the alcohol rich-region are higher than in the water-rich region for both alcohols. In pure alcohols the solubilities of KI are low i.e.

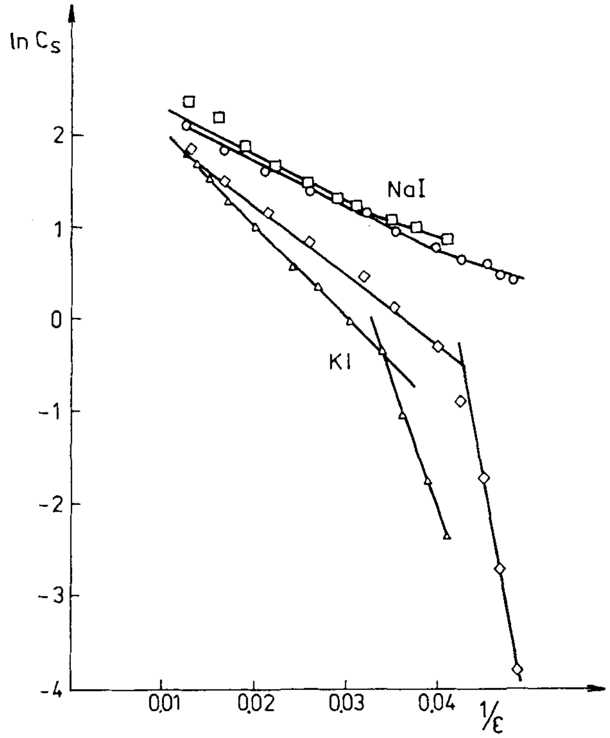

Figure 2 Dependence of the logarithm of the solubility of NaI and KI on the reciprocal of the electric permittivity of water-ethyl and *n*-propyl alcohol mixtures at 25°C; △, □ = data for water-ethyl alcohol from Ref. (9), ○, ◇ = our data.

0.096 mol dm^{-3} in ethyl alcohol and 0.022 mol dm^{-3} in *n*-propyl alcohol, thus the saturated solutions are dilute and the Born's assumption that their electric permittivities are close to their values for the solvent is fulfilled. With the increase of the salt solubility the electric permittivity of the solvent becomes more and more different from the real electric permittivity of the saturated solution, the Born's assumption becomes unjustified and the values of electric permittivity of the solvent should be replaced by those for saturated solution. According to Delesalle *et al.*[9] the extrapolation of the dependencies $\ln c_s = f(1/\varepsilon_x)$ observed in alcohol-rich region to the value of $\ln c_s$ corresponding to pure water should give the value of electric permittivity for saturated solution of KI in water. It is not true because the values of electric permittivity obtained by extrapolation of the straight lines in both alcohols are different. So, the explanation of the existence of two straight sections with different slopes is not simple.

In the case of NaI the straight lines corresponding to different alcohols are very close to each other and their slopes in the water-rich regions are higher than in the mixtures rich in alcohol. This observation is very difficult to explain. The intersection point for both systems is observed at ca. 70 mol% alcohol and corresponds to the change of solid phase composition for both systems.[9] Moreover, the fact that the lines for both systems are very close points out that the decrease of electric permittivity caused by the change of alcohol is not significant in the case of such a well soluble electrolyte like NaI.

My investigations confirm the expected deviation from the Born's equation for sodium and potassium iodides in water-*n*-propyl alcohol system.

Besides, I have observed disagreement of my solubility data for NaI in water with the Delesalle *et al.* value.[9] The values of the solubility in g of salt per 100 g of solutions are the same i.e. 65 g/100 g solution but in moles of salt per dm^3 of solution are different (my value -8.34 and the Delesalle *et al.* -10.91). The error is connected with the determination of density for saturated solution (1.92 g cm^{-3}, my value and 2.5 g cm^{-3}, the Delesalle *et al.* one[9]).

The solubility of several electrolytes in homogeneous mixtures of water-organic solvent was found to obey the equation[21]:

$$S = S_w \exp(-\lambda x) \tag{2}$$

where S_w and S are the solubilities of salt (in moles dm^{-3}) in water and in the mixture, respectively, and x is the molar fraction (or volume fraction) of the organic solvent. The constant, λ, is named the organic solvent precipitating constant for an electrolyte and has the thermodynamic explanation[21]:

$$\lambda = \frac{1}{RT}(\mu^0 - \mu_w^0) \tag{3}$$

where μ^0 and μ_w^0 are standard chemical potentials of electrolyte in the organic solvent and water, respectively. The difference between the standard chemical potentials of the electrolyte in two solvents is the free energy of transfer of electrolyte from one solvent to another.

Rearranging Eq. (3) to the form:

$$\ln \gamma = \ln \frac{S}{S_w} = -\lambda x \tag{4}$$

we can obtain the coefficient λ.

The dependencies of the logarithm of the ratio of solubility in the mixed solvent to the solubility in water, γ, on molar fraction of alcohol, x, are presented in Figure 3 for NaI and KI in water-*n*-propyl alcohol mixtures as well as for both these electrolytes in water-ethyl alcohol systems. As it is seen the straight lines observed for all investigated system in alcohol-rich region break down in the middle range of mixed solvent compositions. So, in all cases the relationship: $\ln \gamma = f(x_a)$ is divided into two straight sections with different slopes. In the case of KI the slopes are significantly different and larger in the alcohol-rich region. The precipitating con-

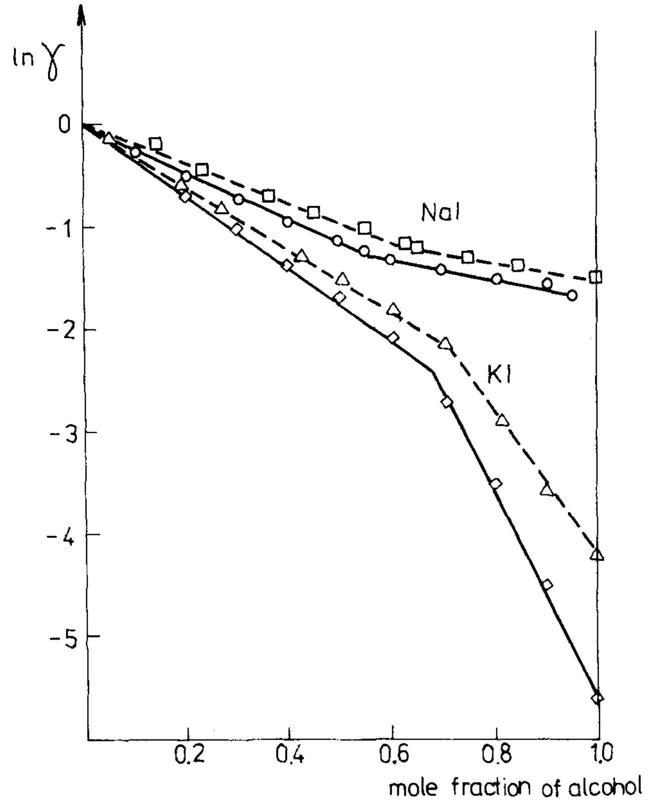

Figure 3 Dependence of the ratio of solubility in water-alcohol mixtures to the solubility in water, γ, as a function of molar fraction of alcohol for KI and NaI in the mixtures of water with ethyl and *n*-propyl alcohol; (——) water-ethyl alcohol and (——) water-*n*-propyl alcohol systems.

stants, λ, are 5.6 and 10 for ethyl and *n*-propyl alcohol, respectively. The larger value of λ for *n*-propyl alcohol agrees with its lower electric permittivity and indicate that *n*-propyl alcohol is a better precipitator than ethanol.

The behavior of NaI is quite different than KI. In the alcohol-rich region the λ constants are very close to each other (0.78 and 1 for ethyl and *n*-propyl alcohol, respectively). So the decrease of the electric permittivity of the solvent does not play such an important role for NaI as for KI and alcohols are not very good precipitators for NaI. Moreover, the slopes of the straight lines in the water-rich region are higher than in alcohol-rich region and the precipitation of NaI by *n*-propyl alcohol is larger in water-rich region than in alcohol region.

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References

1. S. Taniewska-Osińska and P. Chądzyński, *Acta Univ. Lodz.* **II**(6), 37 (1976).
2. S. Taniewska-Osińska and A. Kacperska, *Polish J. Chem.*, **53**, 1351, 1673 (1979).
3. A. Kacperska, S. Taniewska-Osińska, A. Bald and A. Szejgis, *J. Chem. Soc., Faraday Trans. 1*, **85**, 4147 (1989); **86**, 2225 (1990).
4. H. Piekarski, *Can. J. Chem.*, **61**, 2202 (1983).
5. S. Taniewska-Osińska and H. Piekarski, *J. Solution Chem.*, **7**, 891 (1978).
6. B. Nowicka, A. Kacperska, J. Barczyńska, A. Bald and S. Taniewska-Osińska, *J. Chem. Soc., Faraday Trans. 1*, **84**, 3877 (1989).
7. H. Piekarski, A. Piekarska and S. Taniewska-Osińska, *Can. J. Chem.*, **62**, 856 (1984).
8. A. Kacperska and S. Taniewska-Osińska, *Acta Univ. Lodz. Folia Chimica*, **8**, 61 (1988).
9. G. Delesalle and J. Heubel, *Bull. Soc. Chim. France*, **1972**, 2626.
10. A. Watanabe, Reports of the Government Industrial Research Institute, Nagoya, vol. XV, No. 10, p. 335 (1966).
11. H. H. Emons and F. Winkler, *Z. Chem.*, **11**, 293 (1971).
12. G. Akerlof and H. E. Turck, *J. Amer. Chem. Soc.*, **57**, 1746 (1935).
13. M. Born, *Z. Physik.*, **1**, 45 (1920).
14. J. N. Bronsted, A Delbanco and K. Volqvartz, *Z. Phys. Chem.*, **A162**, 128 (1932).
15. T. W. Davies, J. E. Ricci and C. G. Santer, *J. Amer. Chem. Soc.*, **61**, 3274 (1939).
16. P. B. Davies and C. B. Monc, *J. Chem. Soc.*, **1951**, 2718.
17. H. Miyamoto, H. Shimura and K. Sasaki, *J. Solution Chem.*, **14**, 485 (1985).
18. A. Weissberger, E. S. Proskauer, J. A. Riddick and E. E. Toops Jr, *Organic Solvents* (Interscience, New York, 1955).
19. A. R. Martin and A. C. Brown, *Trans. Faraday Soc.*, **34**, 742 (1938).
20. A. D'Aprano, D. I. Donato and E. Caponetti, *J. Solution Chem.*, **8**, 135 (1979).
21. Z. B. Alfassi and J. Weiss, *Ber. Bunsenges. Phys. Chem.*, **87**, 890 (1983).