An Effect of Urea on Association and Solvation of Ions in Aqueous Solutions of Alcohols

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The conductivity of NaI in ternary solvents consisting of water, alcohol and urea has been determined at 25 °C in its dependence on the alcohol concentration. Viscosities and static dielectric constants of these ternary solvents have also been measured. It has been found that in all studied solvents the limiting equivalent conductivities λ^0 are smaller than those in binary solvents despite of the lower viscosities. The observed effect indicates that urea prevents the dehydration of ions and also hinders the ionic association. These phenomena have led to the conclusion that urea molecules are able to solvate alcohol clusters similar to what has been observed for micelles.

Aqueous solutions of higher alcohols serve as model systems to investigate hydrophobic phenomena. Our previous studies of electrolyte solutions in mixtures of water with propanols and *tert*-butanol [1, 2] have shown a correlation between a self-association of alcohols and dehydration of ions. For the same solvent composition, for which the highest concentration of the alcohol clusters has been found, the hydration shells of ions are either noticeably reduced, as for Na^+, or even completely eliminated, as for Et_4N^+ and I^-. This indicates that the hydration of alcohol clusters competes successfully with the ion-water interactions. It has been also noticed, that the appearance of the alcohol aggregates causes a rapid increase of the ionic association. That effect is much greater than it might be due to the decrease of the static dielectric constant. Such a behaviour has been explained as the result of the "lack" of water in the surrounding of ions.

The purpose of the present work was to investigate the effect of urea on the association and solvation of ions. The anomalous behaviour of urea in aqueous solutions is well known. It denatures proteins and nucleic acids [3–5], enhances the solubility of hydrocarbons [6] and inhibits a micellar aggregation [7–9]. The nature of these effects is not yet established. One of the hypotheses is that urea molecules may replace some of the water ones in hydration shells of nonpolar groups [10]. In such a case one may expect that the addition of urea may prevent the ionic association and/or the ionic dehydration. In the present work we determined the conductivity of sodium iodide in ternary solvents, containing water, alcohol and urea.

Experimental

n-Propanol (spectroscopic grade, Merck), *iso*-propanol (spectroscopic grade, Merck), *tert*-butanol (A.C.S. reagent, Aldrich), urea (pro analysi, Merck) and NaI (suprapur, Merck) were used as received. Water was deionized and degassed. Its specific conductivity does not exceed $0.5 \, \mu S \, cm^{-1}$.

Ternary solvents and solutions of NaI were prepared by weight. In all experiments the urea concentration was the same and equal to 2.0 mole per 100 mole of the binary mixture, whereas the concentrations of alcohols in aqueous solutions were varied, but they did not exceed 25 mol%. For all ternary solvents the viscosities were determined using an Ubbelhode type viscosimeter AVS 310 (Schott-Geräte), whereas their static dielectric constants were measured by means the dielectrometer OH 302 (Radelkis).

The molarities of NaI covered the range between 10^{-3} and $5 \cdot 10^{-2}$. The conductivities of the NaI solutions were measured using a CG 855 conductivity meter (Schott-Geräte) with the cell calibrated by the method of Lind et al. [11]. The conductivities of ternary solvents were also measured, and they were subtracted from those of the NaI solutions All experiments were carried out at $25.0 \pm 0.05 \, °C$.

Alcohol	n-propanol		iso-propanol		tert-butanol	
mol%	$\eta \cdot 10^3$ N·s·m^{-2}	ε	$\eta \cdot 10^3$ N·s·m^{-2}	ε	$\eta \cdot 10^3$ N·s·m^{-2}	ε
0.0	0.925	84.32	0.925	84.32	0.925	84.32
5.0	1.570	73.47	1.615	74.81	1.963	70.22
10.0	2.049	63.00	2.284	65.00	2.901	57.85
15.0	2.386	54.93	2.664	56.30	3.635	49.44
20.0	2.559	47.05	2.858	49.65	–	–
25.0	2.650	42.10	2.934	44.10	–	–

Table 1. Viscosities η and static dielectric constants ε of ternary systems: water-alcohol-urea at 25.0 °C. The urea concentration was 2.0 mol/100 mol of mixture.

Results and Discussion

The viscosity η and the static dielectric constant ε of the ternary solvents are summarised in Table 1. An addition of urea to water enhances the static dielectric constant, and the ε value reported here is in very good agreement with that one published previously [12]. Also the viscosity of the aqueous solution of urea exceeds that of pure water, and the value given in Table 1 fits perfectly the dependence of η on the urea concentration reported before [13].

The static dielectric constants of the ternary solvents consisting of n-propanol, water and urea are, within the experimental error, the same as those of the binary solvents, e.g. mixtures of water with n-propanol [14]. Also the viscosities of these ternary solvents are the same as those of the binary systems [15].

The effect of urea on the properties of aqueous solutions of iso-propanol and of tert-butanol is, however, different. The ε-values of these ternary solvents exceed those of the binary mixtures [16, 17], whereas the viscosities are reduced as compared with those of aqueous solutions of alcohols. A similar effect of urea has been reported previously for mixtures of water with tert-butanol [18].

Variations of the equivalent conductivity λ with the molarity of NaI were analysed using the Fuoss and Hsia equation [19], for the partially dissociated electrolyte, with the Fernandez-Prini coefficients [20]. The details of the fitting procedure have been described previously [21]. Three adjustable parameters, e.g. the limiting equivalent conductivity λ^0, the most probable distance R between ions forming an ionic pair, and the degree of the dissociation α have been chosen for the best fit of the experimental data, and the association constant K_A was calculated from the equation

$$K_A = \frac{(1-\alpha) f_p}{\alpha^2 f_i^2 c}, \qquad (1)$$

assuming that the activity coefficient of the ionic pair f_p equals 1, whereas that of free ions f_i was calculated from

$$f_i = \exp\left[-\frac{A(\alpha c)^{0.5}}{1 + BR(\alpha c)^{0.5}}\right] \qquad (2)$$

with $A = 2.791 \cdot 10^3/(\varepsilon T)^{1.5}$, $B = 50.29/(\varepsilon T)^{0.5}$ and the distance R between ions given in Å.

The computed values of R, λ^0, and K_A are summarised in Table 2. For comparison the Bjerrum distances, q, are also presented.

In all studied solvents λ^0 decreases with increasing alcohol concentration, as might be expected because of the viscosity increase. One should however noticed that the λ^0 values determined in ternary solvents are smaller than those in the corresponding binary mixtures despite to the opposite changes of the solvent viscosities, which are either the same, as for systems containing n-propanol, or even smaller, as for mixtures with iso-propanol and tert-butanol. This unexpected influence of urea on λ^0 can be seen from Fig. 1, where variations of the Walden products with the alcohol concentration are shown. The dependencies calculated for the ternary solvents are compared with those reported before for the binary mixtures [1, 22]. Similar as it has been observed before, these functions exhibit maxima. In ternary solvents the observed excess of the Walden products is, however, much smaller than it was in aqueous solutions of alcohols. This indicates that if the solvent contains urea the size of the solvated ions increases. Such an enlargement may be observed for different reasons: (i) if urea molecules, whose diameter is larger than that of water, are able to enter the solvation shells of ions or (ii) if the addition of urea prevents the dehydration of ions, observed in mixtures of water with alcohols [1, 2, 22]. In our opinion the latter supposition is more likely.

As has been mentioned above, the dehydration of ions occurs probably because there is the lack of water
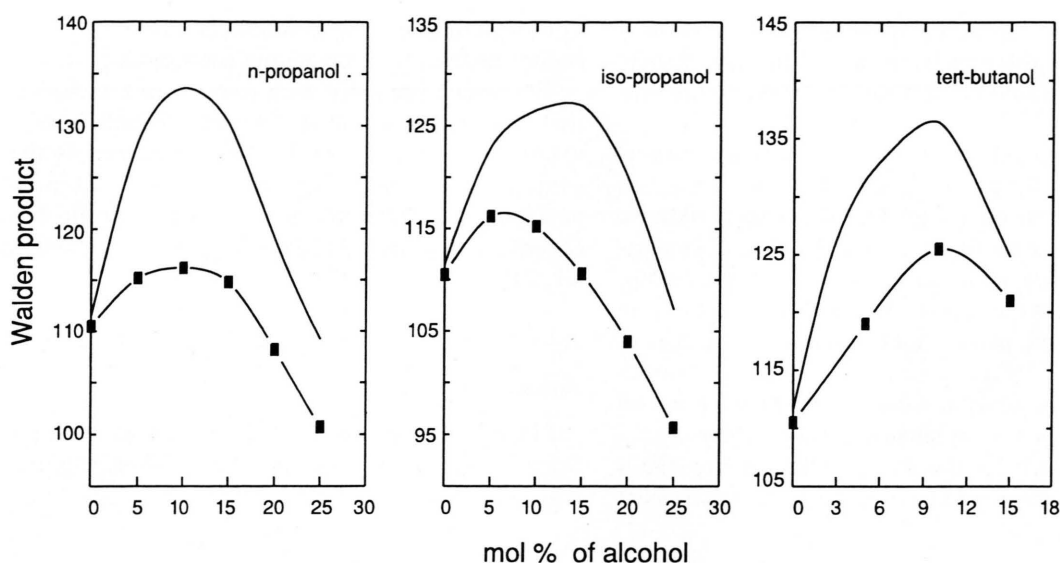
Fig. 1. Walden products of NaI vs. alcohol concentrations in ternary solvents water-alcohol-urea (curves with points) at 25 °C. The urea concentration equals 2.0 mol/100 mol of binary solvent. Upper curves describe the Walden products of NaI reported for binary mixtures of water with n-propanol and iso-propanol [1] and with tert-butanol [22].

Table 2. Limiting equivalent conductivities λ^0 of NaI and association constants K_A in ternary solvents: water-alcohol-urea, obtained for the most probable distance R between ions, at 25.0 °C. Urea concentration: 2 mol/100 mol of mixture.

Alcohol	n-propanol				iso-propanol				tert-butanol			
	R	q^*	λ^0	K_A	R	q^*	λ^0	K_A	R	q^*	λ^0	K_A
mol%	Å	Å	$\dfrac{\text{S cm}^2}{\text{mol}}$		Å	Å	$\dfrac{\text{S cm}^2}{\text{mol}}$		Å	Å	$\dfrac{\text{S cm}^2}{\text{mol}}$	
0.00	3.5	3.4	119.4	<10	3.5	3.4	119.4	<10	3.5	3.4	119.4	<10
5.0	3.5	3.8	73.4	<10	3.5	3.7	71.9	<10	3.5	4.0	60.7	<10
10.0	3.5	4.4	56.7	<10	3.5	4.4	50.5	<10	3.5	4.9	43.3	<10
15.0	3.5	5.1	48.1	<10	3.5	5.0	41.5	<10	3.5	5.6	33.2	<10
20.0	3.5	5.8	42.3	<10	3.5	5.6	36.4	<10	–	–	–	–
25.0	3.5	6.4	38.0	<10	3.5	6.4	32.6	<10	–	–	–	–

* Bjerrum distance.

molecules, they being involved in the hydration of alcohol clusters. It is known that urea molecules are able to enter the vicinity of micelles and to replace water molecules in their hydration shells [23, 24]. Thus it seems to be very probable that urea molecules can also solvate alcohol clusters. In such a case, in the presence of urea the deficit of water would be smaller than in aqueous solutions of alcohols.

As seen from Table 2, the addition of urea prevents not only the dehydration of ions, but also hinders significantly the formation of ionic pairs. In all studied ternary solvents the association of ions is negligible

($K_A < 10$ [25]), whereas for binary solvents it was not [1]. Such a behaviour cannot result from the very slight increase of the static dielectric constant. One should notice that in binary solvents small amounts either of tert-butanol or of n-propanol have caused the rapid increase of K_A. It was explained by assuming that in a binary, inhomogenous solvent which consists of two microphases, e.g. hydrated alcohol clusters and water with alcohol monomers, ions occupy mostly the water microphase. Thus their real concentration is higher than the one calculated for the homogenous distribution. The decrease of K_A observed in the pres-

ence of urea confirms the supposition that urea molecules are able to solvate alcohol clusters, thereby increasing the amount of water molecules to dissolve ions.

As seen from Table 2, in all studied ternary solvents the distances R between ions in the ionic pairs, are smaller than those calculated for the binary mixtures. The R values are independent of the alcohol concentration and they are equal to the sum of the crystallographic radii of the ions. This indicates that formation of contact ionic pairs is more probable than that of ions separated by the solvent. One should also notice that, except the aqueous solution of urea, the R values in ternary solvents are smaller than the Bjerrum distances. Such a behaviour agrees with our hypothesis that ions are dissolved mostly in the water microphase

thus the static dielectric constant of the ternary system cannot be used to calculate the Bjerrum distances.

The results presented here lead to the conclusion that in aqueous solutions of higher alcohols urea is able to prevent both the dehydration as well as the association of ions. They indicate also that urea molecules may enter the solvation shells of alcohol clusters, similar as it has been observed for micelles [23, 24].

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