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STUDY ON SOLVATION OF ALUMINIUM, MAGNESIUM AND SODIUM IONS IN WATER–UREA MIXTURES WITH USE OF ULTRASONIC AND DENSITOMETRIC METHODS

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The measurements of ultrasonic wave velocity and density of ternary mixtures: electrolyte-urea-water and quaternary mixtures electrolyte-urea-water-ethanol with $AlCl_3$, $Al(NO_3)_3$, $MgCl_2$ and NaCl as electrolytes have been carried out in the temperature range of 15 to 35°C. Analysis of the results indicates that urea molecules participate in the solvation structures of the Al^{3+} ions but not those of Mg^{2+} and Na^+ ions. A model for the structure of the mixed solvation sphere around the Al^{3+} ion has been suggested.

1. Introduction

Crystallization performed in electrolyte-urea-water systems can, in certain conditions, lead to compounds of $A_xU_y(H_2O)_z$ type in the solid phase (where A is an electrolyte and U is urea). In these compounds urea molecules replace partly or completely crystallization water of salts [1]. This can be the evidence for a high chemical affinity of urea to many electrolytes. As was shown in verious studies [2–5], aqueous solut ions of aluminium, magnesium and sodium salts have ordered structure both in the immediate vicinity of ions and in the bulk of the solution. Therefore the course of dissolving of urea molecules in solutions of these salts will depend, above all, on mutual correlations of chemical affinities between the components of the system.

In dilute aqueous solutions urea molecules can get built into the existing quasi–crystalline structure of water by replacing two molecules of water without disturbing this structure [6]. Thus the degree of ordering in the solution increases due to urea-water interaction by hydrogen bonds.

In the model of hydration proposed by one of the co–authors [7] this kind of hydration interactions is characterized by negative hydration numbers.

In concentrated aqueous solutions the associated molecules of urea, of U_2 type, can appear [8].

The interactions of 3−1 electrolytes (Al^{3+}) and 2−1 electrolytes (Mg^{2+}) with urea were studies by means of other techniques such as spectroscopic [9−11], isopiestic [12] and conductometric [13]. On the basis of the above studies the formation of various complexes of aluminium and magnesium salts with urea was put forward. Thus far, however, sufficient experimental evidence for their formation has not been reported.

In this paper, results of acoustic and densitometric studies perfrormed in the systems: electrolyte-urea-water and electrolyte-urea-water-ethanol are presented. The studies were undertaken as an attempt to determine the mechanism of formation of solvation complexes of aluminium, magnesium and sodium chlorides and nitrates with urea in aqueous solutions.

These studies, apart from their scientific significance, are also of practical importance, such complexes find application in hydrometallurgy and in production of microelement liquid fertilizers. Determination of the mechanism of formation of these complexes and of their composition can be helpful in preparing technological processes.

2. Experimental

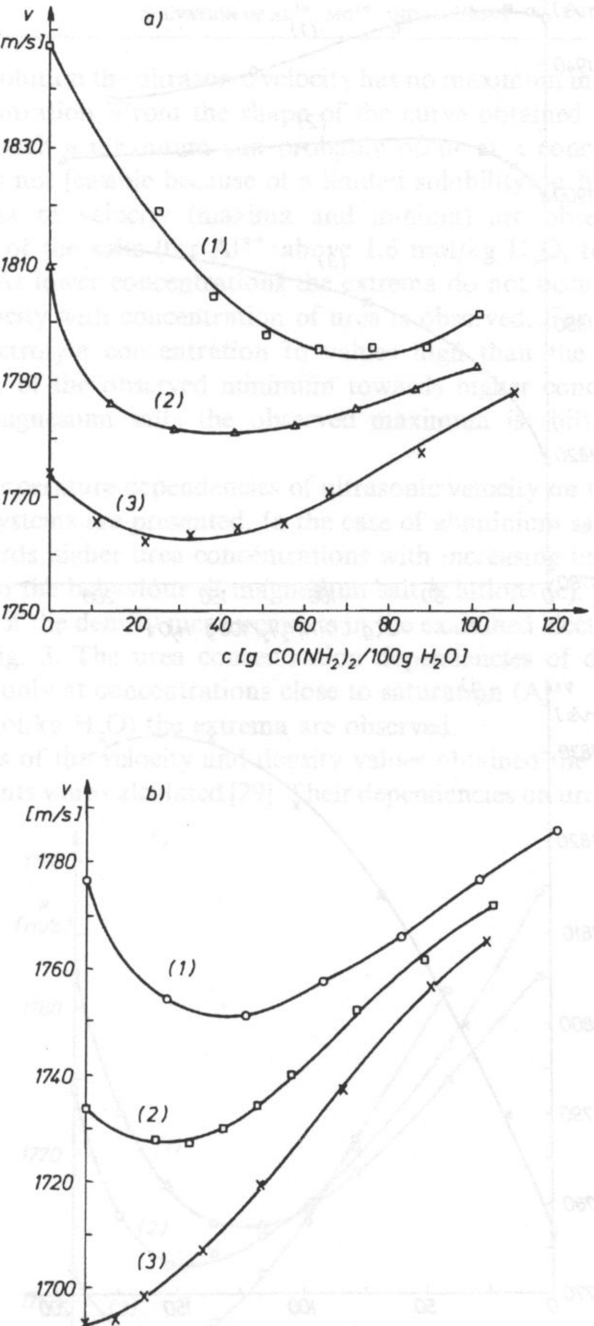
The measurements of velocity of ultrasonic waves propagation and of density in ternary and quartenary mixtures of a broad range of electrolyte and urea concentrations of temperature between 15 and 35°C were performed. The ultrasonic velocity was measured by the „sing around" method and also by the time-interval-averaging method at the frequency of 10 MHz. The accuracy of the velocity measurements was 0.02/s in both methods. The density of the solutions was measured by the vibrating tube method to an accuracy of 0.1 kg/m³. In order to ensure such a high accuracy of velocity and density measurements, the samples were thermostated to an accuracy of 0.01°C in a two-stage water thermostat equipped with a electronic temperature regulator UNIPAN 665. Solutions were prepared in a triple-distilled water in such a way that urea in various amounts was added to an initial salt solution of a know concentration. In the case of quartenary mixtures with ethanol, the concentration of alcohol was changed during the measurement by adding it to the solution in portions (0.2 cm³) with the aid of a metering micropump UNIPAN 335 A.

Al, the substances used in this study were analytically pure POCh, Gliwice, Poland. The obtained results are presented in Figs. 1−6 and listed in Table 1.

3. Discussion

The results of the ultrasonic velocity measurements in electrolyte-water-urea mixtures containing aluminium chloride (a), magnesium chloride (c), sodium chloride (d) and aluminium nitrate (b) are presented in Fig. 1.

As can be seen in Fig. 1, the ultrasonic velocity shows a minimum in the systems containing aluminium salts, and a minimum in the systems containing magnesium


a)
v
[m/s]
1830
1810
1790
1770
1750
(1)
(2)
(3)
0
20
40
60
80
100
120
c [g CO(NH$_2$)$_2$/100g H$_2$O]
b)
v
[m/s]
1780
1760
1740
1720
1700
1680
(1)
(2)
(3)
0
50
100
150
c [g CO(NH$_2$)$_2$/100g H$_2$O]

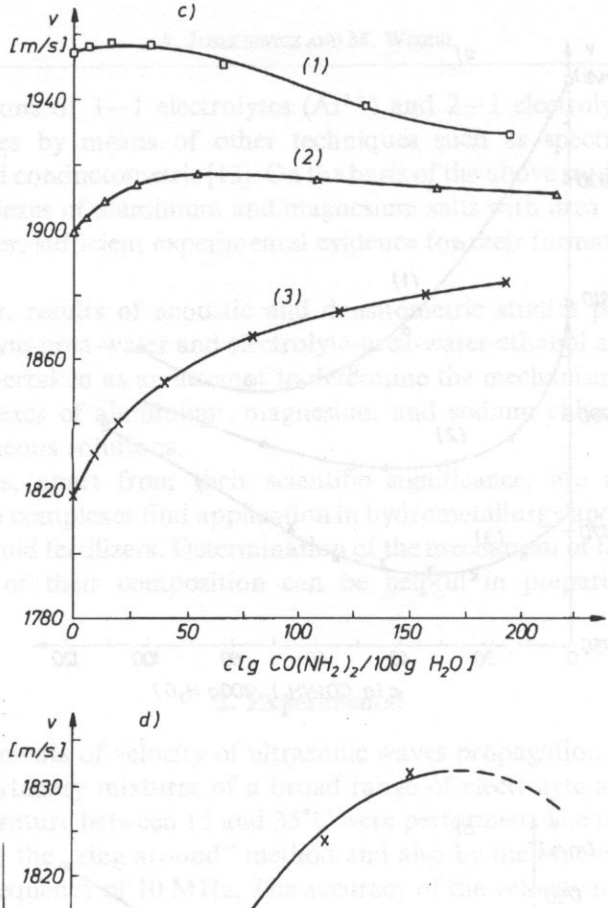


Fig. 1. The dependence of ultrasonic velocity. v [m/s] on the concentration of urea, *c* [g $CO(NH_2)$/100 g H_2O] in aqueous solutions of electrolytes at 25°C.
a) $AlCl_3$ at molal concentrations [mol/kg H_2O] of: (1) 2.41; (2) 2.11; (3) 1.84. b) $Al(NO_3)_3$ at molal concentrations [mol/kg H_2O] of: (1) 2.27; (2) 1.96; (3) 1.66. c) $MgCl_2$ at molal concentrations [mol/kg H_2O] of: (1) 5.43; (2) 4.50; (3) 3.27; d) NaCl at molal concentrations 5.62 [mol/kg H_2O].

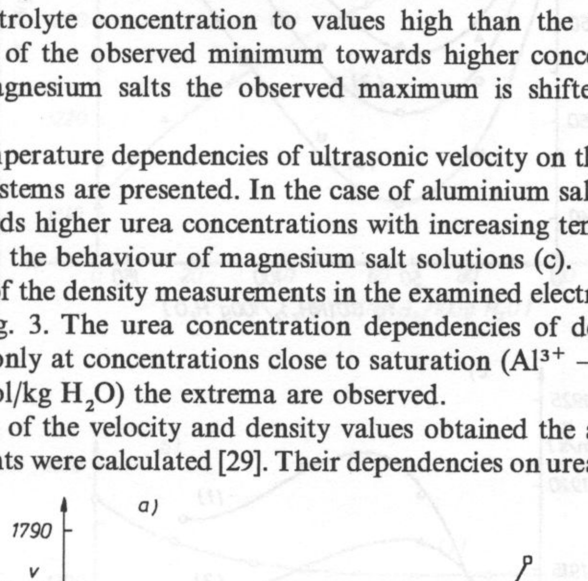
salts. In NaCl solution the ultrasonic velocity has no maximum in the examined range of NaCl concentration. From the shape of the curve obtained it may be deduced, however, that such a maximum can probably occur at a concentration, at which measurement is not feasible because of a limited solubility on NaCl.

The exterma of velocity (maxima and minima) are observed only at high concentrations of the salts (for Al^{3+} above 1.6 mol/kg H_2O, for Mg^{2+} above 3.5 mol/kg H_2O). At lower concentrations the extrema do not occur, and a monotonic increase in velocity with concentration of urea is observed. For aluminium salts an increase in electrolyte concentration to values high than the value given above leads to a shift of the observed minimum towards higher concentrations of urea, whereas for magnesium salts the observed maximum is shifted in the opposite direction.

In Fig. 2 temperature dependencies of ultrasonic velocity on the concentration in the examined systems are presented. In the case of aluminium salts (a) a shift of the minimum towards higher urea concentrations with increasing temperature is observed, contrary to the behaviour of magnesium salt solutions (c).

The results of the density measurements in the examined electrolyte solutions are presented in Fig. 3. The urea concentration dependencies of density are close to montonic, and only at concentrations close to saturation (Al^{3+} — 2.5 mol/kg H_2O; Mg^{2+} — 4.5 mol/kg H_2O) the extrema are observed.

On the basis of the velocity and density values obtained the adiabatic compressibility coefficients were calculated [29]. Their dependencies on urea concentration are



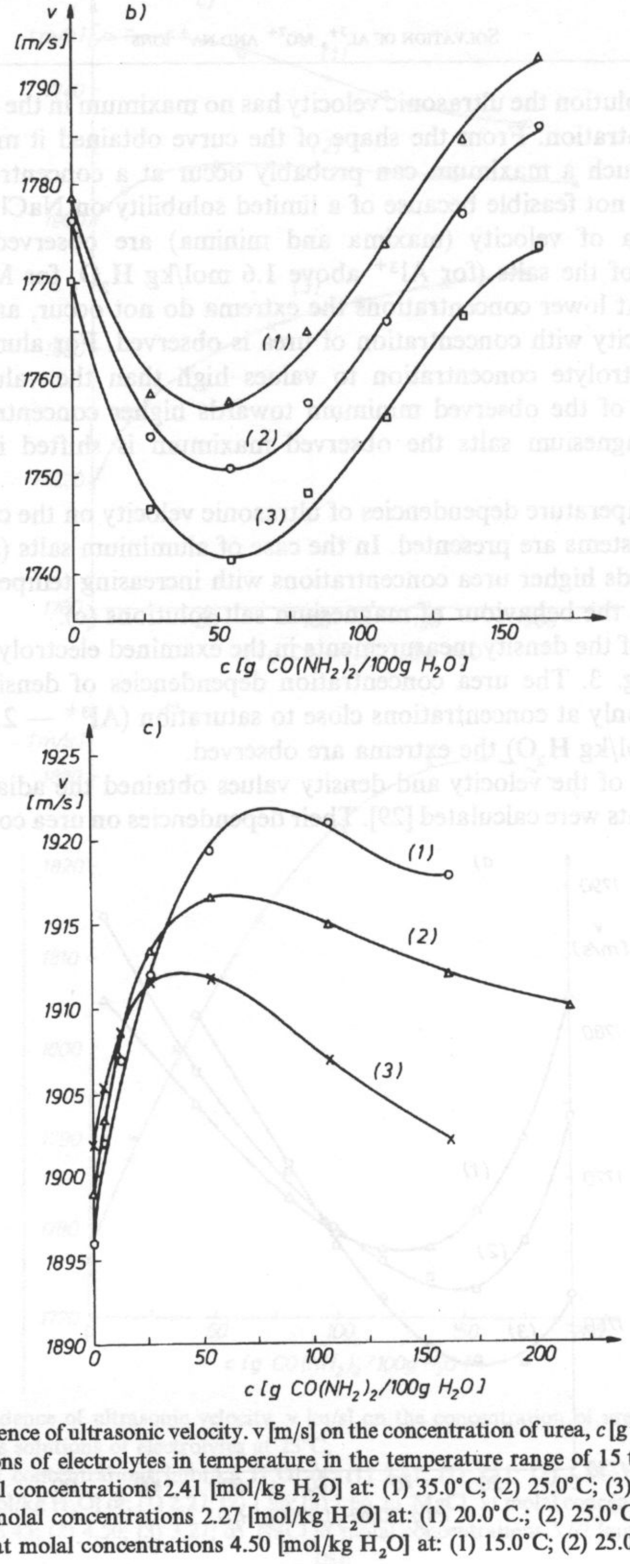
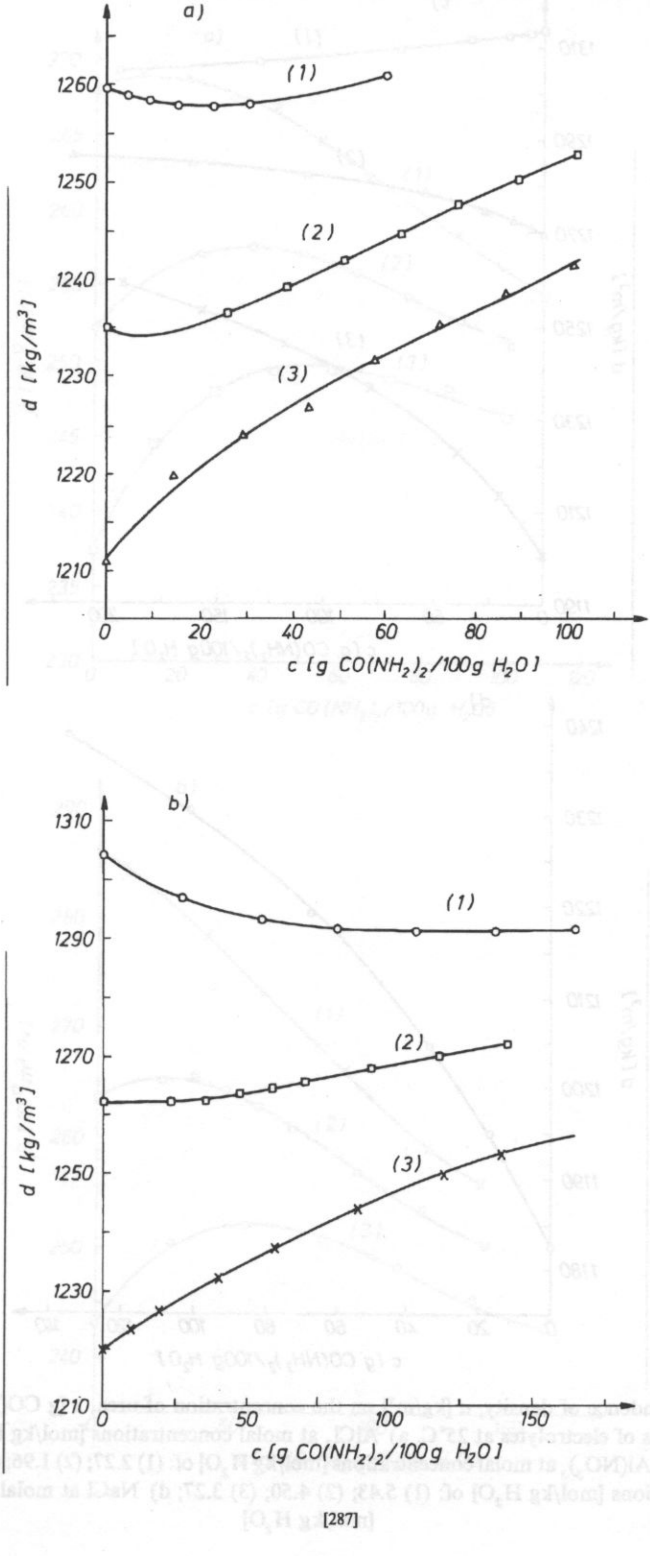


Fig. 2. The dependence of ultrasonic velocity. v [m/s] on the concentration of urea, *c* [g $CO(NH_2)$/100 g H_2O] in aqueous solutions of electrolytes in temperature in the temperature range of 15 to 35°C.

a) $AlCl_3$ at molal concentrations 2.41 [mol/kg H_2O] at: (1) 35.0°C; (2) 25.0°C; (3) 15.0°C.

b) $Al(NO_3)_3$ at molal concentrations 2.27 [mol/kg H_2O] at: (1) 20.0°C.; (2) 25.0°C; (3) 35.0°C.

c) $MgCl_2$ at molal concentrations 4.50 [mol/kg H_2O] at: (1) 15.0°C; (2) 25.0°C; (3) 35.0°C.


a)
d [kg/m³]
1210
1220
1230
1240
1250
1260
(1)
(2)
(3)
0
20
40
60
80
100
c [g CO(NH₂)₂/100g H₂O]
b)
d [kg/m³]
1210
1230
1250
1270
1290
1310
(1)
(2)
(3)
0
50
100
150
c [g CO(NH₂)₂/100g H₂O]

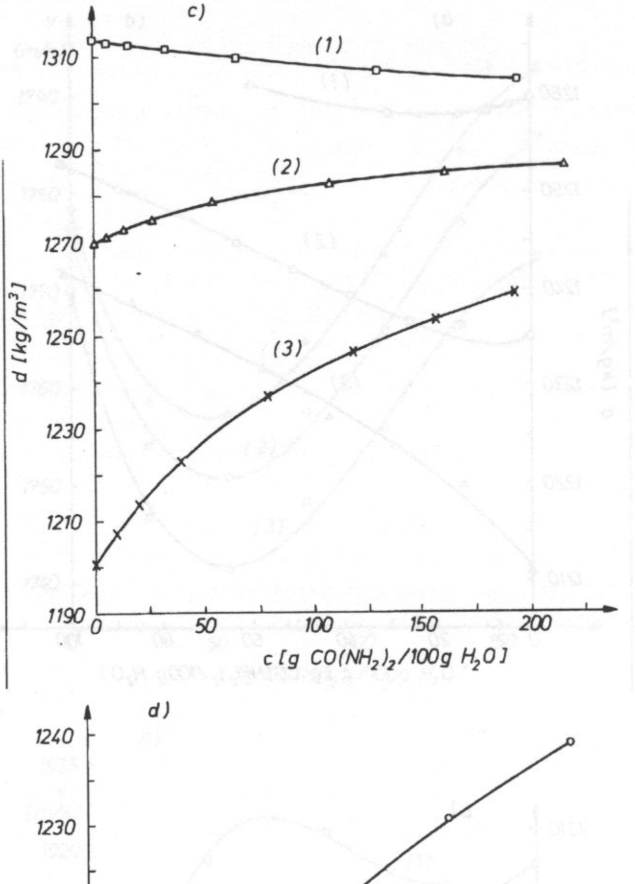
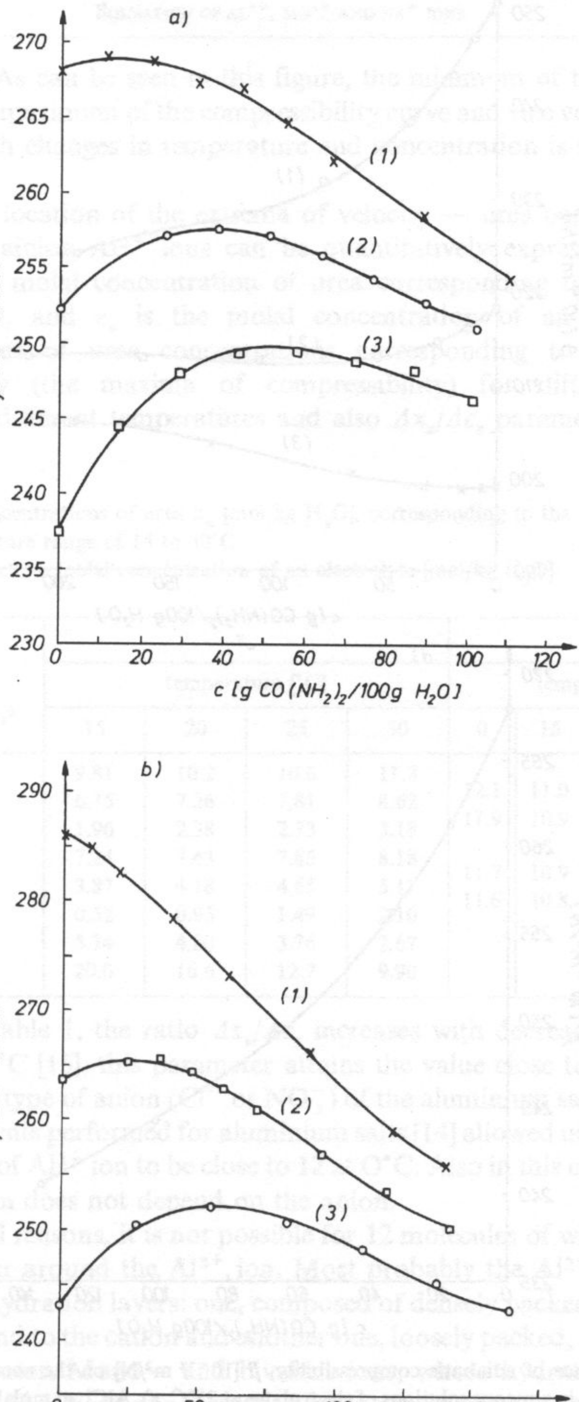


Fig. 3. The dependence of density, *d* [kg/m^3] on the concentration of urea, *c* [g CO(NH$_2$)/100 g H$_2$O] in aqueous solutions of electrolytes at 25°C. a) AlCl$_3$ at molal concentrations [mol/kg H$_2$O] of: (1) 2.69; (2) 2.41; (3) 2.11. b) Al(NO$_3$)$_3$ at molal concentrations [mol/kg H$_2$O] of: (1) 2.27; (2) 1.96; (3) 1.66. c) MgCl$_2$ at molal concentrations [mol/kg H$_2$O] of: (1) 5.43; (2) 4.50; (3) 3.27; d) NaCl at molal concentrations 5.62 [mol/kg H$_2$O]


a)
β [10⁻¹² m²/N]
270
265
260
255
250
245
240
235
230
0
20
40
60
80
100
120
c [g CO(NH₂)₂/100g H₂O]
(1)
(2)
(3)
b)
β [10⁻¹² m²/N]
290
280
270
260
250
240
0
50
100
150
c [g CO(NH₂)₂/100g H₂O]
(1)
(2)
(3)

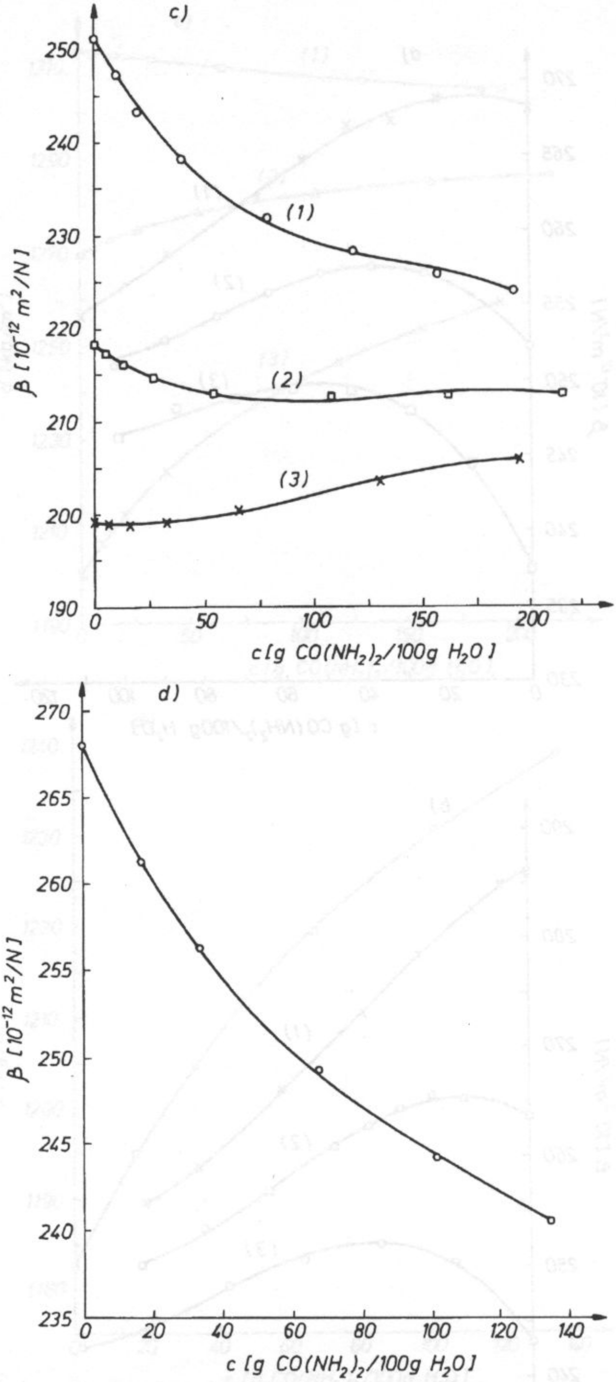


Fig. 4. The dependence of adiabatic compressibility, β [10^{-12} m²/N] on the concentration of urea, c [g $CO(NH_2)$/100 g H_2O] in aqueous solutions of electrolytes at 25°C. a) $AlCl_3$ at molal concentrations [mol/kg H_2O]of: (1) 2.41; (2) 2.11; (3) 1.84. b) $Al(NO_3)_3$ at molal concentrations [mol/kg H_2O] of: (1) 2.27; (2) 1.96; (3) 1.66. c) $MgCl_2$ at molal concentrations [mol/kg H_2O] of: (1) 5.43; (2) 4.50; (3) 3.27; d) NaCl at molal concentrations 5.62 [mol/kg H_2O]

plotted in Fig. 4. As can be seen in this figure, the minimum of the velocity curve corresponds to the maximum of the compressibility curve and vice versa. Also shifting of the extrema with changes in temperature and concentration is similar to that of velocity.

The change in location of the extrema of velocity — urea concentration curve for solutions containing Al^{3+} ions can be quantitatively expressed by the ratio $\Delta x_u/\Delta c_e$, where x_u molal concentration of urea corresponding to the extrema of ultrasonic velocity, and c_e is the molal concentration of an electrolyte. The experimental values of urea concentrations corresponding to the minima of ultrasonic velocity (the maxima of compressibility) for different electrolyte concentrations at different temperatures and also $\Delta x_u/\Delta c_e$ parameters are listed in Table 1.

Table 1. The molal concentrations of urea x_u [mol/kg H_2O], corresponding to the extrema of ultrasonic velocity in the temperature range of 15 to 30°C.
c^e — molal concentration of an electrolyte [mol/kg H_2O].

electr.	C_e mol/dm^3	x_u				$\Delta x_u/\Delta c_e$				
		temperature [°C]				temperature [°C]				
		15	20	25	30	0	15	20	25	30
$AlCl_3$	2.40	9.81	10.2	10.6	11.3	12.1	11.0	10.5	10.1	9.75
$AlCl_3$	2.12	6.75	7.26	7.81	8.62	11.9	10.9	10.4	10.0	9.82
$AlCl_3$	1.75	1.96	2.38	2.73	3.18					
$Al(NO_3)_3$	2.28	7.24	7.43	7.85	8.18	11.7	10.9	10.5	10.3	9.71
$Al(NO_3)_3$	1.97	3.87	4.18	4.65	5.17	11.6	10.8	10.4	10.2	9.89
$Al(NO_3)_3$	1.66	0.52	0.95	1.49	2.10					
$MgCl_2$	4.95	5.74	4.80	3.76	2.67					
$MgCl_2$	4.16	20.0	16.6	12.7	9.90					

As shown in Table 1, the ratio $\Delta x_u/\Delta c_e$ increases with decreasing temperature. Extrapolated to O°C [15], this parameter attains the value close to 6. This value is independent of the type of anion (Cl^- or NO_3^-) of the aluminium salt. The hydration number measurements performed for aluminium salts [14] allowed us to determine the hydration number of Al^{3+} ion to be close to 12 at O°C. Also in this case the hydration number of Al^{3+} ion does not depend on the anion.

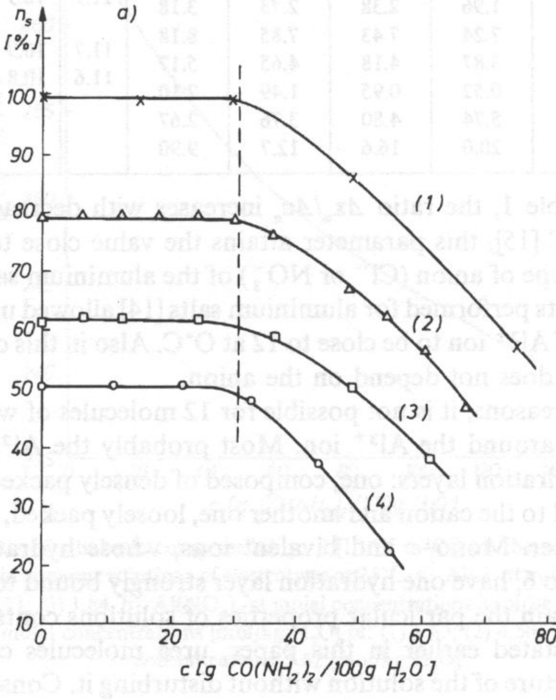
For geometrical reasons, it is not possible for 12 molecules of water to form only one hydration layer around the Al^{3+} ion. Most probably the Al^{3+} ion in aqueous solutions has two hydration layers: one, composed of densely packed six molecules of water strongly bound to the cation and another one, loosely packed, also composed of six molecules of water. Mono— and bivalent ions, whose hydration numbers are lower than or equal to 6, have one hydration layer strongly bound to the ions [15, 16]. The above facts explain the particular properties of solutions containing aluminium salts and urea. As stated earlier in this paper, urea molecules can replace water molecules in the structure of the solution without disturbing it. Consequently they can also get built into these loosely packed outer hydration layer of Al^{3+} ion. Such a phenomenon cannot occur in the case of mono – and bivalent ions.

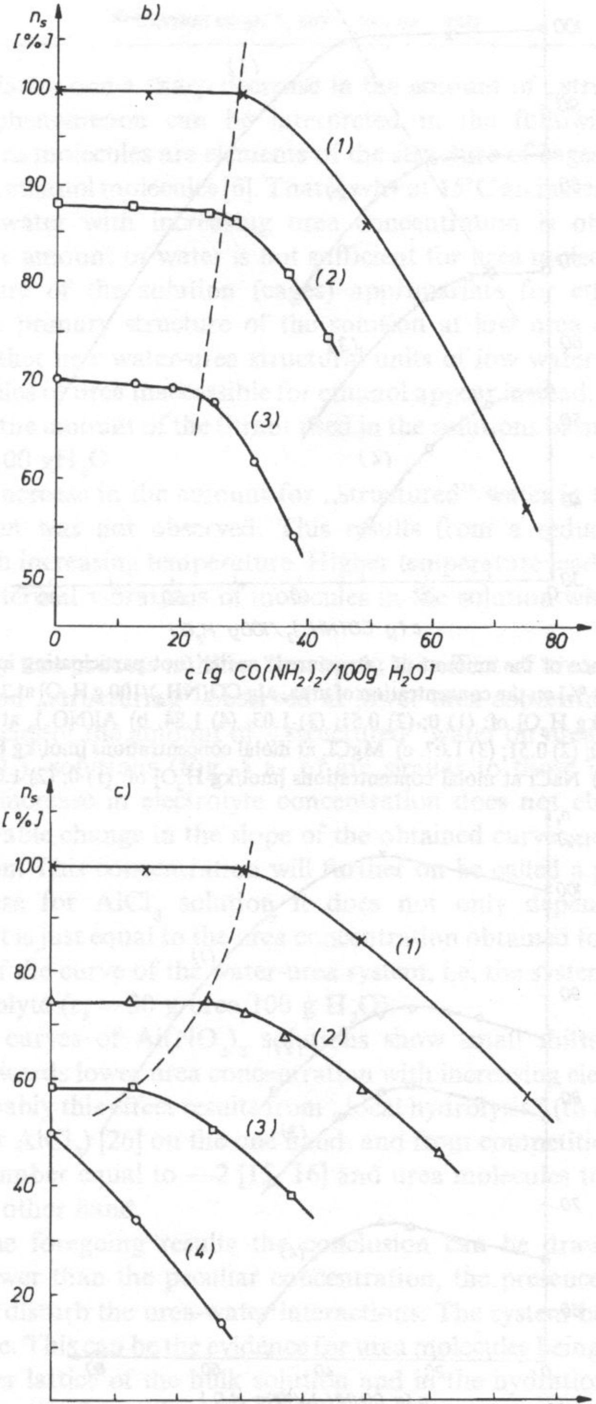
In order to confirm the above conclusion, the measurements of ultrasonic velocity in quartenary electrolyte-urea-water-ethanol systems of different urea end ethanol concentrations were carried out.

Ethanol in such a system plays a role of a titrant enabling to determine the amount of free water (also „structured" to a considerable degree) present in the solution outside the hydration spheres of ions. As reported in previous studies [17 – 25], ethanol molecules enter the cages of water structure. The process of filling these cages with ethanol molecules is accompanied by an increase in ultrasonic velocity, which attains the maximum value when all the cages are filled with ethanol. Therefore the end point of this titration at the concentration of ethanol corresponding to the maximum of ultrasonic velocity.

In this manner the amounts of ethanol corresponding to the ultrasonic velocity maxima were determined for the solutions containing different amounts of urea and electrolyte, and on this basis the equivalent amounts of „structures" water in these solutions (in weight %) were calculated. The results obtained for $AlCl_3$, $Al(NO_3)_3$, $MgCl_2$ and NaCl solutions are presented in Fig. 5 – 6.

The dependencies obtained for aluminium salts (Figs. 5 a, b) consist of two regions: one for urea concentrations lower than 30 g per 100 g H_2O, and another for urea concentrations higher than 30 g per 100 g H_2O. In this former case the amount of „structured" water is either independent of urea concentration (at 25°C) or increases




b)
n_s [%]
100
90
80
70
60
50
(1)
(2)
(3)
0
20
40
60
80
c [g CO(NH$_2$)$_2$/100g H$_2$O]
c)
n_s [%]
100
80
60
40
20
(1)
(2)
(3)
(4)
0
20
40
60
80
c [g CO(NH$_2$)$_2$/100g H$_2$O]

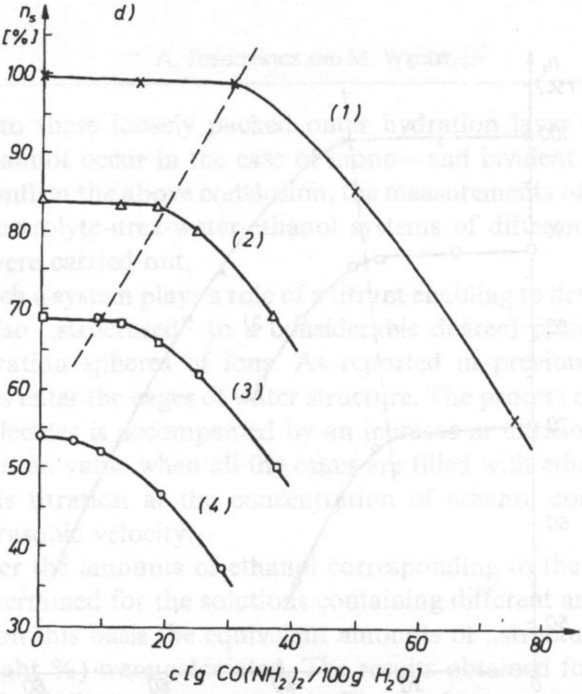


Fig. 5. The dependence of the amount of „structured" water (not participating in the hydration of the electrolyte), n_s [weight %] on the concentration of urea, c [g CO(NH$_2$)/100 g H$_2$O] at 25°C. a) $AlCl_3$ at molal concentrations [mol/kg H$_2$O] of: (1) 0; (2) 0.51; (3) 1.03; (4) 1.84. b) $Al(NO_3)_3$ at molal concentrations [mol/kg H$_2$O] of: (1) 0; (2) 0.51; (3) 1.07. c) $MgCl_2$ at molal concentrations [mol/kg H$_2$O] of: (1) 0; (2) 1.03; (3) 2.11; (4) 3.88. d) NaCl at molal concentrations [mol/kg H$_2$O] of: (1) 0; (2) 1.02; (3) 2.09; (4) 3.20.

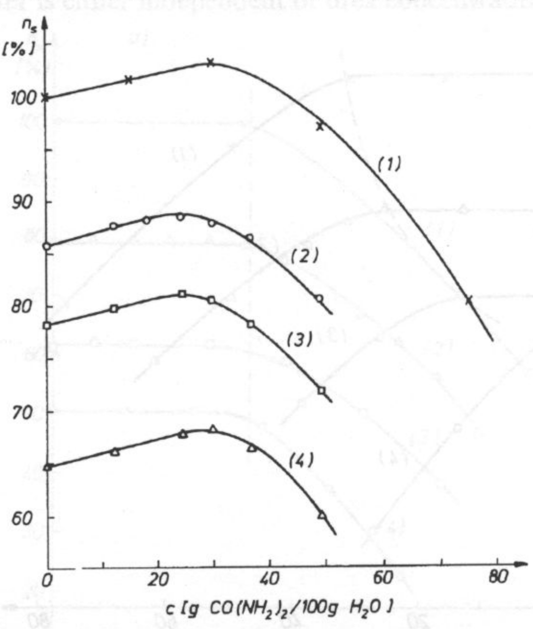


Fig. 6. The dependence of the amount of „structured" water (not participating in the hydration of the electrolyte), n_s [weight %] on the concentration of urea, c [g CO(NH$_2$)/100 g H$_2$O] at 15°C: (1)H$_2$O: (2) NaCl; (3) $MgCl_2$; (4) $AlCl_3$

(at 15°C), in the latter one a sharp decrease in the amount of „structured" water is observed. This phenomenon can be interpreted in the following way: at low concentrations urea molecules are elements of the structure of cages voids which can then be filled with ethanol molecules [6]. That is why at 15°C an increase in the amount of „structured" water with increasing urea concentration is observed. At high concentrations the amount of water is not sufficient for urea molecules to form this particular structure of the solution (cages) appropariate for ethanol molecules. Consequently the primary structure of the solution at low urea concentrations is destroyed, and either new water-urea structural units of low water content or small associated molecules of urea inaccessible for ethanol appear instead. This explains the sharp decrease in the amount of the titrant used in the solutions of urea concentration higher then 30g/100 gH_2O.

For 25°C an increase in the amount for „structured" water in the region of low urea concentration was not observed. This results from a reduction of solution „structuring" with increasing temperature. Higher temperature lead to an increase in the amplitude of termal vibrations of molecules in the solution which consequently breaks bonds.

Most probably this process nullifies thoroguly the effect of urea molecules on the increase in solution „structuring" observed at lower urea concentrations.

The dependencies of the amount of „,structured" water on urea concentration in $AlCl_3$ and $Al(NO_3)_3$ solutions (Fig. 5 a- b) are similar to those in the water-urea system. Also an increase in electrolyte concentration does not change the picture much. A considerable change in the slope of the obtained curves occurs at the same urea concentration. This concentration will further on be called a peculiar concentration, c_s, because for $AlCl_3$ solution it does not only depend on electrolyte concentration, but is just equal to the urea concentration obtained for the point of the change in slope of the curve of the water-urea system, i.e. the system which does not contain an electrolyte ($c_s = 30$ g urea/100 g H_2O).

The titration curves of $Al(NO_3)_3$ solutions show small shifts of the peculiar concentrations towards lower urea concentration with increasing electrolyte concentration. Most probably this effect results from „local hydrolysis" (to a higer degree for $Al(NO_3)_3$ than for $AlCl_3$) [26] on the one hand, and from competition between NO_3^- ions hydration number equal to —2 [15, 16] and urea molecules to bind free water molecules on the other hand.

In view of the foregoing results the conclusion can be drawn that for urea concentrations lower than the peculiar concentration, the presence of Al^{3+} ions in solution does not disturb the urea-water interactions. The system behaves as if these ions were not there. This can be the evidence for urea molecules being fixed both in the „structured" water lattice of the bulk solution and in the hydration sphere of Al^{3+} ions. This leads to the formation of solvation shells composed of water and urea around Al^{3+} ions.

For urea concentrations higher than the peculiar concentration, most probably, in the first place , a decomposition of water-urea structures outside the hydration (solvation) sphere of the ion occurs, and either the associated molecules of urea or water-urea structural units of low water content appear istead.

In the solutions of $MgCl_2$ and NaCl (Fig. 5 c–d), a well–marked decrease in c_s with increasing electrolyte concentration is observed. This results, on the one hand, from a reduction of the amount of water accessible for urea molecules (the water outside the hydration spheres responsible for dissolution of urea). On the other hand, such a big change in c_s following the addition of even a small amounts of urea shows that urea molecules are not capable of getting built into the hydration spheres of mono– and bivalent ions.

5. Conclusion

On the basis of the studies performed in ternary water-urea-electrolyte systems and quartenary water-urea-electrolyte-ethanol systems, the following model of dissolution of urea in aqueous solutions of aluminium, magnesium and sodium salts is proposed.

In aqueous solutions Al^{3+} ions are surrounded by two hydration layers. It seems possible that in these solutions there are two competitive ways for urea to get built into the solution microstructure. The former consists in formation of hydrogen bonds between urea and water not bound to the ions. This leads to an increase in „structuring" of the solution and is followed by an increase in the velocity of ultrasounds. The latter consists in formation of hydrogen bonds between urea and water of Al^{3+} hydration spheres (most probably with the outer hydration layer). A maximum of twelve urea molecules can interact with one Al^{3+} ion (Table 1). This process leads to loosening of Al^{3+} hydration shells and is followed by a decrease in the velocity of ultrasounds. The measured velocity of ultrasounds in the electrolyte-urea-water systems determines the resultant of the two processes. For low electrolyte concentrations the former process is dominant. With increasing concentration of aluminium salt the contribution of the latter process increases, and a certain electrolyte concentration it manifests itself by a decrease in ultrasonic velocity with increasing urea concentration. The minimum velocity (Fig. 1) corresponds to the saturation of Al^{3+} hydration leyers with urea molecules. This model accounts for the fact that there is a constant amount of water accessible for urea independent of the concentration of aluminium salt in the solution.

The hydration numbers of Mg^{2+} and Na^{+} ions are equal to 6 [15, 16, – 27, 28] which means that these ions have one strongly bound hydration layer. In aqueous solutions of these electrolytes urea molecules do not interfere with the hydration layers of the ions. They only interact with witer through hydrogen bonds thus increasing the structuring of the solution accompanied by an increase in ultrasonic velocity. This explains the reduction in the amount of water accessible for urea with increasing electrolyte concentration. In the solutions of $MgCl_2$ of concentrations close to saturation, the urea molecules probably replace hydration water, which leads to losening of the microstructure of the solution. The maximum of the ultrasonic velocity — urea concentration curve is the evidence for that.

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