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Influence of H/D Isotope Substitution on Physicochemical Properties of Aqueous Solutions of Urea and Thiourea

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The influence of the H/D isotope substitution on excess volumes, partial molar volumes, viscosity and ultrasound speed in aqueous solutions of urea and thiourea are studied at 20°C. The excess volume of the solutions studied is relatively small – however, it is negative in urea and positive in thiourea solutions. On the other hand, the deuteration affects the excess volume in both solutions in the same way: deuterated systems show smaller deviation from additivity than regular ones. The speed of sound in the systems studied increases monotonously with concentration, but its isotope effect decreases as the concentration increases. The curves of viscosity are monotonous too, but isotope effect of kinematic viscosity is practically the same in the whole concentration range studied. The present results for urea and thiourea aqueous solutions are compared with those previously obtained for amide–water systems.

Key words: molar volume, viscosity, speed of sound, isotope effect, deuterium, urea, thiourea

Biological importance of urea stimulated very intensive studies of its chemical and physicochemical properties and its aqueous solutions in particular. However, its role as an agent enhancing the solubility of nonelectrolytes in water is not clear as yet. Among many theories trying to explain this phenomenon, Frank and Franks [1] in their approach assume that urea is a chaotic agent whose interactions with water destroy its ice-like structure. This means that the interaction of urea counteracts the hydrophobic effects. On the other hand, according to Schellman's model, refined by Kreschek and Scheraga [2] and by Stokes [3], urea does not destroy the water structure. The molecules of urea are supposed to form dimers and oligomers and they can replace water in the solvation shall of the solute. (It enhances the solubility and in colloids prevents the aggregation of micells.) The study of hydration numbers [4] shows that the molecule of urea builds in the ice-like structure of water to form strong hydrogen bonds. This is supported by NMR [5], Raman [6] and theoretical studies [7], where the possibility of the replacement of water molecules in its net by amine groups is also taken into account. Further studies by Hoccart and Turnel [8] as well those by Hawlicka and Grabowski [9] have not removed some discrepancies concerning the structure of aqueous solution of urea. Moreover, it seems that the problem is much deeper and extends far beyond urea solutions, namely it touches the mechanism of hydrophobic and hydrophilic hydration.

A new approach to this problem is based on the isotope effect method. Some years ago Conway and Laliberte [10] suggested that the direction of the solvent isotope effect on the molar volume could be used as a criterion of the classification of the substances to those enhancing or destroying the structure of water. They found that some ions strongly interacting with water and perturbing (or destroying) its ice-like structure, have a smaller partial molar volume in D_2O than in H_2O, whereas ions which enhance the water structure, *i.e.* they undergo hydrophobic hydration (as tetraalkylammonium ions) have a greater volume in heavy water.

Recent papers of Sacco and Mateoli [11] and Miyai and Nakamura [12] present new data concerning the influence of H/D substitution on the molar volume and viscosities of the aqueous solutions of DMSO and dimethylamides. The conclusions reached in these papers contradict those drawn by Conway and Laliberte [10]. Our recent results [13], concerning the isotope effects on viscosity, speed of sound and molar volumes in aqueous solutions of simple amides, show that the direction of the isotope effect on the molar volume is not a sufficient criterion of the classification of the substances, thus, the isotope effects of other physicochemical properties of solution should be also taken into account.

This paper presents the results of density, viscosity, speed of sound and the influence of H/D isotope substitution on these properties in aqueous solutions of urea and thiourea. The latter has been included in the study, because the substitution S for O results in the worsening the solubility of thiourea as a consequence of the weaker interaction of the solute with water. Hence, it seemed to be interesting to compare the influence of H/D substitution on the physicochemical properties in both solutions. The data obtained enabled us to calculate the excess molar volumes, partial molar volume and the isotope effects of the properties studied.

EXPERIMENTAL

Urea and thiourea (from Sigma) were dried under vacuum. Urea and thiourea used in heavy water were deuterated by triple exchange with D_2O. Water was distilled 4 times but D_2O (99.5%) was used without further purification. All samples were prepared gravimetrically before measurements. The error in the mole fraction is estimated to be less than 10^{-3}. All measurements were performed at 20°C.

Densities were measured in a vibrating densimeter with a precision of 10^{-5} g/cm^3. The kinematic viscosity was determined by an optoelectronic capillary viscosimeter with an accuracy of 10^{-4} cSt. The speed of sound was measured in an acoustic wave time of flight gauge with a precision of 1 cm/s. These three instruments were produced by "ECOLAB" Poland and equipped with Peltier thermostats. The temperature was constant within ±0.01°C.

RESULTS AND DISCUSSION

All measurements have been carried out over the concentration range limited by solubility of the compounds studied, *i.e.* to the mole fraction of about 0.2 for urea and 0.03 for thiourea. Densities, given in Table 1, were used to calculate the average molar volumes (V^A) and the excess volumes (V^E) of the solutions studied. $V^A = (M_o x_o + M_w x_w)/\rho$, where: M_o, M_w and x_o, x_w are molar masses and mole fractions of the components, respectively and ρ is the experimental mixture density, $V^E = V^A - (V_o x_o + V_w x_w)$, where V_o and V_w are molar volumes of pure components (“o” refers to the organic compound and “w” to water).

Table 1. Density of urea and thiourea aqueous solutions.

urea				thiourea			
regular system		deuterated system		regular system		deuterated system	
x_u	ρ [g/cm^3]	x_u	ρ [g/cm^3]	x_t	ρ [g/cm^3]	x_t	ρ [g/cm^3]
0.0000	0.9982	0.0000	1.1050	0.0000	0.9982	0.0000	1.1050
0.0098	1.0065	0.0089	1.1119	0.0011	0.9992	0.0009	1.1061
0.0196	1.0148	0.0195	1.1204	0.0011	0.9992	0.0019	1.1072
0.0213	1.0163	0.0291	1.1276	0.0020	1.0004	0.0029	1.1082
0.0255	1.0199	0.0387	1.1346	0.0023	1.0005	0.0039	1.1092
0.0299	1.0235	0.0487	1.1390	0.0029	1.0018	0.0049	1.1105
0.0360	1.0280	0.0579	1.1480	0.0034	1.0021	0.0059	1.1115
0.0397	1.0315	0.0679	1.1546	0.0047	1.0038	0.0070	1.1125
0.0438	1.0343	0.0777	1.1609	0.0056	1.0047	0.0079	1.1137
0.0494	1.0385	0.0917	1.1643	0.0059	1.0051	0.0087	1.1144
0.0498	1.0390	0.0949	1.1700	0.0071	1.0060	0.0098	1.1156
0.0572	1.0442	0.1013	1.1701	0.0081	1.0075	0.0108	1.1166
0.0596	1.0464	0.1091	1.1754	0.0093	1.0090	0.0119	1.1177
0.0633	1.0486	0.1192	1.1790	0.0104	1.0105	0.0132	1.1193
0.0699	1.0535	0.1298	1.1895	0.0116	1.0117	0.0145	1.1205
0.0798	1.0602	0.1394	1.1929	0.0122	1.0121	0.0157	1.1215
0.0899	1.0670	0.1492	1.1989	0.0128	1.0128	0.0168	1.1228
0.1004	1.0737	0.1598	1.2038	0.0140	1.0145	0.0181	1.1240
0.1100	1.0798	0.1693	1.2076	0.0155	1.0159	0.0194	1.1255
0.1196	1.0854	0.1789	1.2114	0.0163	1.0170	0.0205	1.1265
0.1297	1.0914	0.1892	1.2161	0.0173	1.0178	0.0214	1.1275
0.1390	1.0967	0.1982	1.2202	0.0184	1.0193	0.0224	1.1284
0.1494	1.1023	0.2089	1.2243	0.0197	1.0204	0.0235	1.1293
0.1592	1.1076			0.0207	1.0220	0.0254	1.1314
0.1623	1.1088			0.0217	1.0227	0.0265	1.1323
0.1681	1.1107			0.0219	1.0231	0.0280	1.1338
0.1686	1.1117			0.0229	1.0242	0.0285	1.1345
0.1794	1.1175			0.0241	1.0255	0.0295	1.1352
0.1890	1.1223			0.0252	1.0267		
0.1992	1.1272			0.0264	1.0278		
0.2091	1.1317			0.0268	1.0280		
0.2193	1.1361			0.0275	1.0289		
0.2296	1.1408			0.0286	1.0302		
0.2393	1.1449			0.0297	1.0312		

The excess volumes are presented in Fig. 1. A computer program has been used to fit a curve composed of third order splines [14] to values of V^A as a function of x_1 (mole fraction of non-aqueous component) and V^A derivatives (dV^A/dx) were determined. Then, the partial specific volumes of the components (V_o^p and V_w^p) have been calculated according to the equations [15]: $V_w^p = V^A - (dV^A/dx)x_o$ and $V_o^p = V^A - (dV^A/dx)\ x_o + (dV^A/dx)$. The results obtained are shown in Fig. 2.

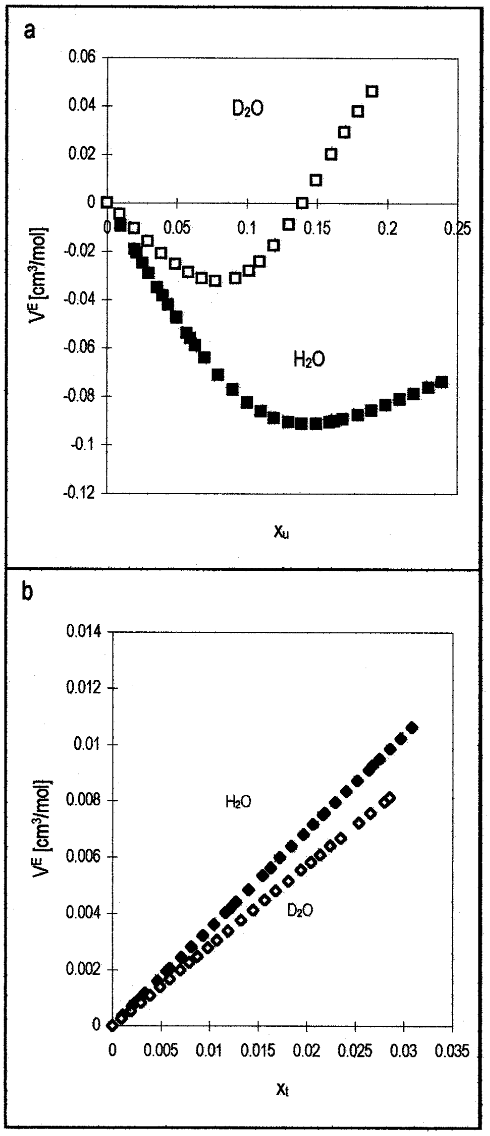

Figure 1. Excess volume of urea (a) and thiourea (b) solutions.

The experimental values of speed of sound (u) in the mixtures studied are presented in Table 2 and Fig. 3a,b. The splines method has been used for the interpolation of the results obtained for systems with hydrogen and deuterium to the same values of x_1. The calculated isotope effects on the speed of sound are presented in Fig. 3c,d.

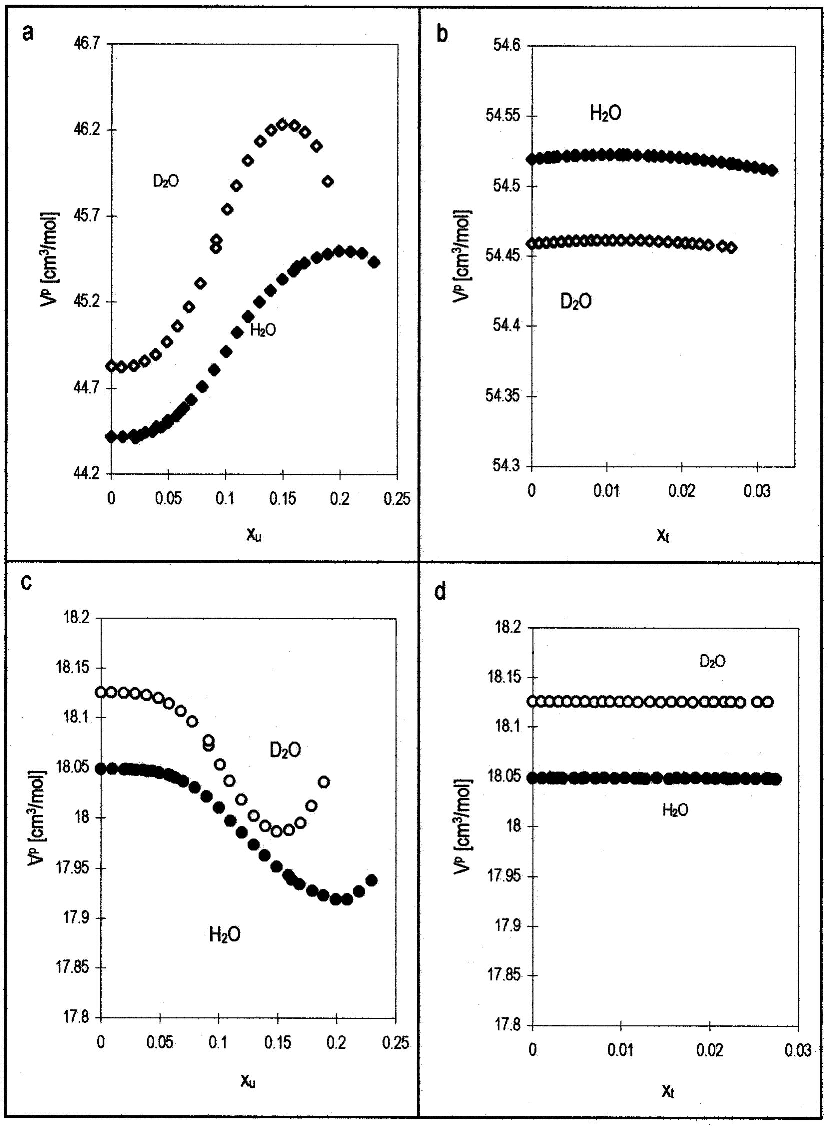

Figure 2. Partial specific volume of urea (a) and thiourea (b) in aqueous solutions. Partial specific volume of water, in urea (c) and thiourea (d) solutions.

The results of kinematic viscosity measurements (ν) in urea solution are shown in Table 3. The concentration dependences of kinematic and dynamic viscosity are presented in Fig. 4.a,b followed by their isotope effects in Fig. 4c,d.

As can be seen in Figure 1a, the excess molar volume of urea is negative in the concentration range studied. This is a typical behavior of most water–organic compound mixtures and a similar course has been observed for amide solutions except of acetamide [13]. However, the deviation of the mean molar volume from additivity is very small. This is not due to the limited solubility of urea in water, which reaches 0.20

mole fraction in room temperature. For other nonelectrolytes well miscible with water, the minimum of V^E lies around mole fraction of 0.4 and the excess molar volumes have the following values at the mole fraction of 0.2: –0.8 cm^3/mol, –1.1 cm^3 /mol for dimethylformamide, dimethylacetamide respectively, but only –0.15 cm^3 /mol for formamide. The large negative deviation of the mean molar volume from the additivity is explained by the penetration of the nonelectrolyte molecules into the gaps of ice-like structure of water. Such a deep minimum is characteristic for systems containing substances enhancing this structure (acetone, ethanol, dimethylamides) [16]. As can be seen, urea, similarly to formamide, does not exhibit such an action.

Table 2. Speed of sound in urea and thiourea aqueous solutions.

urea				thiourea			
regular system		deuterated system		regular system		deuterated system	
x_u	u [m/s]	x_u	u [m/s]	x_t	u [m/s]	x_t	u [m/s]
0.0000	1482.5	0.0000	1385.5	0.0000	1482.5	0.0000	1385.5
0.0098	1489.0	0.0089	1399.8	0.0011	1484.3	0.0009	1387.7
0.0196	1496.0	0.0195	1416.4	0.0020	1485.9	0.0019	1389.5
0.0213	1497.3	0.0291	1430.8	0.0029	1487.7	0.0029	1391.1
0.0255	1500.8	0.0387	1444.2	0.0047	1490.4	0.0039	1392.7
0.0299	1504.7	0.0487	1457.6	0.0056	1491.8	0.0049	1394.9
0.0360	1510.5	0.0579	1469.3	0.0081	1496.0	0.0059	1396.5
0.0397	1514.1	0.0679	1481.5	0.0093	1497.9	0.0070	1398.2
0.0438	1518.2	0.0777	1493.3	0.0104	1499.8	0.0079	1400.1
0.0494	1523.5	0.0917	1508.8	0.0116	1501.5	0.0087	1401.2
0.0498	1523.9	0.0949	1513.9	0.0122	1502.5	0.0098	1403.1
0.0572	1530.6	0.1013	1519.4	0.0140	1505.4	0.0108	1404.8
0.0596	1532.8	0.1091	1527.2	0.0163	1508.9	0.0119	1406.8
0.0633	1536.1	0.1192	1539.2	0.0173	1510.3	0.0132	1409.2
0.0699	1541.9	0.1298	1549.4	0.0184	1511.9	0.0145	1410.9
0.0798	1550.9	0.1394	1558.3	0.0197	1514.2	0.0157	1413.0
0.0899	1560.5	0.1492	1566.7	0.0217	1517.1	0.0168	1415.0
0.1004	1570.3	0.1598	1576.3	0.0219	1517.1	0.0181	1416.9
0.1100	1578.7	0.1693	1585.9	0.0229	1519.2	0.0194	1419.2
0.1196	1586.5	0.1789	1593.8	0.0241	1520.8	0.0205	1421.2
0.1297	1594.2	0.1892	1601.7	0.0252	1522.4	0.0214	1422.4
0.1390	1600.7	0.1982	1608.8	0.0264	1524.1	0.0224	1424.2
0.1494	1606.9	0.2089	1617.0	0.0268	1524.7	0.0235	1427.0
0.1592	1612.2			0.0275	1525.8	0.0254	1429.1
0.1623	1614.0			0.0286	1527.4	0.0265	1430.6
0.1686	1617.7			0.0297	1529.0	0.0280	1433.0
0.1794	1624.9			0.0319	1532.2	0.0285	1433.7
0.1890	1631.4					0.0295	1435.4
0.1992	1637.3						
0.2091	1642.5						
0.2193	1648.4						
0.2296	1655.3						
0.2393	1662.2						

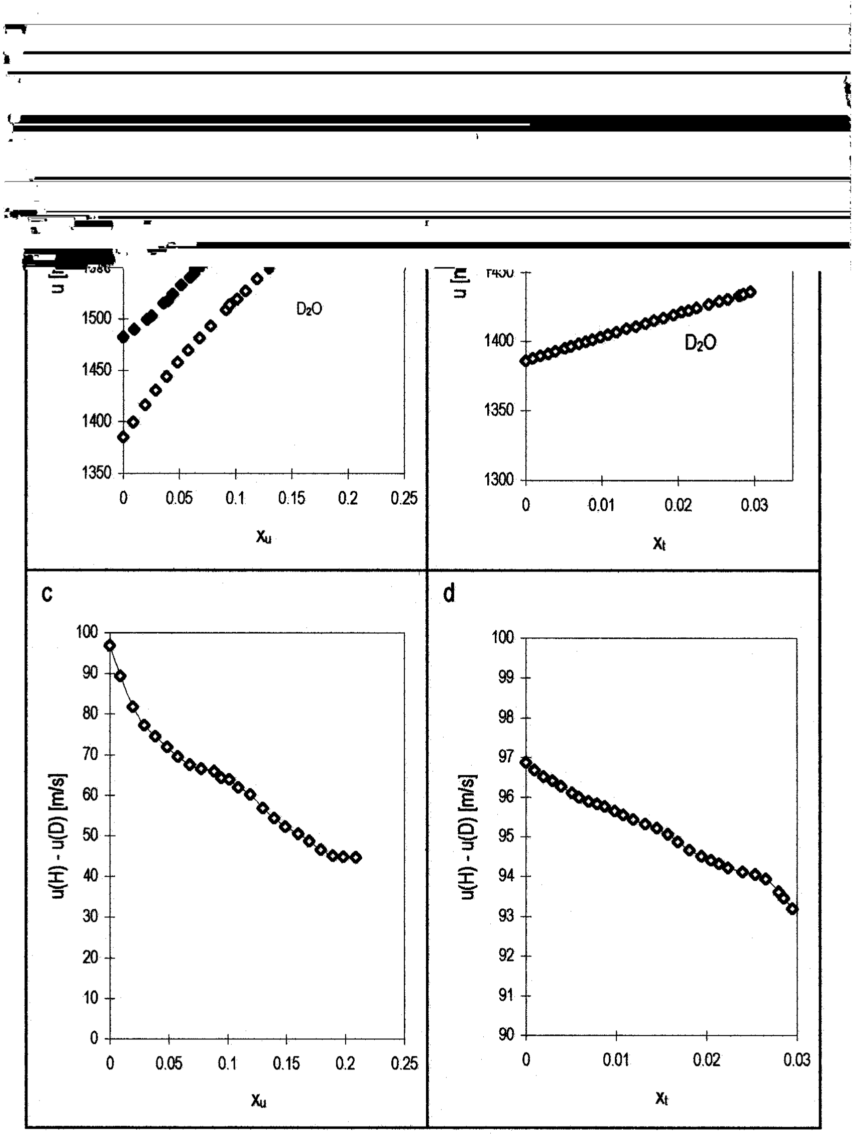

Figure 3. Speed of sound in urea (a) and thiourea (b) aqueous solutions. Isotope effect of speed of sound in urea (c) and thiourea (d) solutions.

The excess molar volume of thiourea (Figure 1b) is very small as well, but it is positive and this behavior resembles acetamide [13]. The opposite direction of the excess molar volume of urea and thiourea solutions can be considered as a result of a different energy of hydrogen bonding formed with the participation of oxygen and sulfur atoms.

The excess molar volumes of urea and thiourea are characterized by relatively large isotope effects (as compared with simple amides). This seems to be related with the large content of deuterium in the molecule, *i.e.* four D atoms in the relatively small molecules. It is worth to mention, that for most substances studied previously the system with deuterium showed a bigger deviation from the additivity and only acetamide presented a different behavior [13]. A similar behavior to that observed for acetamide is found in the present study. As can be seen in Fig. 1a and Fig. 1b, both urea and thiourea show smaller deviations from additivity for deuterated systems. Some analogy could be also found with formamide solution, however, in this case the isotope effect of excess molar volume was negligible and consequently the sign could not be unambiguously determined.

Table 3. Viscosity of aqueous urea solutions.

regular system		deuterated system	
x_u	ν [cSt]	x_u	ν [cSt]
0.0000	1.0039	0.0000	1.1293
0.0133	1.0179	0.0076	1.1343
0.0195	1.0246	0.0151	1.1482
0.0232	1.0258	0.0258	1.1648
0.0302	1.0434	0.0327	1.1736
0.0398	1.0518	0.0393	1.1858
0.0535	1.0868	0.0446	1.1971
0.0607	1.0982	0.0578	1.2257
0.0701	1.1182	0.0756	1.2648
0.0828	1.1508	0.0922	1.2981
0.0921	1.1757	0.1071	1.3470
0.1038	1.2064	0.1220	1.3930
0.1189	1.2502	0.1416	1.4662
0.1239	1.2680	0.1587	1.5129
0.1296	1.2850	0.1803	1.5972
0.1410	1.3256		
0.1578	1.3845		
0.1793	1.4645		

The partial molar volume of urea (Fig. 2a) increases with concentration, passes through a maximum and in the saturated solution reaches the value corresponding to molar volume of the pure substance. No minimum (characteristic for substances enhancing the water structure) is found at low concentration. A similar behavior was previously observed for acetamide–water and formamide–water systems [13], although in the latter the plateau was seen at high concentration of amide.

The isotope effect of partial molar volume of urea is relatively large and in the whole concentration range the volume of urea in D_2O is bigger than in H_2O. Sometimes the direction of the isotope effect of the partial molar volume is taken as a criterion to distinguish between substances enhancing or destroying the structure of water.

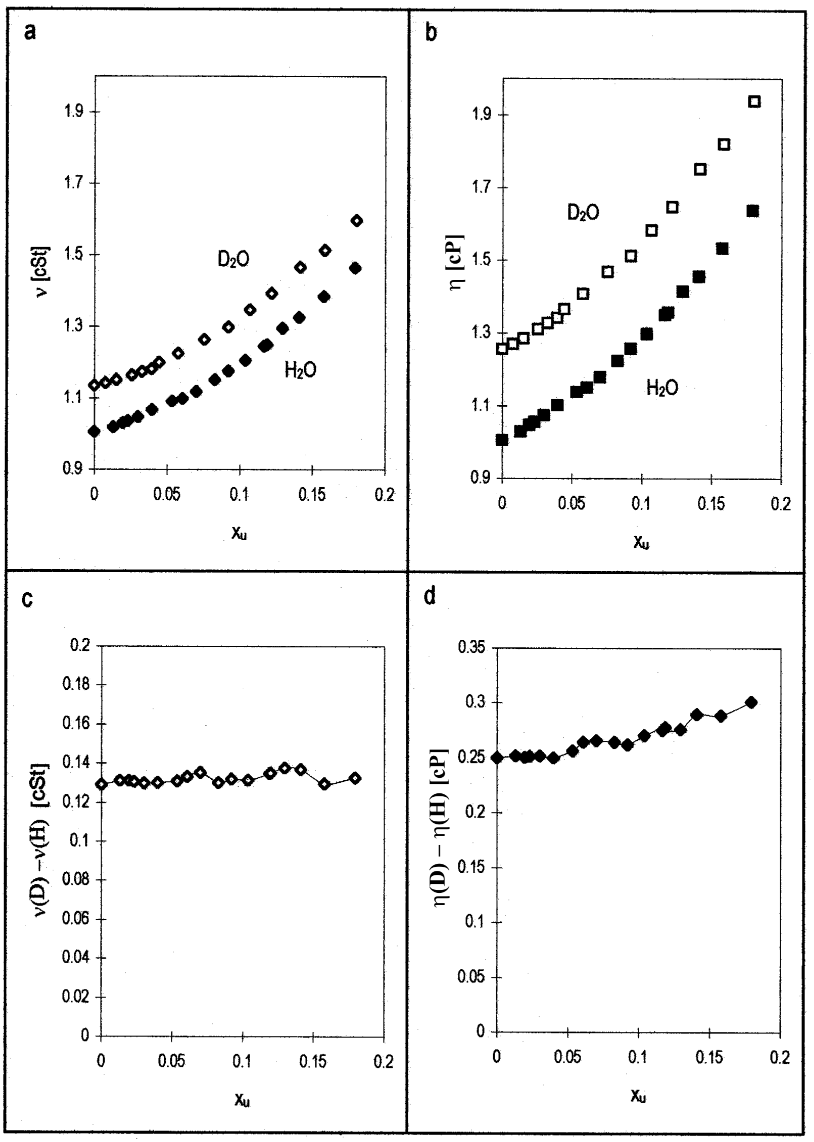

Figure 4. Kinematic viscosity (a) and dynamic viscosity (b) of aqueous solutions of urea. Isotope effect of kinematic (c) and dynamic (d) viscosity of urea solutions.

It was suggested [10], that the so called “promotors” of water structure have a larger molar volume in heavy water. Although such a correlation has been found for electrolytes [11] (inorganic and tetraalkylammonium salts), it does not seem to be valid for aqueous solutions of nonelectrolytes. Namely, it has been shown that for both formamide and dimethylformamide [13] the partial molar volumes in D_2O are smaller than in H_2O, although it is well known that they influence the water structure differently. On the other hand, acetamide, like urea, has a larger molar volume in D_2O

in the broad concentration range although other measurements show rather its destructive influence on water.

The partial molar volume of thiourea in water (Fig. 2b) does not present such big changes as that of urea, what is undoubtedly related to the much worse solubility of thiourea. In the concentration range studied (up to mole fraction of 0.03) no minimum was found, however, the direction of isotope effect is opposite to that found for urea, *i.e.* the partial molar volume of thiourea in D_2O is smaller than in H_2O. It is thus obvious, that the sign of the isotope effect on partial molar volume cannot be a useful criterion of the interaction type of nonelectrolyte with water.

The partial molar volume of water (Fig. 2c,d) is characterized by a large isotope effect and the volume of D_2O is bigger than that of H_2O.

The sound velocity in the system studied (Fig. 3a,b) increases monotonously with concentration. The maximum characteristic for substances enhancing the water structure (alcohols, dimethylamides) does not appear here, however, a visible deviation from additivity is well seen. A similar shape of the concentration dependence has been observed previously for formamide and acetamide. It suggests that the compressibility monotonously decreases with the concentration increase.

The same direction of the isotope effect is observed in urea–water and thiourea–water systems and the systems with deuterium exhibit lower sound velocities. This isotope effect (Fig. 3d,e) is relatively large, because isotope effects of density and compressibility contribute in the same direction. This effect decreases with concentration. The same behavior was observed in the solutions of simple amides.

The viscosity measurements gave very interesting results. The concentration dependences are presented in Figure 4a, as a directly measured kinematic viscosity, and Figure 4b presents the calculated dynamic viscosity. The curves are monotonous and the negative deviation from additivity is well seen. This behavior is similar to that observed for formamide. No minimum characteristic for substances enhancing water structure is seen at low concentrations.

According to the expectation, the deuteration rises the viscosity of the system, however, the isotope effect of viscosity depends on concentration in another way than the isotope effect on speed of sound. The direct comparison of the isotope effect on kinematic and dynamic viscosities reveals some interesting features. Namely, the isotope effect of dynamic viscosity increases slowly, whereas the isotope effect of kinematic viscosity is practically constant. In the first case, the increase of the isotope effect is very likely caused by the density changes in the deuterated system and does not reflect the real changes in the viscous flow upon isotopic substitution. Therefore, it seems that in analysis of the isotope effect of viscosity it is better to use kinematic viscosity. Comparing the concentration dependence of the kinematic viscosity of urea solution with those obtained previously for simple amides, the close similarity of urea and formamide is readily seen. Formamide solution was the only system, where in the concentration range 0–0.2 the isotope effect practically did not change, while for dimethylamides, especially for dimethylacetamide, a strong increase of the isotope effect on viscosity with a maximum below mole fraction of 0.2 was observed.

The comparison of the results obtained for urea and thiourea solutions does not lead to unequivocal conclusions, concerning the influence of S to O change on the interaction of the solute with water. Although the excess molar volumes and the isotope effects thereon behave differently (opposite direction) the speed of sound does not exhibit any visible differences between these two solutions. These results support our previous observations [13], that the isotope effect on the molar volume is not a sufficient criterion of the classification of the substances and the isotope effects of other physicochemical properties of solution should be taken into account.

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