Temperature and Concentration Dependence of Apparent Molar Volumes and Viscosities of NaCl, NH_4Cl, $CuCl_2$, $CuSO_4$, and $MgSO_4$ in Pure Water and Water + Urea Mixtures

M. A. Motin*

Department of Chemistry, Khulna University of Engineering and Technology (KUET), Khulna-9203, Bangladesh

Apparent molar volumes (ϕ_v) and viscosities (η) of NaCl, NH_4Cl, $CuCl_2$, $CuSO_4$, and $MgSO_4$ in water and water + urea solutions as a function of concentration are reported at (308.15, 313.15, and 323.15) K. The apparent molar volumes at infinite dilution of these electrolytes were determined by extrapolating ϕ_v values to zero concentration, which is practically equal to the partial molar volume. Viscosity coefficients (A and B) for these systems were also determined for the Jones−Dole equation. Apparent molar volumes (ϕ_v) and viscosities of these electrolytes were found to be higher in water + urea solutions than those in water solutions. All these electrolytes, except NH_4Cl, exhibit structure making behavior in water and water + urea solutions. Ammonium chloride showed structure breaking properties in water and 1 mol·kg^{-1} water + urea solutions. In 5 mol·kg^{-1} urea solution ammonium chloride showed structure making behavior at the temperature range studied. Electrolytes in water + urea solutions are seen to be more structured than those in water solutions. The properties of these electrolytes in water and water + urea solution systems are discussed in terms of the charge, size, and hydrogen bonding effect.

Introduction

A large number of researchers reported that urea acts as a net structure breaker for water.[1−10] On the other hand, another researcher reported that urea enhances water structure.[11] The later view has been supported by our recent studies.[12−14] The structure making or breaking property of urea in aqueous solution was found to be a temperature-dependent property. It will be interesting to see what happens when some water structure making and breaking salts are added in water + urea solution systems to substantiate the former studies. Urea + water and salt + water mixtures are of great importance in protein stability and denaturation phenomena.[15−17] The effects of added urea and salt upon the properties of water continue to be investigated to understand the mechanism of the protein stability and denaturation by urea and salts. Although volumetric and viscometric results on water solution systems of electrolytes are available, no data are yet available for them in water + urea solution systems. Here, we report the effect of some simple inorganic electrolytes on the structure of water and water + urea solution systems using apparent molar volume and viscosity coefficient data. Two types of electrolytes were chosen for the purpose. In one type of the salts the anions were the same but the cations were different. In other types, the cations were the same but the anions were different. The electrolytes possessing different charge and size of the ions may affect water and water + urea solution structure differently, which may be reflected in the apparent molar volume and viscosity coefficient data. This type of study on simple systems sometimes provides very useful information regarding the structure for more complex systems.

Experimental Section

Materials. Urea (99%), sodium chloride (>99%), ammonium chloride (99%), copper chloride (>98%), copper sulfate (98%), and magnesium sulfate (99%) were procured from E. Merck. The chemicals with quoted purities were dried first in an oven at 110 °C and then at room temperature in a vacuum over phosphorus pentoxide for at least 24 h and were then used without further purification.

Density Measurements. Densities were measured by using 5 mL pycnometers. The volumes of the pycnometers were calibrated with deionized and doubly distilled water at (308.15, 313.15, and 323.15) K. The densities of electrolyte in water and water + urea solutions were determined from the mass of the solution in the pycnometer after reaching thermal equilibrium with a water bath at the studied temperatures. A Mettler PM-200 electronic balance with an accuracy of ±0.0001 g was used for the mass determination.

Determination of Apparent Molar Volumes. Apparent molar volumes were determined using the measured densities of solvent and solution in eq 1[18]

$$\phi_v = [1000(\rho_0 - \rho)/(m\rho_0)] + M_w/\rho_0 \qquad (1)$$

where ϕ_v is the apparent molar volume, m is the molality, M_w is the molecular weight of the solute, and ρ_0 and ρ are the densities of the solvent and the solution, respectively.

The molalities of the solutions were calculated from the molarities C (mol·L^{-1}) using eq 2

$$m = \frac{1}{(\rho/C) - M_w/1000} \qquad (2)$$

In general, ϕ_v was found to vary linearly with concentration for the systems studied. The uncertainty of ϕ_v was (0.1−

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* To whom correspondence should be addressed. E-mail: abdulmotin75@yahoo.com.

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Table 1. Apparent Molar Volumes (ϕ_v) for NaCl, NH_4Cl, $CuCl_2$, $CuSO_4$, and $MgSO_4$ in Pure Water, Water + 1 mol·kg^{-1} Urea, and Water + 5 mol·kg^{-1} Urea Solutions at (308.15, 313.15, and 323.15) K

	ϕ_v/cm^3·mol^{-1} at T = 308.15 K					ϕ_v/cm^3·mol^{-1} at T = 313.15 K					ϕ_v/cm^3·mol^{-1} at T = 323.15 K				
m/mol·kg^{-1}	NaCl	NH_4Cl	$CuCl_2$	$CuSO_4$	$MgSO_4$	NaCl	NH_4Cl	$CuCl_2$	$CuSO_4$	$MgSO_4$	NaCl	NH_4Cl	$CuCl_2$	$CuSO_4$	$MgSO_4$
In Pure Water Solution															
0.0625	17.2	37.2	53.8	91.0	128.1	17.8	37.7	54.3	91.8	129.2	18.4	38.2	54.9	92.5	130.1
0.1250	17.7	37.3	54.4	91.9	129.6	18.1	37.8	54.9	92.6	130.7	18.7	38.3	55.5	93.3	131.7
0.2500	18.3	37.4	54.9	92.9	131.0	18.7	37.9	55.4	93.6	132.1	19.4	38.5	55.9	94.4	133.1
0.5000	19.0	37.6	56.1	94.6	132.9	19.5	38.0	56.6	95.4	133.9	20.2	38.6	57.1	96.0	135.0
1.0000	20.7	37.7	57.6	96.4	134.5	21.3	38.2	58.2	97.1	135.5	21.8	38.7	58.6	97.8	136.6
In Water + 1 mol·kg^{-1} Urea Solution															
0.0625	17.8	37.6	54.0	91.6	129.2	18.4	38.1	54.5	92.4	130.3	19.0	38.6	55.1	93.1	131.3
0.1250	18.3	37.7	54.5	92.6	130.7	18.9	38.2	55.1	93.3	131.8	19.4	38.8	55.7	94.1	132.8
0.2500	18.9	37.8	55.0	93.6	132.2	19.5	38.4	55.6	94.3	133.3	20.0	38.9	57.0	95.1	134.4
0.5000	19.6	38.0	56.2	95.1	133.7	20.2	38.5	56.8	95.9	134.8	20.8	39.1	57.4	96.6	135.9
1.0000	20.7	38.2	57.8	96.7	135.2	21.3	38.8	58.0	97.4	136.4	21.8	39.3	58.7	98.2	137.5
In Water +5 mol·kg^{-1} Urea Solution															
0.0625	18.5	38.1	54.6	92.5	130.4	19.1	38.6	55.1	93.2	131.5	19.7	39.2	55.7	93.9	132.5
0.1250	19.0	38.6	55.1	93.4	131.6	19.7	39.1	55.7	94.1	132.7	20.2	39.9	56.3	94.8	133.8
0.2500	19.7	39.2	55.7	94.4	133.0	20.3	39.7	56.3	95.1	134.0	20.9	40.2	56.9	95.8	135.1
0.5000	20.5	40.1	57.0	95.8	134.5	21.1	40.6	57.5	97.3	135.6	21.7	41.2	58.5	98.1	136.7
1.0000	22.4	42.2	59.2	98.9	137.1	22.9	43.1	60.4	100.0	138.8	23.5	42.7	61.8	101.5	139.3

0.5)%. The reliability of ϕ_v values at low concentrations (<0.0625 mol·kg^{-1}) is expected to be poorer than that at high concentrations (>0.0625 mol·kg^{-1}).

Viscosity Measurement. Viscosities were measured with a calibrated U-type Ostwald viscometer of the British standard institution with sufficiently long efflux time to avoid kinetic energy correction. The provided calibration constants were checked with water, ethanol, and *n*-hexane. Temperatures were controlled by a thermostatic water bath fluctuating to ±0.01 °C. The uncertainty of η in the present experiments was less than 2 × 10^{-4} mPa·s. The absolute viscosities of solutions η were calculated from

$$\eta = A\rho t \tag{3}$$

where t is the flow time, ρ is the density of the solution, and A is the viscometer constant.

Viscosity Coefficients A and B Measurement. The coefficients A and B for the electrolyte solutions were calculated using the empirical equations of Jones−Dole[19]

$$\eta_r = 1 + A\sqrt{C} + BC \tag{4}$$

where η_r is the relative viscosity = viscosity of solution (η)/viscosity of solvent (η_0). The values of the coefficients A and B were obtained from the intercept and slope of the plot $(\eta_r - 1)/\sqrt{C}$ against $\sqrt{C}$, respectively.

Results and Discussion

The apparent molar volumes (ϕ_v) of the studied electrolytes were tabulated in Table 1, and their representative plots are shown in Figure 1 as examples (figures for the other electrolytes $CuCl_2$, $CuSO_4$, and $MgSO_4$ in water and 1 and 5 mol·kg^{-1} urea solutions are not shown for similar nature). The apparent molar volume is found to be dependent upon the electrolyte concentration as well as on the temperature. The increase of ϕ_v with molality is seen to be significant for all studied electrolytes except NH_4Cl (shown in Figure 1). The change of ϕ_v with molality is not significant for NH_4Cl in water and in 1 mol·kg^{-1} water + urea solution systems, but in 5 mol·kg^{-1} water + urea solutions systems the change is significant. This indicates that the electrolytes studied except for NH_4Cl are structure makers in water and in water + urea solution systems. The structure breaking tendency of NH_4Cl is probably counteracted by the structure making tendency of urea, and at higher urea concentration (5 mol·kg^{-1}), urea nullifies the structure breaking effect of NH_4Cl and forces water to be more structured.

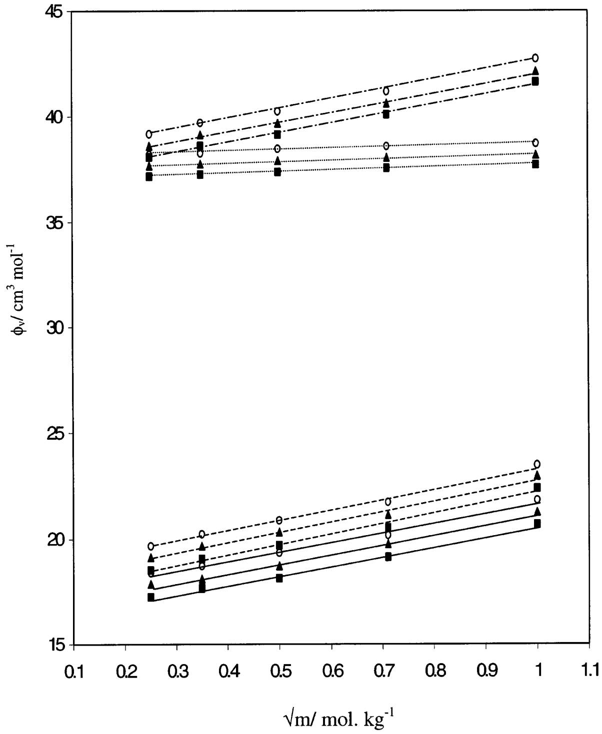

Figure 1. Plots of apparent molar volume (ϕ_v) versus $\sqrt{m}$ for (a) sodium chloride (solid line) and ammonium chloride (dashed line) in water and (b) sodium chloride (dotted line) and ammonium chloride (dashed−dotted line) in water + 5 mol·kg^{-1} urea solutions at the following temperatures: ■, 308.15 K; △, 313.15 K; ○, 323.15 K.

Plots of ϕ_v versus square root of the molality of the electrolytes show a linear relationship. This relation is also seen in the case of temperature rise; that is, as temperature is increased, the ϕ_v value is also increased, at least at the chosen three temperatures. The increase of ϕ_v with molality of the electrolyte suggests that the ion−solvent interactions increase with the increase in molality of the electrolytes. The limiting apparent molar volume (ϕ_v°), which is taken to be the partial molar volume of the solute at infinite dilution ($\bar{V}_2^\circ$), slightly changes with the rise of tempera-

Table 2. Viscosity (η) for NaCl, $NaNO_3$, KNO_3, NH_4Cl, $CuCl_2$, $CuSO_4$, and $MgSO_4$ in Pure Water, Water + 1 mol·kg^{-1} Urea, and Water + 5 mol·kg^{-1} Urea Solutions at (308.15, 313.15, and 323.15) K

	η/mPa·s at T = 308.15 K					η/mPa·s at T = 313.15 K					η/mPa·s at T = 323.15 K				
m/mol kg^{-1}	NaCl	NH_4Cl	$CuCl_2$	$CuSO_4$	$MgSO_4$	NaCl	NH_4Cl	$CuCl_2$	$CuSO_4$	$MgSO_4$	NaCl	NH_4Cl	$CuCl_2$	$CuSO_4$	$MgSO_4$
In Pure Water Solution															
0.0625	0.7238	0.7299	0.7390	0.7420	0.7400	0.6610	0.6608	0.6675	0.6730	0.6745	0.5516	0.5560	0.5770	0.5823	0.5642
0.1250	0.7353	0.7289	0.7708	0.7918	0.7982	0.6700	0.6597	0.6970	0.7176	0.7215	0.5585	0.5555	0.6010	0.6001	0.6050
0.2500	0.7441	0.7281	0.8088	0.8376	0.8401	0.6786	0.6590	0.7375	0.7579	0.7600	0.5678	0.5551	0.6370	0.6314	0.6392
0.5000	0.7642	0.7279	0.8790	0.9348	0.9420	0.6950	0.6586	0.7940	0.8476	0.8575	0.5870	0.5547	0.6967	0.7076	0.7330
1.0000	0.7990	0.7315	0.9692	1.0890	1.0939	0.7220	0.6610	0.8595	0.9770	0.9550	0.6200	0.5570	0.7595	0.8170	0.8368
In Water + 1 mol.kg^{-1} Urea Solution															
0.0625	0.7354	0.7390	0.7675	0.7738	0.7742	0.6674	0.6701	0.6977	0.6990	0.6994	0.5570	0.5645	0.5881	0.5828	0.5962
0.1250	0.7475	0.7384	0.7872	0.8056	0.8187	0.6785	0.6697	0.7140	0.7345	0.7345	0.5673	0.5642	0.6188	0.6068	0.6160
0.2500	0.7561	0.7380	0.8249	0.8488	0.8847	0.6867	0.6692	0.7579	0.7741	0.7787	0.5774	0.5638	0.6528	0.6492	0.6621
0.5000	0.7749	0.7377	0.8807	0.9485	0.9589	0.7066	0.6690	0.8162	0.8733	0.8825	0.5974	0.5635	0.7200	0.7258	0.7500
1.0000	0.7995	0.7398	0.9397	1.0498	1.0531	0.7295	0.6710	0.8845	0.9825	0.9963	0.6274	0.5651	0.7892	0.8124	0.8472
In Water + 5 mol·kg^{-1} Urea Solution															
0.0625	0.8872	0.8917	0.8998	0.9191	.0.9199	0.8127	0.8118	0.8194	0.8397	0.8392	0.6846	0.6921	0.7157	0.7184	0.7188
0.1250	0.8932	0.8932	0.9356	0.9423	0.9557	0.8297	0.8142	0.8621	0.8826	0.8891	0.6914	0.6940	0.7407	0.7437	0.7489
0.2500	0.9001	0.8950	0.9809	0.9985	0.9976	0.8402	0.8177	0.9062	0.9207	0.9258	0.7005	0.6976	0.7928	0.7989	0.8031
0.5000	0.9174	0.8998	1.1024	1.1075	1.1096	0.8601	0.8230	1.0156	1.0186	1.0211	0.7198	0.7028	0.8609	0.8701	0.8942
1.0000	0.9480	0.9149	1.2039	1.2940	1.2595	0.8930	0.8379	1.1250	1.1870	1.1357	0.7990	0.7170	0.9372	0.9940	0.9980

ture. Such temperature dependence may be interpreted using the model suggested by Frank and Wen for aqueous electrolyte solutions.[20] According to this model, water molecules from the intermediate region (region B), which is more random, have been transferred to the more structured bulk region (region C) due to thermal agitation resulting in an increase in ϕ_{v}°. Due to the increased thermal energy at higher temperature, the relaxation to the bulk of the electrostricted water molecules from the solvation sphere of the ions results in a positive volume change. Increase in temperature may also decrease the water + water interactions, thereby breaking the tetrahedral cluster of bulk water, giving a negative volume change. The predominance of the positive contributions due to the former overcomes the small negative contribution due to the latter effect, giving rise to a net positive change in volume. However, the temperature coefficients of $CuSO_4$ and $MgSO_4$ are seen to be much higher than any of those of the other salts listed in this study. Weak ion + water interactions in the case of large sized SO_4^{2-} perhaps transfer water molecules from the structure broken region to the structured bulk region, easily producing a large positive volume change at higher temperatures.

The limiting apparent molar volume (ϕ_{v}°) reflects the true volume of the solute and the volume change arising from the solute−solvent interactions. The change in this property for an additive as a function of urea concentration and temperature may reflect the change in its environment in the solution systems. The values of ϕ_{v}° for all the electrolytes studied are higher in water + urea solutions than those in water solutions only.

The salts sodium chloride and ammonium chloride contain monovalent, dissimilar cations but the same anion. The cations are of different nature and are hydrated by water dipoles. The crystallographic radii of Na^+ and NH_4^+ are (0.95 and 1.44) Å, respectively.[21] According to Vaslow's[22] concept of hydration, small cations normally enhance hydrogen bonded structural grouping in liquid water. As the radius of Na^+ is the smallest among the two, it may occupy the smallest space in the hydration sheath. For the larger radius of NH_4^+, it occupies a larger space in the hydration sheath than the Na^+; thus, the limiting apparent molar volumes of NaCl and NH_4Cl in water and in water + urea solution should follow the order $\phi_{\text{v}}^{\circ}(NH_4Cl) > \phi_{\text{v}}^{\circ}(NaCl)$. That is, the interaction of these electrolytes with the water dipole will increase in the order NaCl + H_2O < NH_4Cl + H_2O. This sequence is in reasonable agreement with the experimental values obtained in this study (Table 3).

In water and in water + urea solutions, the electrolytes $CuSO_4$ and $MgSO_4$ have the same anions (SO_4^{2-}) but their cations are of different nature. Both cations are divalent and the difference between their crystallographic radii is negligible,[16] which influences the ϕ_{v}° values. The crystallographic radius of Cu^{2+} is less than that of Mg^{2+}.[21] Thus, the limiting apparent molar volume of copper sulfate is expected to be less than that of magnesium sulfate. The results obtained in this study (Table 3) are in reasonable agreement with the expected value on the basis of the ionic radius.

Copper(II) chloride ($CuCl_2$) and copper(II) sulfate ($CuSO_4$) contain the same cations, but their anions are Cl^- and SO_4^{2-}, respectively. The behaviors of cations and anions differ essentially in the presence of each other, which may influence the water structure differently. The large size of Cl^- and SO_4^{2-} anions may occupy a larger space in the hydration sheath. The SO_4^{2-} should be more highly solvated than the Cl^- due to its higher number of electronegative groups. Sulfate ion, containing four oxygen atoms, may enhance the formation of hydrogen bonding in water solutions.[23]

Among the electrolytes studied (NaCl, NH_4Cl, $CuCl_2$, $CuSO_4$, and $MgSO_4$), the ϕ_{v}° value obtained for $MgSO_4$ is seen to be abnormally higher than those of the other electrolytes (shown in Table 3). This abnormality may be accounted for by the fact that Mg^{2+} can form an octahedral complex with water.

The viscosity (η) and viscosity A and B coefficients for the chosen electrolytes in water and in water + urea solutions at (308.15, 313.15, and 323.15) K are shown in Tables 2 and 3, respectively. The representative plots of η versus molality are shown in Figure 2 as examples (figures for the other electrolytes $CuCl_2$, $CuSO_4$, and $MgSO_4$ in water and 1 and 5 mol·kg^{-1} urea solutions are not shown for similar nature). The values of η are seen to increase with the increase in molality for all studied electrolytes except NH_4Cl. The B coefficient values for all the electrolytes in water and in water + urea solutions at all temperatures are seen to be positive, except that for NH_4Cl. The value is negative for NH_4Cl salt in water and in a low concentration of urea (1 mol·kg^{-1}) solution. The B coefficient values for all the electrolytes are seen to be higher in water + urea solvent systems than those in a water system alone and show an increasing trend as the

Table 3. Partial Molar Volumes at Infinite Dilution ϕ_v^o, Viscosity Coefficients A and B for Different Electrolytes in Pure Water, Water +1m Urea and Water +5m Urea Solutions at (308.15, 313.15 and 323.15) K

		ϕ_v^o/cm^3 mol^{-1} at			A- coefficient values at			B− coefficient values at		
Salts	Solvent systems	308.15 K	313.15 K	323.15 K	308.15 K	313.15 K	323.15 K	308.15 K	313.15 K	323.15 K
NaCl	H_2O	17.1	17.2	17.6	0.0247	0.0390	0.0590	0.0152	0.0278	0.0317
	H_2O+1 mol.kg^{-1} urea	17.3	17.5	17.9	−0.0151	−0.0251	−0.0292	0.0524	0.0728	0.0822
	H_2O+5 mol.kg^{-1} urea	17.9	18.2	18.6	−0.1256	−0.0329	−0.0935	0.1521	0.1625	0.1124
NH_4Cl	H_2O	36.5	36.8	37.2	0.0289	0.0342	0.0489	−0.0397	−0.0265	−0.0424
	H_2O+1 mol.kg^{-1} urea	36.7	37.0	37.5	−0.0376	−0.0348	−0.0236	−0.0056	−0.0032	−0.0019
	H_2O+5 mol.kg^{-1} urea	37.3	37.6	38.0	−0.0356	−0.0365	−0.0308	0.0269	0.0388	0.0494
$CuCl_2$	H_2O	51.6	51.9	52.3	0.0359	0.0369	0.0309	0.2662	0.2722	0.3059
	H_2O+1 mol.kg^{-1} urea	52.1	52.6	53.0	−0.0167	−0.0199	−0.0545	0.3255	0.3390	0.3795
	H_2O+5 mol.kg^{-1} urea	52.9	53.2	53.8	−0.0684	−0.0741	−0.0500	0.4533	0.4585	0.4793
$CuSO_4$	H_2O	88.0	88.3	88.9	−0.0130	0.0152	−0.0287	0.6768	0.7034	0.7207
	H_2O+1 mol.kg^{-1} urea	88.8	89.2	88.9	−0.0844	−0.0769	−0.0566	0.7618	0.7490	0.7721
	H_2O+5 mol.kg^{-1} urea	89.5	89.9	40.3	−0.0429	−0.0904	−0.0652	0.6835	0.8097	0.8598
$MgSO_4$	H_2O	126.2	126.6	126.9	0.0056	0.0002	0.0134	0.6800	0.6948	0.6898
	H_2O+1 mol.kg^{-1} urea	127.1	127.5	127.9	−0.0745	−0.0533	0.0445	0.8194	0.8091	0.8304
	H_2O+5 mol.kg^{-1} urea	128.0	128.3	128.8	−0.0462	−0.0910	−0.1372	0.8609	0.8865	0.9006

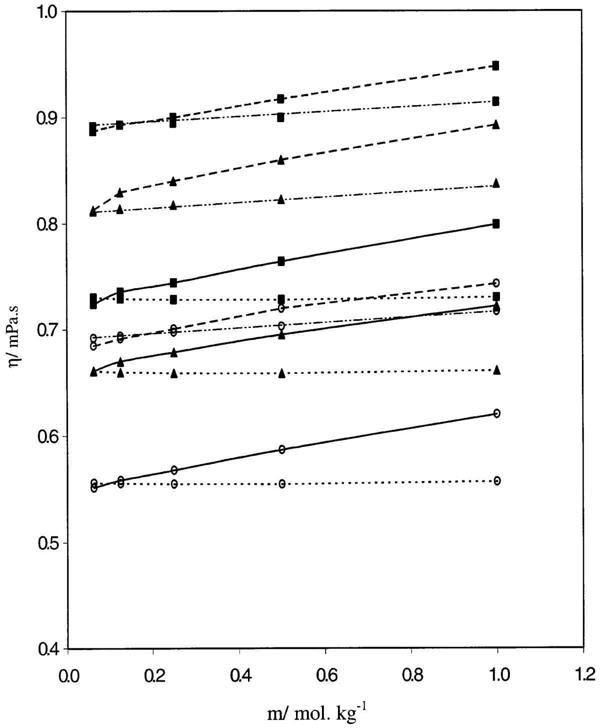

Figure 2. Plots of viscosity (*η*) versus *m* for (a) ammonium chloride (dotted line) and sodium chloride (solid line) in water and (b) ammonium chloride (long dashed–dotted line) and sodium chloride (dashed line) in water + 5 mol·kg^{-1} urea solutions at the following temperatures: ■, 308.15 K; ▲, 313.15 K; ○, 323.15 K.

concentration of urea is increased. The positive value of the *B* coefficient corresponds to the structure making behavior, and the negative values correspond to the structure breaking behavior of the solutes for water. The negative *B* coefficient values for NH_4Cl clearly indicate that it acts as a water structure breaker.

It is seen from Table 3 that in water solution $CuCl_2$, $CuSO_4$, and $MgSO_4$ have large positive *B* coefficient values. This indicates that these electrolytes exhibit structure making behavior in water. The divalent cations of these electrolytes are of the same nature, and their sizes are approximately equal to one another.[21] The viscous abilities as well as the structure making abilities of these electrolytes are seen to be approximately equal. Their *B* coefficient values are comparatively larger than those of the other electrolytes containing chloride as the anion. This indicates that in the presence of SO_4^{2-} the structure making ability of these electrolytes is higher than those in the presence of the Cl^-. The high structure making ability of SO_4^{2-} is due to its electrostatic charge and four oxygen atoms, which may enhance the formation of hydrogen bonds in water solution.[23] Thus, the solution is highly viscous in the presence of SO_4^{2-} and the viscosity coefficient *B* is large.

The increase in the *B* coefficient values for $CuCl_2$, $CuSO_4$, and $MgSO_4$ with the increase in urea molality indicates that these electrolytes must be in a progressively more structured environment as urea molality is increased. In ternary (H_2O + urea + electrolytes) solutions, urea + polar group interactions disrupt the less structured region around them and the water molecules move toward the more structured bulk region, resulting in an increase in viscosity. The urea + hydrophobic group interactions decrease the structure enforcing ability, thereby decreasing the viscosity. The predominance of urea–polar group interactions over urea + hydrophobic group interactions gives a net increase in viscosity. The urea + electrolytes, urea + urea, and urea + water interactions progressively enhance the overall structure of the solution as the molality of urea is increased, accounting thereby for the increase in the *B* coefficient value with the molality of urea.

In the case of NaCl, the viscosity coefficient *B* is very small and positive in water solution. The small size as well as the monovalent nature of the cation and the anion of the electrolyte is in agreement with its low viscous ability. The *B* coefficient value for NaCl increases with the increase in urea molality. Ammonium chloride causes no significant change in *η* values in water and in 1 mol·kg^{-1} water + urea solution systems (shown in Table 2). The initial slight decease in viscosity may be attributed to the destruction of the tetrahedrally bonded water clusters.

The *B* coefficient values for NH_4Cl are positive in 5 mol·kg^{-1} urea solution. Due to high concentration (5 mol·kg^{-1}) of urea, the water molecules are more structured. The NH_4Cl salt, a relatively weaker water structure breaker, cannot overcome the structure making ability of urea solution at high concentration (5 mol·kg^{-1} urea solution), causing the *B* coefficient value for NH_4Cl to be positive.

For an ion to fit into a cavity formerly occupied by a water molecule, its radius must be less than or equal to that of a water molecule (1.38 Å). This type of ions should fit into such a cavity without disruption of the water structure (the primary and secondary hydration layers about this cavity).[23] Ammonium ion, whose radius is 1.44 Å,[21] would be expected to disrupt the primary hydration layer. Furthermore, this would also result in a disruption of the secondary hydration layer. This disruption should lead to a weakening of the bonds holding this water molecule together in this hydration layer. These disruptions always lead to structure breaking effects in water and in water + 1 mol·kg^{-1} urea solution. Thus, the large monovalent NH_4^+ ions generally have a net structure breaking or entropy increasing effect. Because of the dipole−dipole repulsion between solvation shell molecules, the relatively weak electrostatic field about such ions can cause polarization, immobilization, and electrostriction of water molecules only in the first layer. Beyond this layer, a strong structure breaking effect persists. Thus, ions such as $NH_4^+$and Cl^- actually increase the fluidity of the solvent. These viscometric data are in excellent agreement with those obtained from volumetric data.

The coefficient *A* represents the solute−solute interactions coupled with the size and shape effects of the solute and to some extent solute−solvent interactions. Due to the lack of adequate theoretical knowledge, its significance is not fully understood.[24] In this study an irregular variation in the values of *A* coefficient is found (shown in Table 3).

The value of *A* has been found to decrease with the rise of temperature. This is probably due to the greater thermal agitation and reduction of attractive forces between the ions.[25] The increase in the *A* value can be explained by the interpenetration effect, which brings the ions closer together.[26] It is found that the majority of *A* coefficient values are negative in aqueous urea solutions and positive in aqueous solutions. This indicates that, in aqueous solution, ion−ion interactions are not prevented by the solvent (relatively low structural) but, in aqueous urea solution, the solvent (relatively high structural) prevents the ion−ion interaction. Positive *A* values for aqueous solutions of NaCl or NH_4Cl and negative values for $MgSO_4$, $CuSO_4$, or $CuCl_2$ were observed. This may be due to the higher charge-to-radius ratio for Mg^{2+} and Cu^{2+} in comparison to those of the other cations. For this reason, these ions cannot come closer for repulsion, but the Na^+ and NH_4^+, having relatively smaller charge-to-radius ratios, come closer for the weaker repulsive forces, increasing the *A* values.

Conclusions

Urea acts as a structure maker for water at the studied temperatures. Sodium chloride acts as a weak structure maker for water. Ammonium chloride, on the other hand, exhibits structure breaking behavior in water and in water + 1 mol·kg^{-1} urea solution. In 5 mol·kg^{-1} urea solution, NH_4Cl acts as a structure maker; that is, the structure breaking tendency of NH_4Cl is overcome by the structure making behavior of urea in solution. Copper(II) chloride, copper sulfate, and magnesium sulfate exhibit structure making behavior in water and in water + urea solutions.

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