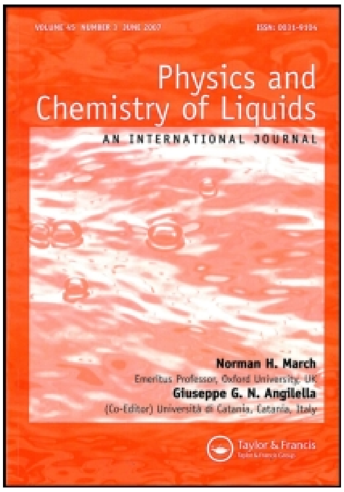

Physics and Chemistry of Liquids
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

Volumetric and Viscometric Studies on Some Inorganic Electrolytes in Water and in Water-SDS Solution Systems

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To cite this Article Afroz, Shahina , Motin, Muhammad A. , Biswas, Tapan K. and Huque, Entazul M.(2003) 'Volumetric and Viscometric Studies on Some Inorganic Electrolytes in Water and in Water-SDS Solution Systems', Physics and Chemistry of Liquids, 41: 3, 249 — 262

To link to this Article: DOI: 10.1080/0031910021000061033

URL: http://dx.doi.org/10.1080/0031910021000061033

Physics and Chemistry of Liquids
2003, Vol. 41, No. (3), pp. 249–262

VOLUMETRIC AND VISCOMETRIC STUDIES ON SOME INORGANIC ELECTROLYTES IN WATER AND IN WATER–SDS SOLUTION SYSTEMS

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(Received 13 August 2002)

The apparent molal volumes (ϕ_v) of NaCl, $NaNO_3$, NH_4Cl, $CuCl_2$, $CuSO_4$, $CoSO_4$ and $MgSO_4$ in water and in water–SDS (Sodium dodecyl sulphate) solutions were determined from density measurements at 308.15, 313.15 and 323.15 K respectively. The limiting apparent molal volume at infinite dilution (ϕ_v^o) which is practically equal to the partial molal volume ($\bar{V}_2^o$) of these electrolytes were found to be higher in water–SDS solution systems than those in water solutions. Viscosity coefficients (A and B) for these systems were also determined by Jones–Dole equation. All these electrolytes, except NH_4Cl exhibit structure making behaviour in water and in water–SDS solutions. Ammonium chloride showed structure breaking properties in water and in 0.01 molar water–SDS solutions. In 0.1 molar SDS solution, it showed structure making behaviour at the temperature range studied. The properties of these electrolytes in water and in water–SDS solution systems have been discussed in terms of the charge, size and hydrogen bonding effect.

Keywords: Apparent molal volume; Viscosity coefficient; Activation parameters; Hydrogen bonding

1. INTRODUCTION

Surfactant molecules in water solution at low concentration exist in monomeric form and behave like normal electrolyte or non-polar molecule. However, increase concentration of the surfactant an abrupt change in several physicochemical properties of the solution such as osmotic pressure, electrical conductance, surface tension, viscosity, apparent molal volume etc. is observed. This behaviour of surfactant solution is ascribed to be due to the formation of multi-molecular aggregates, called micelles [1]. Micelle formation is a typical hydrophobic process [2]. In water medium, surfactant molecules with their long hydrophobic tails undergo hydrophobic hydration. The concentration at which the micelle first appears is referred to as the critical micelle concentration (CMC). Above this concentration micelles are in dynamic equilibrium with monomeric form of the surfactant in the bulk phase. Surfactants in water solutions generally form spherical micelles just above the CMC and associate further to form

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ISSN 0031-9104 print: ISSN 1029-0451 online
DOI: 10.1080/0031910021000061033

rod-like micelles at higher concentration. An increase in size and polydispersity of SDS (sodium dodecyl sulphate) micelles with increase surfactant concentration in solutions of high salt concentration has been reported by a number of researchers [3–5]. Ikeda *et al.* [5] explained these changes as due to the equilibrium between two types of micelles; a small micelle formed at the CMC and a larger micelle formed at a higher concentration. A limited thermodynamic analysis of the growth of SDS micelles with increase surfactant and electrolyte concentration has been studied earlier [6]. The changes occur on addition of electrolyte to water solutions of SDS have been gaining interest in recent years. Mazer and co-workers [3,4] reported that at a fixed SDS concentration and temperature, an increase concentration of added sodium chloride over the range 0–0.6 M resulted a dramatic increase in micellar weight and a change in shape from roughly spheroidal aggregates to a polydisperse distribution of spherocylindrical aggregates. The presence of rod-like micelles in water solution of SDS in 0.6 M NaCl at temperature below 40°C was later confirmed by Young *et al.* [7]. Some limitations of these studies were pointed out by Hayashi and Ikeda [8] who investigated the effect of electrolyte on SDS micelles using classical light scattering methods. A transition from spherical to rod-like-micelles was noted when the concentration of added sodium chloride was increased beyond 0.45 M and the concentration of the SDS was well in excess of the CMC.

Here we report the effect of some simple inorganic electrolytes on the structure of water and water–SDS solution systems using apparent molal volume and viscosity coefficient data. Micelle forming molecules SDS may force water to be in certain structural form in the water–SDS system. The perturbations of this forced structure of water in water–SDS system, by some electrolytes are expected to be appreciable than the perturbation caused by these salts in water system alone. Two types of electrolytes were chosen for the purpose. In one type the anions were same but the cations were different. In other, 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–SDS structure differently which may be reflected in the apparent molal volume and viscosity coefficient data. This type of study on simple systems, sometimes provides very useful information regarding the structure of many complex systems.

2. EXPERIMENTAL

Sodium dodecyl sulphate and sodium nitrate (>98%), sodium chloride (>99%), ammonium chloride (99%), copper chloride (>98%), copper sulphate (98%) and magnesium sulphate (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 vacuum over phosphorus pentoxide for at least 24 h and were then used without further purification. Doubly distilled water were used for making solution and density were measured by using a 10 mL bicapillary pycnometer previously calibrated by water. Viscosity were measured by calibrated U-type Ostwald viscometer of the British standard institution with sufficiently long efflux time to avoid kinetic energy correction. Time of flow was recorded by a timer accurate up to ±0.01 s. A METTLER PM-200 electronic balance with an accuracy of ±0.0001 g was used for weighing. Temperatures were controlled by a thermostatic water bath fluctuating to ±0.1°C.

3. RESULTS AND DISCUSSION

Volumetric properties of the electrolytes NaCl, $NaNO_3$, NH_4Cl, $CuCl_2$, $CuSO_4$, $CoSO_4$ and $MgSO_4$ in water and in water–SDS solutions were measured at 308.15, 313.15 and 323.15 K respectively. The apparent molal volume (ϕ_v) of the electrolytes were tabulated in Table I and their representative plots are shown in Figs. 1 and 2 (for similar nature, figures for the electrolytes in 0.01 M SDS and for $NaNO_3$, $CuSO_4$ and $CuCl_2$ in water and in water–0.1 M SDS solutions are not shown). The apparent molal volume is found to be dependent upon the electrolyte concentration as well as on the temperature. Plots of ϕ_v *versus* square root of the molality of the electrolytes show a linear relationship. This relation is also seen in case of temperature rise i.e. at higher temperature, the ϕ_v value is also higher at least at the chosen three temperatures. The increase value of ϕ_v with molality of the electrolyte suggests that the ion-solvent interactions increase with the increase in molality of the electrolytes. At a fixed concentration of SDS and at a certain temperature the increase of ϕ_v with the concentration of added electrolytes in the range 0.05–0.45 M is probably due to the increase in micellar weight and a change in shape from roughly spheroidal aggregates to a spherocylindrical aggregates. The limiting apparent molal volume (ϕ_v^o) which is taken to be the partial molal volume of the solute slightly changes with the temperature. Such temperature dependence may be interpreted using the model suggested by Frank and Wen for water solutions of electrolyte [9]. 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 an increase in ϕ_v^o. 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 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 a net positive change in volume. However, the temperature coefficient of $CuSO_4$, $CoSO_4$ and $MgSO_4$ are seen to be much higher than any other salt in this study. Weak ion–water interactions in the case of large-sized SO_4^{2-} perhaps transfers water molecules from structure broken region to the structured bulk region easily producing large positive volume change at higher temperatures.

The limiting apparent molal volume (ϕ_v^o) reflects 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 surfactant concentration and temperature may reflect the change in its environment in the micellar systems. Increase temperature may cause the desolvation of micelle and their counterions providing thus an easier access for additive into the more hydrophobic-like interior of the micelle. The value of ϕ_v^o for all the electrolytes studied are higher in water–SDS solutions than those in water solutions only. This suggests that electrolyte molecules are likely to be in a micellar-like environment where there is relatively less free space than in the electrolyte in water environment.

The salt sodium chloride and ammonium chloride contain monovalent dissimilar cations but same anion. The cations are of different nature. Both the ions are hydrated by water dipole. The crystallographic radius of Na^+ and NH_4^+ are 0.95 and 1.44 Å respectiely [10]. According to Vaslows [11] concept of hydration, small cations normally

TABLE I Apparent molal volumes (ϕ_v in cm^3 mol^{-1}) for NaCl, $NaNO_3$, NH_4Cl, $CuC1_2$, $CuSO_4$, $CoSO_4$ and $MgSO_4$ in water, water–0.01M SDS and water–0.1M SDS solutions at 308.15, 313.15 and 323.15 K respectively

Concentration (mol kg^{-1})	ϕ_v *at* 308.15 K							ϕ_v *at* 313.15 K							ϕ_v *at* 323.15 K						
	NaCl	*$NaNO_3$*	*NH_4Cl*	*$CuCl_2$*	*$CoSO_4$*	*$CuSO_4$*	*$MgSO_4$*	*NaCl*	*$NaNO_3$*	*NH_4Cl*	*$CuCl_2$*	*$CuSO_4$*	*$CoSO_4$*	*MgSo$_4$*	*NaCl*	*$NaNO_3$*	*NH_4Cl*	*$CuCl_2$*	*$CuSO_4$*	*$CoSO_4$*	*$MgSO_4$*
In water solution																					
0.0503	17.45	28.10	37.25	52.91	91.10	113.98	128.75	17.95	28.70	37.70	54.22	91.90	117.43	130.05	18.75	29.90	38.25	55.54	93.75	120.91	132.06
0.1513	17.89	28.90	37.51	54.45	91.90	116.93	130.60	18.39	29.55	37.92	55.27	93.30	119.80	132.14	19.35	30.80	38.55	56.02	94.80	122.66	134.01
0.2526	18.28	29.61	37.79	54.94	92.95	118.55	131.36	18.75	30.25	38.28	55.75	94.18	121.71	133.18	19.70	31.19	38.80	56.94	95.49	124.83	135.69
0.3544	18.50	30.01	38.02	55.65	93.84	120.55	132.94	19.10	30.90	38.50	56.55	95.05	123.77	134.22	20.05	31.98	39.10	57.76	96.69	126.88	137.87
0.4566	19.05	30.90	38.35	56.28	95.10	122.95	133.96	19.40	31.40	38.80	56.96	96.55	125.05	135.79	20.40	32.55	39.38	58.58	97.62	128.34	138.91
In water + 0.01 M SDS solution																					
0.0503	18.05	29.20	37.61	53.75	91.76	117.59	130.18	18.52	29.92	37.98	54.47	92.66	120.05	131.23	19.25	30.68	38.50	55.68	94.31	112.07	135.00
0.1511	18.48	30.10	37.98	54.72	92.74	119.89	131.74	18.91	30.85	38.25	55.25	93.72	122.27	133.39	19.70	31.45	38.78	56.57	95.51	124.27	136.54
0.2526	18.95	30.83	38.22	55.04	93.57	120.49	132.92	19.41	31.51	38.55	55.96	94.85	123.24	134.14	20.15	32.26	39.19	56.93	96.55	125.99	137.14
0.3542	19.30	31.55	38.50	55.92	94.69	121.90	133.86	19.80	32.15	38.85	56.75	95.99	124.43	135.13	20.50	32.80	39.46	58.04	97.32	127.62	138.97
0.4565	19.80	32.20	38.80	56.45	95.82	123.69	134.23	20.26	32.80	39.14	57.28	96.28	125.13	136.01	20.90	33.38	39.88	58.47	98.74	128.65	139.77
In water + 0.1 M SDS solution																					
0.0503	18.90	30.35	37.98	54.45	92.71	119.90	131.48	19.45	31.10	38.45	55.50	93.54	121.95	133.35	20.15	31.75	38.87	56.70	95.40	123.98	136.66
0.1518	19.30	31.23	38.46	55.50	93.80	121.71	133.05	19.90	31.85	38.70	56.46	95.37	123.98	134.75	20.62	32.50	39.20	57.51	96.88	126.50	137.39
0.2542	19.78	31.90	38.75	56.08	94.87	123.26	133.55	20.41	32.58	39.15	56.95	96.45	125.61	135.71	21.21	33.25	39.66	57.97	97.99	127.88	138.90
0.3581	20.20	32.50	38.85	56.78	95.78	125.36	134.64	20.88	33.15	39.50	57.72	98.37	127.62	136.12	21.60	33.75	40.02	58.83	99.07	129.98	139.81
0.4632	20.51	32.90	39.25	57.15	96.80	127.07	135.92	21.05	33.55	39.79	58.71	99.44	129.35	137.60	22.00	34.30	40.39	59.50	100.10	131.95	140.87

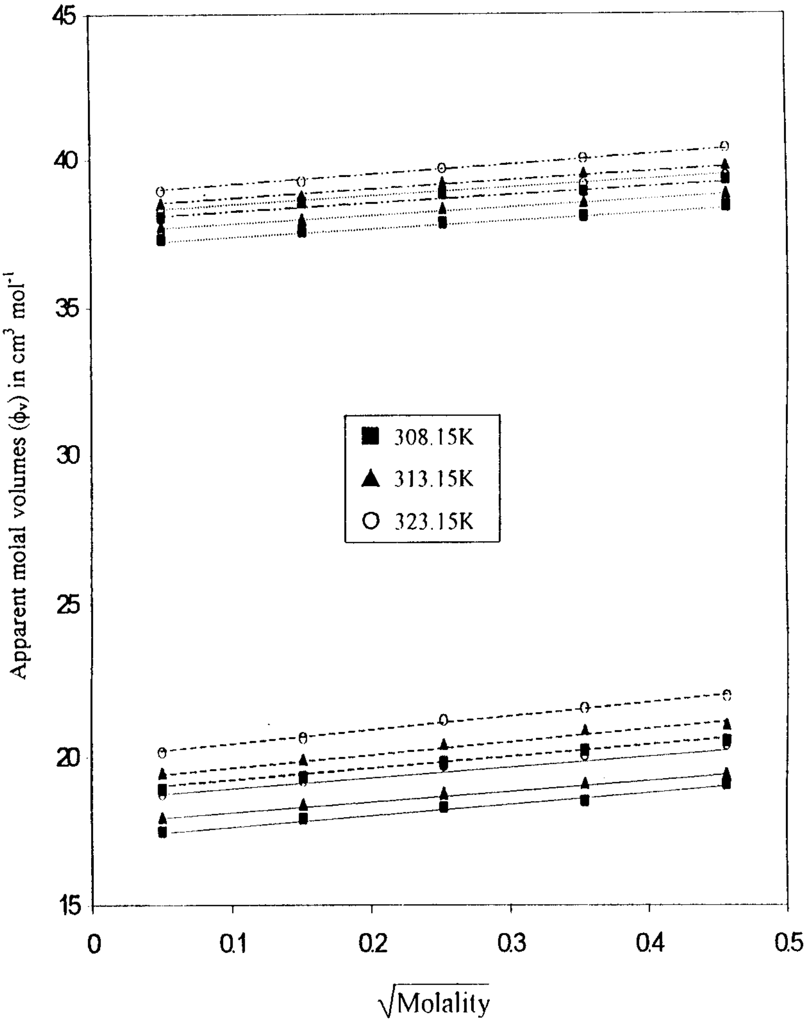

FIGURE 1 Plots of apparent molal volume (ϕ_v) *versus* $\sqrt{\text{Molality}}$ for (a) Sodium chloride (solid line) and ammonium chloride (dotted line) in water; (b) Sodium chloride (dashed line) and ammonium chloride (dashed–dotted line) in water–0.1 M SDS solutions at 308.15, 313.15 and 323.15 K respectively.

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 large space in hydration sheath than the Na^+, thus the limiting apparent molal volume of NaCl and NH_4Cl in water and in water–SDS solution should follow the order ϕ_v^o NH_4Cl > ϕ_v^o NaCl. That is the interaction of these electrolytes with 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 III).

In case of NaCl and $NaNO_3$ the cations are the same but the anions are of different nature. The cation is Na^+ and anions are Cl^- and NO_3^-. The latter ions must play an important role in determining the structure of water and forces it to get final configuration of the solution [12]. For large size of Cl^- and NO_3^-, they occupy relatively larger

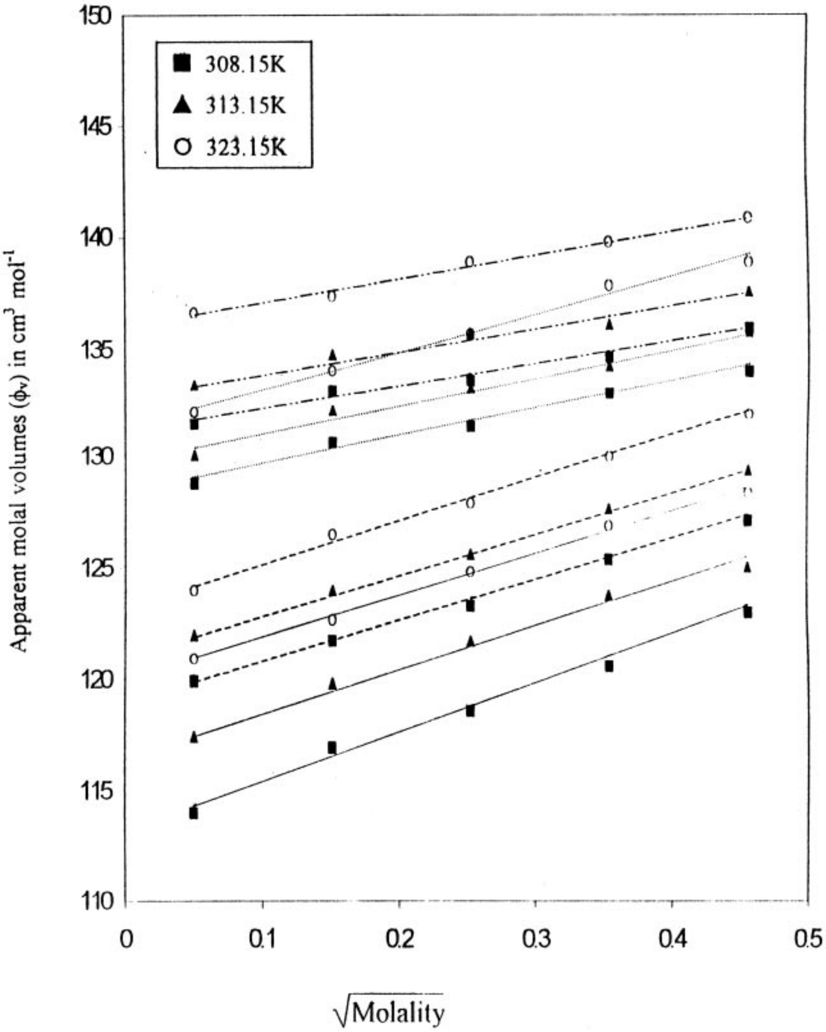

FIGURE 2 Plots of apparent molal volumes (ϕ_v) *versus* $\sqrt{\text{Molality}}$ for (a) Cobalt sulphate (solid line) and magnesium sulphate (dotted line) in water; (b) Cobalt sulphate (dashed line), magnesium sulphate (dashed–dotted line) in water–0.1 M SDS solutions at 308.15, 313.15 and 323.15 K respectively.

space in the hydration sheath. The NO_3^- is highly polar than Cl^- due to its higher oxygen content (three oxygen atoms) which may enhance the formation of hydrogen bond in water solution [13]. This is clearly indicated in the higher ϕ_v^o values of nitrate ion containing electrolyte than the Cl^- containing electrolyte i.e. ϕ_v^o of $NaNO_3 > \phi_v^o$ of NaCl.

In water and in water–SDS solutions, the electrolytes $CuSO_4$, $CoSO_4$ and $MgSO_4$ have the same anions (SO_4^{2-}) but their cations are of different nature. The three cations are divalent and their Crystallographic radius has very little difference [10] which influence the ϕ_v^o values. The crystallographic radius of Cu^{2+} is less than that of Co^{2+} [10]. Thus the limiting apparent molal volume of copper sulphate is expected to be less than those of cobalt sulphate. The results obtained in this study (Table III) are in reasonable agreement with the expected value on the basis of the ionic radius.

Copper(II) chloride ($CuCl_2$) and copper(II) sulphate ($CuSO_4$) contain same cations but their anions are Cl^- and SO_4^{2-} respectively. The behaviour of cations and anions differ essentially in presence of each other which may influence the water structure differently. The large size of Cl^- and SO_4^{2-} anions may occupy larger space in the hydration sheath. The SO_4^{2-} should be highly solvated than the Cl^- due to its higher electronegative group. Sulphate ion containing four oxygen atoms may enhance the formation of hydrogen bond in water solutions [13]. The higher ϕ_v^o values of sulphate containing salt than those of Cl^- containing salt can be accounted for by this reasoning i.e. ϕ_v^o of $CuSO_4$ > ϕ_v^o of $CuCl_2$.

The variation of ϕ_v^o values with SDS molarity can be rationalized in terms of the cosphere overlap model [14]. According to this model, the overlap of the cospheres of two ions or polar groups and an ion with that of a hydrophilic groups, always produces positive volume change. On the other hand the overlap of cosphere of an ion with that of a hydrophobic group results in a negative volume change. In the present ternary system, the overlap of cospheres of SDS–SDS and SDS–hydrophilic groups of electrolyte interactions takes place. The overlap of cospheres of SDS gives positive change in volume due to the relaxation of the electrostricted water molecules from its cosphere to the bulk. The overlap of the cospheres of SDS with those of hydrophilic group of salts results positive change in volume. The relaxation of the electrostricted water molecules due to strong localized interactions from the cospheres of both salts and SDS causes an increase in volume. The postive volume change due to overlap of the cospheres of SDS with those of SDS and hydrophilic part of the salts outweighs the negative volume change due to the overlap of hydrophobic part of SDS and salts (negligible) giving greater ϕ_v^o value in SDS compared to that in water. The water–water and water–SDS interaction seems to be the same and do not produce considerable change in volume.

The viscosity (η) and viscosity A and B-coefficient for the chosen electrolytes in water and in water–SDS solutions at 308.15, 313.15 and 323.15 K are shown in Tables II and III respectively. The representative plots of η *versus* molality are shown in Figs. 3 and 4. The values of η are seen to increase with the increase in molality for all studied electrolytes except NH_4Cl in both the solvent systems. The B-coefficient value for all the electrolytes in water and in water–SDS solutions at all temperatures are seen to be positive except NH_4Cl. The value, is negative for NH_4Cl salt in water and in low concentration of SDS (0.01 M) solution. The B-coefficient values for all the electrolytes are seen to be higher in water–SDS solvent systems than those in water system alone and show an increasing trend as the concentration of SDS is increased. The positive value of the B-coefficient corresponds to the structure making behaviour and the negative values correspond to the structure breaking behaviour of the solutes for water. The negative B-coefficient values for NH_4Cl clearly indicate that it acts as water structure breaker.

It is seen from the Table III that in water solution $CuCl_2$, $CuSO_4$, $CoSO_4$ and $MgSO_4$ have large positive B values. This indicates that these electrolytes exhibits structure making behaviour in water. The divalent cations of these electrolytes are of same nature and their size is approximately equal to one another [10]. The viscous ability as well as structure making ability of these electrolytes are seen to be approximately equal and their viscosity coefficient B is very similar. Their B values are comparatively larger than those of the other electrolytes containing chloride as the anion. This indicates that in presence of SO_4^{2-} the structure making ability of these electrolytes is

TABLE II Viscosity (η in cP) for NaCl, NaNO$_3$, NH$_4$Cl, CuCl$_2$, CuSo$_4$, CoSO$_4$ and MgSO$_4$ in water, water–0.01 M SDS and water–0.1 M SDS solutions at 308.15, 313.15 and 323.15 K respectively

Concentration (mol kg^{-1})	η *at* 308.15 K							η *at* 313.15 K							η 323.15 K						
	NaCl	*NH$_4$Cl*	*NaNO$_3$*	*CuCl$_2$*	*CuSO$_4$*	*CoSO$_4$*	*MgSo$_4$*	*NaCl*	*NH$_4$Cl*	*NaNO$_3$*	*CuCl$_2$*	*CuSO$_4$*	*CoSO$_4$*	*MgSO$_4$*	*NaCl*	*NH$_4$Cl*	*NaNO$_3$*	*CuCl$_2$*	*CuSo$_4$*	*CoSo$_4$*	*MgSo$_4$*
In water solution																					
0.0503	0.7247	0.7306	0.7324	0.7395	0.7428	0.7454	0.7405	0.6616	0.6614	0.6609	0.6680	0.6739	0.6751	0.6750	0.5522	0.5565	0.5655	0.5775	0.5628	0.5699	0.5648
0.1513	0.7364	0.7295	0.7422	0.7712	0.7922	0.7990	0.7988	0.6705	0.6608	0.6695	0.6975	0.7182	0.7255	0.7220	0.5590	0.5560	0.5705	0.6015	0.6005	0.6065	0.6054
0.2526	0.7450	0.7288	0.7525	0.8092	0.8380	0.8405	0.8405	0.6792	0.6603	0.6763	0.7380	0.7585	0.7615	0.7605	0.5682	0.5556	0.5784	0.6375	0.6319	0.6420	0.6398
0.3544	0.7542	0.7285	0.7606	0.8409	0.8866	0.8970	0.8890	0.6858	0.6598	0.6855	0.7620	0.8013	0.8140	0.8025	0.5742	0.5544	0.5858	0.6685	0.6685	0.6890	0. 6695
0.4566	0.7646	0.7310	0.7705	0.8790	0.9348	0.9490	0.9420	0.6959	0.6620	0.6992	0.7945	0.8482	0.8555	0.8580	0.5877	0.5570	0.5986	0.6972	0.7082	0.7390	0.7335
In water + 0.01 M SDS solution																					
0.0503	0.7360	0.7395	0.7403	0.7481	0.7545	0.7705	0.7548	0.6678	0.6706	0.6716	0.6781	0.6895	0.6795	0.6760	0.5574	0.5649	0.5725	0.5885	0.5732	0.5796	0.5767
0.1511	0.7481	0.7390	0.7495	0.7879	0.8062	0.8063	0.8192	0.6789	0.6702	0.6795	0.7145	0.7350	0.7386	0.7350	0.5679	0.5645	0.5756	0.6192	0.6071	0.6323	0.6165
0.2526	0.7569	0.7383	0.7585	0.8255	0.8495	0.8565	0.8852	0.6870	0.6695	0.6865	0.7585	0.7745	0.7758	0.7793	0.5780	0.5638	0.5840	0.6530	0.6497	0.6706	0.6626
0.3542	0.7660	0.7380	0.7675	0.8570	0.8992	0.9107	0.9012	0.6961	0.6691	0.6968	0.7890	0.8270	0.8339	0.8305	0.5877	0.5635	0.5925	0.6925	0.6794	0.7145	0.7100
0.4565	0.7744	0.7398	0.7820	0.8812	0.9485	0.9625	0.9590	0.7066	0.6710	0.7085	0.8167	0.8733	0.8763	0.8825	0.5974	0.5651	0.6085	0.7205	0.7262	0.7565	0.7502
In water + 0.1 M SDS solution																					
0.0503	0.8237	0.8412	0.8250	0.8151	0.8527	0.8283	0.8355	0.7475	0.7513	0.7390	0.7370	0.7855	0.7671	0.7797	0.6287	0.6382	0.6293	0.6247	0.6505	0.6315	0.6545
0.1518	0.8297	0.8362	0.8305	0.8756	0.8823	0.8833	0.8957	0.7535	0.7466	0.7487	0.7865	0.8070	0.8028	0.8095	0.6351	0.6299	0.6336	0.6581	0.6782	0.6896	0.6852
0.2542	0.8365	0.8222	0.8425	0.9709	0.9385	0.9396	0.9376	0.7646	0.7387	0.7550	0.8506	0.8451	0.8465	0.8452	0.6442	0.6205	0.6395	0.7325	0.7295	0.7260	0.7333
0.3581	0.8439	0.8480	0.8495	1.1324	0.9845	0.9942	0.9862	0.7732	0.7440	0.7650	0.9800	0.8980	0.9028	0.8990	0.6529	0.6450	0.6485	0.7729	0.7767	0.7653	0.7712
0.4632	0.8539	0.9034	0.8525	1.2400	1.0475	1.0556	1.0496	0.7845	0.8209	0.7705	1.1504	0.9432	0.9551	0.9455	0.6635	0.6850	0.6560	0.8896	0.8298	0.8178	0.8335

TABLE III Partial molal volumes at infinite dilution ($\phi_v^o \approx \overline{V}{}_2^o$), viscosity coefficients A and B, free energy of activation for viscous flow ($\Delta G^{o\ddagger}$) for different electrolytes in water, water–0.01 M SDS and water–0.1 M SDS solutions at 308.15, 313.15 and 323.15 K respectively

Salts	*Solvent systems*	ϕ_v^o ($cm^3 mol^{-1}$) *at*			*A-coefficient values at*			*B-coefficient values at*			$\Delta G^{o\ddagger}$ ($kJ mol^{-1}$) *at*		
		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	308.15 K	313.15 K	323.15 K
NaCI	H_2O	16.90	17.40	18.25	0.0050	0.0055	0.0050	0.0951	0.0940	0.0925	22.1657	22.1845	22.2626
	$H_2O + 0.01$ M SDS	17.30	17.75	18.55	0.0120	0.0125	0.0100	0.1178	0.1150	0.1125	25.6196	25.2283	25.5423
	$H_2O + 0.1$ M SDS	18.15	18.73	19.40	−0.365	−0.335	−0.325	0.5280	0.5250	0.5210	81.1814	81.1814	82.6356
$NaNO_3$	H_2O	26.90	27.45	28.50	0.008	0.006	0.010	0.1529	0.1520	0.1500	31.7433	31.9364	32.2344
	$H_2O + 0.01$ M SDS	27.77	28.35	29.25	0.006	0.004	0.015	0.1595	0.1560	0.1520	31.3976	31.3165	31.4770
	$H_2O + 0.1$ M SDS	29.10	29.70	30.60	−0.430	−0.425	−0.350	0.5909	0.5880	0.5790	92.0624	92.8754	93.8410
NH_4Cl	H_2O	36.82	37.20	37.75	0.030	0.028	0.025	−0.0375	−0.0360	−0.0350	6.3184	6.3916	6.3999
	$H_2O + 0.01$ M SDS	37.10	37.43	37.95	0.038	0.036	0.036	−0.0380	−0.0370	−0.0360	6.2929	6.1985	6.1600
	$H_2O + 0.1$ M SDS	37.45	37.80	38.30	−0.385	−0.380	−0.379	0.6660	0.6560	0.6170	103.4625	103.5105	103.6640
$CuCl_2$	H_2O	51.85	52.75	54.10	0.008	0.006	0.007	0.3850	0.3830	0.3810	68.0554	68.6661	69.8778
	$H_2O + 0.01$ M SDS	52.50	53.15	54.62	0.008	0.010	0.009	0.4250	0.4210	0.4180	73.3243	73.4037	75.0656
	$H_2O + 0.1$ M SDS	53.45	54.37	55.57	0.030	0.025	−0.200	1.0480	1.0450	1.0400	158.1147	157.9333	161.3617
$CuSO_4$	H_2O	89.55	90.50	92.05	0.015	0.014	0.0139	0.6115	0.6105	0.6070	104.6943	106.6786	108.8935
	$H_2O + 0.01$ M SDS	90.05	91.02	92.65	0.016	0.015	0.014	0.6550	0.6500	0.6480	110.8327	111.2038	114.2214
	$H_2O + 0.1$ M SDS	91.02	92.42	93.90	−0.387	−0.365	−0.337	1.1096	1.0720	1.0520	169.8430	18.5098	170.5832
$CoSO_4$	H_2O	111.50	114.30	117.90	0.008	0.007	0.007	0.6875	0.6860	0.6828	119.5124	120.8989	123.8479
	$H_2O + 0.01$ M SDS	114.55	116.60	118.95	0.010	0.009	0.008	0.7500	0.7450	0.7350	127.5560	128.9592	130.7549
	$H_2O + 0.1$ M SDS	116.70	118.60	120.85	−0.317	−0.303	−0.362	1.1271	1.1084	1.0650	170.3366	173.6965	176.3082
$MgSO_4$	H_2O	125.45	127.32	129.30	0.020	0.019	0.018	0.6500	0.6480	0.6430	114.0065	113.9192	119.6800
	$H_2O + 0.01$ M SDS	127.80	128.90	132.50	0.022	0.021	0.019	0.6865	0.6798	0.6650	120.3702	120.6005	122.5266
	$H_2O + 0.1$ M SDS	129.75	131.10	134.50	−0.377	−0.367	−0.347	1.0950	1.0780	1.0450	175.0287	175.1055	175.3911

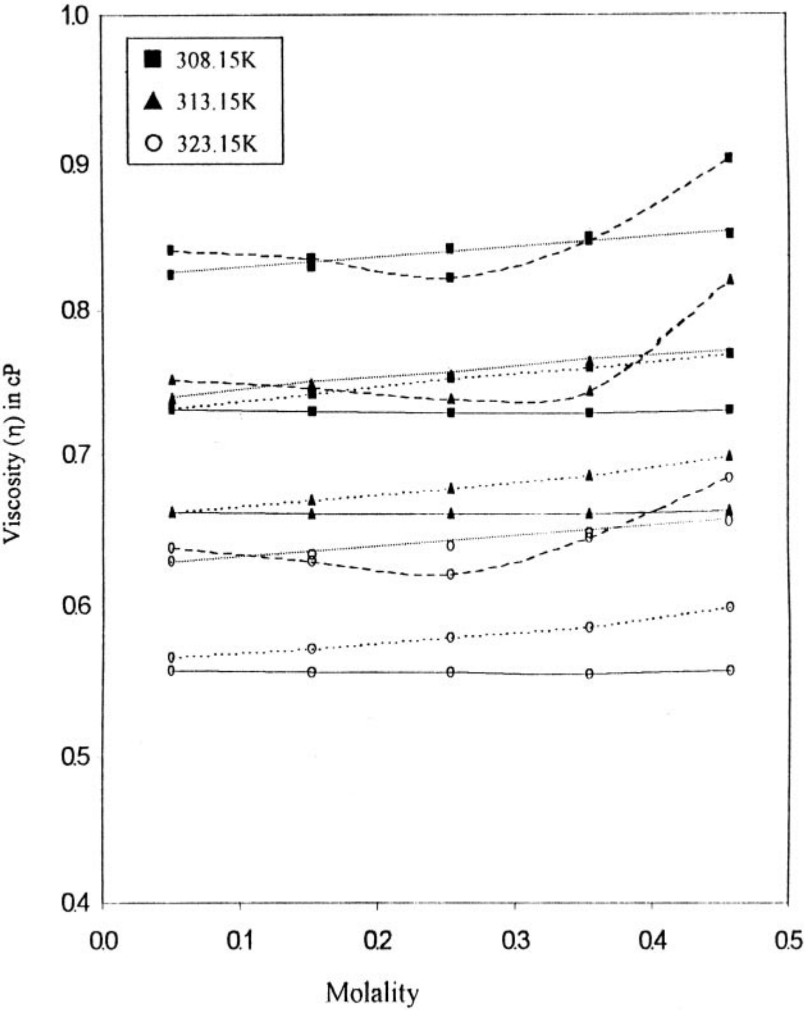

FIGURE 3 Plots of viscosity (η) *versus* molality for (a) Ammonium chloride (solid line) and sodium nitrate (dashed line) in water; (b) Ammonium chloride (long dashed line) and sodium nitrate (dotted line) in water–0.1 M SDS solutions at 308.15, 313.15 and 323.15 K respectively.

higher than those in 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 bond in water solution [13]. Thus the solution is highly viscous in presence of SO_4^{2-} and the viscosity coefficient B is large. This tendency is also observed in partial molal volume properties (described earlier).

The increase in B-coefficient value for $CuCl_2$, $CuSO_4$, $CoSO_4$ and $MgSO_4$ with the increase in SDS molality reveals that these electrolytes must be in a progressively more structured environment as SDS molarity is increased. In ternary ($H_2O + SDS +$ electrolytes) solutions, SDS–polar group interactions disrupt the less structured region around them and the water molecules move towards the more structured bulk region resulting in an increase in viscosity.

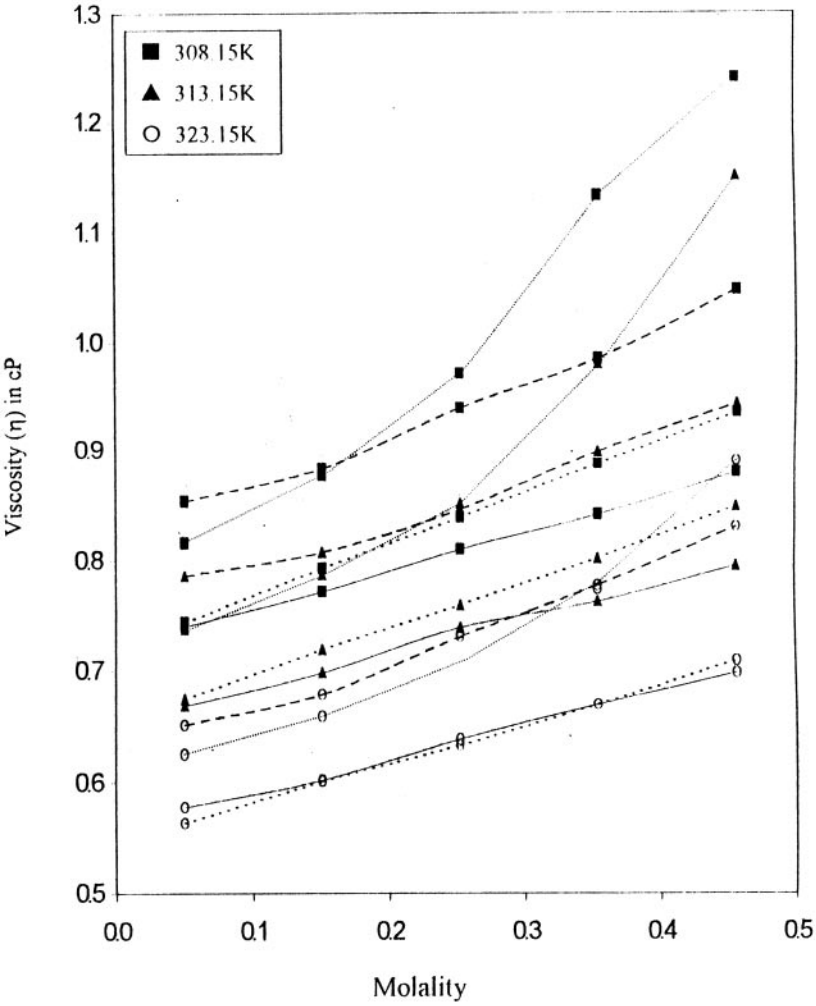

FIGURE 4 Plots of viscosity (η) *versus* molality for (a) Copper (II) chloride (solid line) and copper sulphate (dashed line) in water; (b) Copper (II) chloride (dotted line) and copper sulphate (long dashed line) in water–0.1M SDS solutions at 308.15, 313.15 and 323.15 K respectively.

The SDS–hydrophobic group interactions decrease the structure enforcing ability thereby decreasing the viscosity. The predominance of SDS–polar group interactions over SDS–hydrophobic group interactions gives a net increase in viscosity. The SDS–electrolytes, SDS–SDS and SDS–water interactions progressively enhance the overall structure of the solution as the molality of SDS is increased accounting thereby for the increase in B-Coefficient value with the molality of SDS.

In case of NaCl and $NaNO_3$ the viscosity coefficient B is very small and positive in water solution. Small sizes as well as the monovalent nature of the cations and anions of the electrolytes are in agreement with its low viscous ability. The B-coefficient value for NaCl and $NaNO_3$ increases with the increase in SDS molality. The viscosity (η) of NaCl and $NaNO_3$ solutions in SDS–water are smaller than the viscosity of SDS–water only. SDS contains Na^+ and the electrolytes also contain Na^+. For the common ion effect, probably the viscosity of those solutions becomes less than the viscosity of the solvent.

For NH_4Cl in water and in water–0.01 M SDS solution the viscosity decreases slightly with the concentration of salt and in water–0.1 M SDS solution the viscosity first decreases, then after certain concentration of the salt, the viscosity starts increasing (shown in Fig. 3). This indicates that NH_4Cl behaves as structure breaker in pure water and in dilute (0.01 M) SDS–water solution. The plots of the viscosity against molality for NH_4Cl (Fig. 3) in water–0.1 M SDS solution show a minimum, after which the viscosity starts increasing with the increase in salt molality. The initial decease in viscosity may be attributed to the destruction of the tetrahedrally bonded water clusters. However, the increase in viscosity with the increase in molality after the minimum may de due to the stiffness of the solution resulting from the hydrodynamic distortion of the fluid streamlines by the relatively large number of ions because such incremental contribution overcome the decrease in viscosity due to water structure breaking effect. The B-coefficient for NH_4Cl is positive in 0.1 molar SDS solution. Due to high concentration of (0.1 molar) SDS the water molecules are probably more structured. The NH_4Cl salt, a relatively weaker water structure breaker, perhaps cannot overcome the structure making ability of SDS solution at high concentration (0.1 M SDS solution) causing the B-coefficient value for NH_4Cl positive.

For an ion to fit into a cavity formerly occupied by water molecule, its radius must be less than or equal to that of water molecule (1.38 Å). This type of ions should fit into such cavity without disruption of the water structure (the primary and secondary hydration layers about this cavity) [13]. Ammonium ion whose radius is 1.44 Å [10] 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 molecules together in these hydration layer. These disruptions are always leads to structure breaking effects in water and in water–0.01 M SDS 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 solvent.

The coefficient ‘A’ represents the solute–solute interactions coupled with size and shape effect of the solute and to some extent solute–solvent interactions. Due to the lack of adequate theoretical knowledge its significance is not understood [15]. In the present study no regularity in ‘A’ value is found. Majority of ‘A’ values are positive. These positive ‘A’ value represents that the increase in viscosity with solute concentration is due to some additional factors other than the solute–solvent interactions (i.e. B-coefficient). Not only the solute–solvent interaction imparts positive contribution to the increase in viscosity with the increase electrolyte concentration, positive and negative contributions may also be operative as represented by the positive and negative sign of the A-coefficient respectively.

It is seen in the Table III that the free energy of activation per mole of solute ($\Delta G^{o\ddagger}$) for viscous flow of all the electrolytes in water, water–0.01 M and in water–0.1 M SDS solutions at the studied temperatures is positive. A positive $\Delta G^{o\ddagger}$ value indicates that the viscous flow is not favoured. During the viscous flow the molecules have to overcome the transition state of higher energy compared to that of the ground state. The positive free energy of activation of viscous flow has been studied earlier [13]. According to this concept, kinetic species involved in the viscous flow move into a cavity as hole and the work involved in forming this hole in the liquid medium is given by the work required in forming the hole against surface tension of the liquid. The higher positive $\Delta G^{o=}$ value indicates strong solute–solvent interaction rendering the solution more structured and difficult for hole creation. The positive $\Delta G^{o\ddagger}$ value indicates that the viscous flow is not favoured. This may be attributed to the fact that the ground state of the ternary system is more organized than the transition state which the system has to traverse during the viscous flow. In traversing the transition state significant bond breaking takes place resulting a positive free energy of activation for viscous flow. This means that the ground state is more organized and structured while the transition state is comparatively disordered due to the break down of the bond responsible for enforcement of solvent structure. As the concentration of SDS increases the ground state becomes more organized, as a result the net work done in traversing the transition state during viscous flow increases.

4. CONCLUSION

Volumetric and viscometric studies on the inorganic electrolytes in water and in water–SDS solutions reveal the following:

1. The electrolytes NaCl, $NaNO_3$ and NH_4Cl in water and in water–SDS solutions interact with the solvent differently. Sodium chloride and sodium nitrate interacts with the solvent and acts as a weak structure maker for water. Ammonium chloride on the other hand exhibits structure breaking behaviour for water in water and in water–0.01 M SDS solution. In 0.1 M SDS solution NH_4Cl acts as structure maker i.e. the structure breaking tendency of NH_4Cl is overcome by the structure making behaviour of SDS in solution.
2. Copper (II) chloride, copper sulphate, cobalt sulphate and magnesium sulphate exhibits structure making behaviour in water and in water–SDS solutions.
3. The higher structure making ability of all the studied electrolytes are higlier in water–SDS solution than those in water solutions indicates that electrolyte molecules are likely to be in a micellar like environment in water–SDS solution where there is relatively less free space than in the electrolyte in water environment. At a fixed SDS concentration and temperature, an increase concentration of added electrolytes results an increase in micellar size and micellar weight.
4. The positive free energy of activation, $\Delta G^{o\ddagger}$ for viscous flow for these electrolytic solutions indicate that the viscous flow is not favoured. As the concentration of SDS increase the ground state becomes more organized, as a result the net work done in traversing the transition state during viscous flow increases.

Acknowledgements

We acknowledge the Department of Chemistry, University of Rajshahi for providing laboratory facilities for the work. Muhammad A. Motin acknowledges the financial support of the ministry of science and technology, the government of the peoples republic of Bangladesh in the form of fellowship.

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