

# Volumetric studies of some electrolytes in water and in aqueous sodium dodecylsulfate solutions at different temperatures

Dulal Chandra Kabiraz · Tapan Kumar Biswas ·  
M. Entazul Huque

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**Abstract** The apparent molar volumes ( $\phi_v$ ) of KCl,  $\text{KNO}_3$ ,  $\text{MgCl}_2$ , and  $\text{Mg}(\text{NO}_3)_2$  have been determined in water and in aqueous sodium dodecylsulfate solutions from density measurements at 303.15, 308.15, 313.15, 318.15, and 323.15 K. The limiting apparent molar volumes ( $\phi_v^0$ ) and experimental slopes ( $S_v$ ) were derived from the Masson equation. The partial molar volume transfer ( $\Delta\bar{V}_{tr}$ ) of the electrolytes were obtained from limiting apparent molar volume data from water to aqueous sodium dodecylsulfate solutions and have been interpreted in terms of ion–ion, hydrophilic–hydrophilic, and hydrophobic–hydrophobic interactions on the basis of a co-sphere overlap model. It is shown that the transfer volumes ( $\Delta\bar{V}_{tr}$ ) are positive and increase with increasing sodium dodecylsulfate concentration for all electrolytes. The structure making or breaking capacities of the electrolytes have been inferred from the sign of  $[\partial^2\phi_v^0/\partial T^2]_p$ , i.e., the second derivative of the limiting apparent molar volume with respect to temperature at constant pressure. In water, KCl and  $\text{KNO}_3$  exhibit structure breaking and  $\text{MgCl}_2$  and  $\text{Mg}(\text{NO}_3)_2$  exhibit structure making behavior. All the studied electrolytes were found to act as structure makers in aqueous sodium dodecylsulfate solutions.

**Keywords** Apparent molar volume · Partial molar volume transfer · Sodium dodecylsulfate · Partial molar volume expansibility

## Introduction

Partial molar volumes of electrolytes provide valuable information about ion–ion and ion–solvent interactions in ionic solutions [1–12]. This information is of fundamental importance for understanding reaction rates and equilibria involving dissolved electrolytes. Surfactants are extensively employed in pharmaceutical [13, 14] and biotechnological processes [15, 16]. In protein solution, surfactants are known as protein destabilizers, due to their strong binding with protein molecules [17]. A literature survey showed that, although many studies on thermodynamic properties of various solutes have been carried out in single-component and in mixed solvent systems, little attention has been paid to the behavior of salts in binary aqueous solution of sodium dodecylsulfate (SDS). In the present work we tried to review our knowledge of liquid water, its remarkable physical properties in the presence of some electrolytes and how these give rise to a unique liquid “structure,” and its influence on interactions between dissolved solutes. The study deals with the determination of the apparent molar volume, partial molar volume, and the volumes of transfer of several electrolytes at various temperatures. Two types of electrolyte were chosen for the study. In one type, monovalent cations ( $\text{K}^+$ ) were the same but anions were different ( $\text{Cl}^-$ ,  $\text{NO}_3^-$ ); in the other, divalent cations ( $\text{Mg}^{2+}$ ) were the same but anions were different ( $\text{Cl}^-$ ,  $\text{NO}_3^-$ ). Different charge and size of the ions may affect water structure differently, which may be reflected in the partial molar volume measurement data. Sodium dodecylsulfate is a strong water structure maker. The hydrophobic tail of SDS forces water molecules to be compactly structured. With this in view, it was considered interesting to investigate the effect of some electrolytes on aqueous solutions of SDS as a function of temperature. The structure making and breaking effects of

D. C. Kabiraz · T. K. Biswas · M. E. Huque (✉)  
Department of Chemistry, University of Rajshahi,  
Rajshahi 6205, Bangladesh  
e-mail: tapankb@ru.ac.bd

electrolytes will probably be more pronounced in this highly structured SDS solution in comparison with in pure water. The effects may mainly be due to the formation and breaking of the spherical micelles formed by SDS. In this study, densities and viscosities of some electrolytes in water and in water-SDS solution were measured. The experimentally measured data were then used to determine the limiting apparent molar volume. The results are discussed on the basis of the change in solute-solvent interaction induced by the solutes. Emphasis is given to the change of solvent structure making and structure breaking behavior of the solute in the solution.

## Results and Discussion

Apparent molar volumes ( $\phi_v$ ) were calculated using density data and the following equation:

$$\phi_v = \frac{M_2}{\rho_0} + \frac{1,000}{C} \left[ \frac{\rho - \rho_0}{\rho_0} \right], \quad (1)$$

where  $\rho$  and  $\rho_0$  are the densities of the solution and pure water in  $\text{g cm}^{-3}$ ,  $C$  is the molar concentration of the solution in  $\text{mol dm}^{-3}$ , and  $M$  is the molar mass of the solute. The apparent molar volume at infinite dilution ( $\phi_v^0$ ) was calculated using least-squares fit to linear plots of experimental values of  $\phi_v$  versus the square root of molar

concentration ( $\sqrt{C}$ ) using the following Masson equation [18]:

$$\phi_v = \phi_v^0 + S_v C^{1/2}, \quad (2)$$

where  $\phi_v^0$  is the partial molar volume at infinite dilution (limiting apparent molar volume) and  $S_v$  is the experimental slope. The values of  $\phi_v^0$  and  $S_v$  along with standard errors are given in Tables 1 and 2. It is evident from the data that  $S_v$  is positive for the entire electrolyte in water as well as in aqueous SDS solutions at different temperatures, which shows the presence of specific ion-ion interactions in both systems. It is noted that the value of  $S_v$  for all electrolytes increases in magnitude with increasing SDS content in water, thereby suggesting that ion-ion interactions further strengthen with increasing SDS content. The interactions decrease with increasing temperature. This is caused by more violent thermal agitation at higher temperatures, resulting in diminishing force of the ion-ion interaction [19]. This tendency is supported by the densities, viscosities, and adiabatic compressibility studies on some mineral salts in water at different temperatures [20]. It is reported that the solute-solute interactions decrease with increasing temperature for lithium nitrate, sodium nitrate, potassium nitrate, magnesium nitrate, and calcium nitrate.

In case of metal chlorides ( $\text{KCl}$ ,  $\text{MgCl}_2$ ) and metal nitrates [ $\text{KNO}_3$ ,  $\text{Mg}(\text{NO}_3)_2$ ], the anions are the same but the cations are of different nature. The cations are  $\text{K}^+$  and

**Table 1** Limiting apparent molar volumes ( $\phi_v^0$ ), experimental slopes ( $S_v$ ), and limiting apparent molar volume expansibilities ( $\phi_E^0$ ) for some electrolytes in water at different temperatures

Electrolyte	Temperature (K)	$\phi_v^0$ ( $\text{cm}^3 \text{ mol}^{-1}$ )	$S_v$ ( $\text{cm}^3 \text{ l}^{1/2} \text{ mol}^{-3}$ )	$\phi_E^0$ ( $\text{cm}^3 \text{ mol}^{-1} \text{ K}^{-1}$ )	$[\partial^2 \phi_v^0 / \partial T^2]_p$
KCl	303.15	27.85 ( $\pm 0.08$ )	26.8341 ( $\pm 1.04$ )	0.218	
	308.15	28.88 ( $\pm 0.04$ )	25.2195 ( $\pm 0.48$ )	0.203	
	313.15	29.90 ( $\pm 0.04$ )	23.3535 ( $\pm 0.56$ )	0.188	-0.0030
	318.15	31.09 ( $\pm 0.04$ )	22.6327 ( $\pm 0.55$ )	0.173	
	323.15	31.93 ( $\pm 0.04$ )	20.7287 ( $\pm 0.52$ )	0.158	
	303.15	38.21 ( $\pm 0.03$ )	24.1963 ( $\pm 1.09$ )	0.352	
$\text{KNO}_3$	308.15	38.76 ( $\pm 0.06$ )	21.5065 ( $\pm 0.87$ )	0.313	
	313.15	39.65 ( $\pm 0.03$ )	16.6555 ( $\pm 0.50$ )	0.274	-0.0078
	318.15	40.97 ( $\pm 0.03$ )	16.5712 ( $\pm 0.47$ )	0.235	
	323.15	41.10 ( $\pm 0.02$ )	14.9825 ( $\pm 1.11$ )	0.196	
$\text{MgCl}_2$	303.15	104.27 ( $\pm 0.07$ )	34.7897 ( $\pm 0.95$ )	0.193	
	308.15	105.63 ( $\pm 0.06$ )	32.7980 ( $\pm 0.89$ )	0.218	
	313.15	106.77 ( $\pm 0.04$ )	25.0850 ( $\pm 0.59$ )	0.243	+0.0050
	318.15	108.08 ( $\pm 0.02$ )	17.8906 ( $\pm 0.25$ )	0.268	
	323.15	109.40 ( $\pm 0.03$ )	13.1422 ( $\pm 0.41$ )	0.293	
$\text{Mg}(\text{NO}_3)_2$	303.15	159.07 ( $\pm 0.06$ )	40.4747 ( $\pm 0.85$ )	0.424	
	308.15	160.84 ( $\pm 0.04$ )	28.3628 ( $\pm 0.53$ )	0.431	
	313.15	162.50 ( $\pm 0.03$ )	22.3341 ( $\pm 0.44$ )	0.438	+0.0014
	318.15	164.29 ( $\pm 0.05$ )	21.0474 ( $\pm 0.71$ )	0.445	
	323.15	166.00 ( $\pm 0.05$ )	17.3143 ( $\pm 0.61$ )	0.452	

Standard errors are given in parentheses

**Table 2** Limiting apparent molar volumes ( $\phi_v^0$ ), experimental slopes ( $S_v$ ), limiting apparent molar volume expansibilities ( $\phi_E^0$ ), and partial molar volumes of transfer ( $\Delta\bar{V}_{tr}^0$ ) for some electrolytes in aqueous SDS solutions at different temperatures

Temperature (K)	$\phi_v^0$ (cm <sup>3</sup> mol <sup>-1</sup> )	$S_v$ (cm <sup>3</sup> l <sup>1/2</sup> mol <sup>-3</sup> )	$\phi_E^0$ (cm <sup>3</sup> mol <sup>-1</sup> K <sup>-1</sup> )	[ $\partial^2\phi_v^0/\partial T^2$ ]p	$\Delta\bar{V}_{tr}^0$ (cm <sup>3</sup> mol <sup>-1</sup> )
<i>0.007 m SDS</i>					
KCl					
303.15	28.80 (±0.04)	15.4604 (±0.53)	0.405		0.95
308.15	29.97 (±0.03)	16.1616 (±0.48)	0.412		0.95
313.15	30.89 (±0.03)	10.1818 (±0.43)	0.419	+0.0014	0.99
318.15	32.24 (±0.05)	20.0075 (±0.67)	0.426		1.15
323.15	33.20 (±0.02)	20.6071 (±0.30)	0.433		1.27
KNO <sub>3</sub>					
303.15	29.00 (±0.03)	16.9381 (±0.31)	0.139		0.79
308.15	39.76 (±0.06)	15.2856 (±0.67)	0.188		1.00
313.15	40.78 (±0.03)	12.1626 (±0.35)	0.236	+0.0097	1.13
318.15	42.22 (±0.03)	8.8468 (±0.35)	0.285		1.25
323.15	43.56 (±0.02)	7.1200 (±0.28)	0.334		1.76
MgCl <sub>2</sub>					
303.15	105.38 (±0.07)	15.6617 (±0.12)	0.277		1.11
308.15	106.95 (±0.07)	14.8038 (±0.13)	0.306		1.32
313.15	108.29 (±0.04)	14.2205 (±0.23)	0.335	+0.0058	1.52
318.15	109.67 (±0.02)	14.0413 (±0.30)	0.364		1.59
323.15	111.72 (±0.03)	13.8207 (±0.40)	0.393		1.68
Mg(NO <sub>3</sub> ) <sub>2</sub>					
303.15	159.07 (±0.09)	42.3304 (±0.36)	0.424		1.110
308.15	160.84 (±0.03)	26.1392 (±0.42)	0.431		1.560
313.15	162.65 (±0.09)	26.0688 (±1.16)	0.438	+0.0014	1.600
318.15	164.29 (±0.03)	25.2288 (±0.45)	0.445		1.850
323.15	165.68 (±0.05)	18.2689 (±0.70)	0.452		2.000
<i>0.01 m SDS</i>					
KCl					
303.15	29.56 (±0.07)	44.8653 (±0.88)	0.078		0.80
308.15	30.40 (±0.04)	12.1563 (±0.54)	0.165		1.71
313.15	30.88 (±0.06)	19.2159 (±0.85)	0.252	+0.0174	1.51
318.15	32.80 (±0.05)	29.7511 (±0.61)	0.339		0.98
323.15	34.47 (±0.06)	21.5118 (±0.80)	0.426		1.71
KNO <sub>3</sub>					
303.15	39.20 (±0.15)	28.0838 (±1.81)	0.102		0.99
308.15	39.91 (±0.08)	29.4016 (±0.91)	0.166		1.15
313.15	41.17 (±0.08)	21.5595 (±0.93)	0.230	+0.0129	1.52
318.15	42.23 (±0.05)	17.3873 (±0.54)	0.295		1.26
323.15	43.16 (±0.55)	9.3223 (±0.65)	0.358		2.06
MgCl <sub>2</sub>					
303.15	105.48 (±0.06)	22.2100 (±0.82)	0.217		1.21
308.15	106.92 (±0.02)	19.9347 (±0.32)	0.280		1.29
313.15	108.19 (±0.03)	16.7013 (±0.44)	0.345	+0.0128	1.42
318.15	110.27 (±0.03)	17.8407 (±0.34)	0.408		2.19
323.15	111.67 (±0.02)	12.3433 (±0.20)	0.473		2.27
Mg(NO <sub>3</sub> ) <sub>2</sub>					
303.15	159.92 (±0.12)	44.4647 (±0.16)	0.328		1.96
308.15	161.36 (±0.03)	27.1540 (±0.46)	0.343		2.08
313.15	163.28 (±0.07)	33.2207 (±0.91)	0.358	+0.0030	2.23
318.15	165.04 (±0.08)	29.6398 (±1.13)	0.373		2.60
323.15	166.82 (±0.06)	23.3773 (±0.86)	0.388		3.14

Standard errors are given in parentheses

$Mg^{2+}$  and the anions are  $Cl^-$  and  $NO_3^-$ , respectively. Owing to the large size of  $Cl^-$  and  $NO_3^-$ , they occupy a large space in the hydration sheath, but  $NO_3^-$ , being more polar than  $Cl^-$  due to its higher oxygen content, occupies more space. Nitrate has three oxygen atoms, which may enhance the formation of hydrogen bonds in aqueous solution [21, 22]. For this reason  $\phi_v^0$  values of nitrate-containing electrolyte are greater than those of  $Cl^-$ . Desnoyers and Jolicoeur [23] have reported that the strength of ion–solution interactions decreases with increasing charge of the ions. The value of partial molar volumes for magnesium salts is higher than that of potassium salts owing to the higher charge and small size of  $Mg^{2+}$  ions.

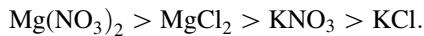
The measured partial molar volume can be considered to be a sum of the geometric volume of the solute and the change. This simple approach has been widely used in many models [24–30] to interpret partial molar volume for a broad range of solutes. When two charged centers are not separated by a distance of 3–4 Å, their hydration co-spheres overlap, which results in a decrease in the electrostriction [31]. The overlap of two co-spheres of two ionic species shows an increase in volume, whereas the overlap of hydrophobic–hydrophobic species results in an increase in volume and the overlap of hydrophobic groups and ion–hydrophobic groups results in a decrease in volume. The increase of  $\phi_v^0$  values with increasing temperature may also be attributed to the reduction in electrostriction with temperature. From these data it may be concluded that the solution of cations in water follows the order:  $Mg^{2+} > K^+$ . The same results were reported for some metal sulfates in water earlier [32].

The partial molar volume of transfer ( $\Delta\bar{V}_{tr}$ ) for electrolytes from water to surfactant solution are presented in Tables 1 and 2, being calculated as follows:

$$(\Delta\bar{V}_{tr}) = \phi_v^0(MS) - \phi_v^0(W), \quad (3)$$

where  $\phi_v^0(MS)$  and  $\phi_v^0(W)$  are the partial molar volumes at infinite dilution of the salts in mixed solvent (SDS–water) and in pure water, respectively. The increase of  $\phi_v^0$  and  $\Delta\bar{V}_{tr}$  for all salts may be attributed to the decrease in electrostriction in the presence of SDS. Thus, the electrostriction effect, which brings about shrinkage in the volume of the solvent, is decreased in the mixed solvent as compared with in pure water.

The  $\Delta\bar{V}_{tr}$  values are positive for potassium chloride, potassium nitrate, magnesium chloride, and magnesium nitrate at very low concentrations. The observed  $\Delta\bar{V}_{tr}$  values of these salts from water to aqueous SDS system follow the order:



The  $\Delta\bar{V}_{tr}$  values for the magnesium salts are higher than those for the potassium salts in aqueous SDS

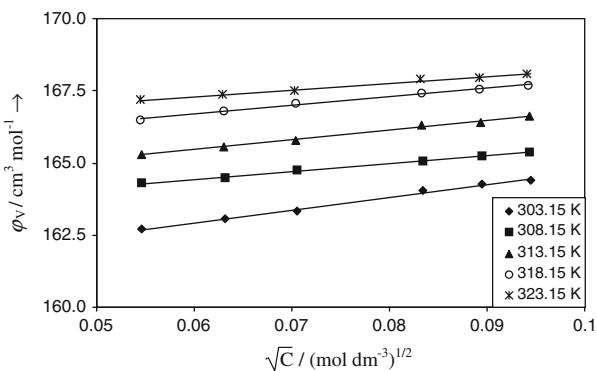
solutions. This trend may be due to its higher charge and the small size of the  $Mg^{2+}$  ion (radius = 0.82 nm). Similar data have been presented by Badarayani and Kumar [33], who reported that 1:2 and 2:1 electrolytes such as  $Na_2SO_4$  and  $MgCl_2$ , respectively, influence the apparent molar volume and transport properties of volumes and compressibilities of an aqueous amino acid solution more strongly than do 1:1 electrolytes such as  $KCl$ ,  $KBr$ , and  $NaBr$ . Banipal et al. also reported significant positive  $\Delta\bar{V}_{tr}$  values for some polyols and mono-, di-, and trisaccharides in presence of electrolytes such as  $NaCl$  [34],  $KCl$ ,  $SrCl_2$ ,  $BaCl_2$ ,  $Gu-HCl$  [35],  $CuCl_2$ , and  $ZnCl_2$  [36], and suggested that hydrophilic–ionic-type interaction dominates over the hydrophobic–ionic-type interactions. The  $\Delta\bar{V}_{tr}$  values for saccharides in solutions of  $CuCl_2$  and  $ZnCl_2$  reported in [36] are almost twice those in  $NH_4Br$ . This again supports the view that divalent cations interact more strongly than monovalent cations with the salts.

The volume transfer values increase with increasing molalities of SDS. This can be rationalized by the co-sphere overlap model, as developed by Friedman and Krishnan [37]. The interaction between the salts and SDS molecules can be classified as follows:

- (a) Ion–ion interactions between  $SO_4^{2-}$  of SDS and the  $K^+/Mg^{2+}$  group of salts
- (b) Ion–ion interactions between the  $Na^+$  of SDS and the  $Cl^-/NO_3^-$  ion of salts
- (c) Hydrophilic–hydrophobic interactions between the hydrophilic/hydrophobic parts of the SDS and anion/cation part of the salts

Taking the co-sphere overlap model [29] as the guideline, (a) and (b) type of interactions would lead to positive  $\Delta\bar{V}_{tr}$ , since there is a reduction in the electrostriction effect and the overall water structure is enhanced. Interactions of type (c) would lead to negative  $\Delta\bar{V}_{tr}$ , because of the reduction of water structure that is formed around those groups as a result of co-sphere overlap. Since we have observed positive  $\Delta\bar{V}_{tr}$  for the four electrolytes it is concluded that ion–ion and hydrophilic–hydrophilic group interactions are overall predominant over the hydrophobic–hydrophobic group interactions in the ternary system. The temperature dependence of  $\phi_v$  for the mineral salts was studied in water and in different compositions (Fig. 1).

The values of  $\phi_v^0$  increase with increasing temperature for all salts, in water as well as in 0.007 and 0.01 m aqueous SDS solutions, thereby showing that solute–solute interactions are further strengthened with increasing temperature. The temperature dependence of  $\phi_v^0$  ( $cm^3 mol^{-1}$ ) in water for all salts can be expressed by the following expressions:



**Fig. 1** Plots of apparent molar volume ( $\phi_v$ ) versus  $\sqrt{C}$  for magnesium nitrate in 0.007 m aqueous SDS solution at different temperatures

$$\phi_v^0 = 26.714 + 1.1270T - 0.0150T^2 \quad (4)$$

for potassium chloride,

$$\phi_v^0 = -431.98 + 2.7167T - 0.0039T^2 \quad (5)$$

for potassium nitrate,

$$\phi_v^0 = 271.35 - 1.322T + 0.0025T^2 \quad (6)$$

for magnesium chloride,

$$\phi_v^0 = 157.35 + 1.7267T + 0.0007T^2 \quad (7)$$

for magnesium nitrate.

In 0.007 m SDS–water solution the expressions are:

$$\phi_v^0 = 27.704 + 1.1027T + 0.0007T^2 \quad (8)$$

for potassium chloride,

$$\phi_v^0 = 447.70 - 2.832T + 0.0049T^2 \quad (9)$$

for potassium nitrate,

$$\phi_v^0 = 291.99 - 1.4814T + 0.0029T^2 \quad (10)$$

for magnesium chloride,

$$\phi_v^0 = 157.32 + 1.7567T + 0.0007T^2 \quad (11)$$

for magnesium nitrate.

In 0.1 m SDS–water solution the expressions are:

$$\phi_v^0 = 806.79 - 5.197T + 0.0087T^2 \quad (12)$$

for potassium chloride,

$$\phi_v^0 = 599.08 - 3.778T + 0.0064T^2 \quad (13)$$

for potassium nitrate,

$$\phi_v^0 = 627.97 - 3.6635T + 0.0064T^2 \quad (14)$$

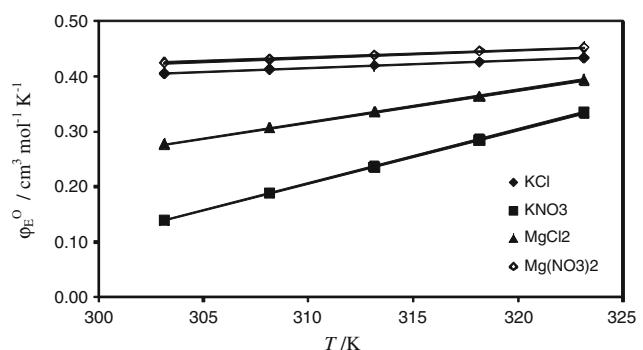
for magnesium chloride,

$$\phi_v^0 = 199.43 - 0.5809T + 0.0015T^2 \quad (15)$$

for magnesium nitrate.

In all expressions the temperature  $T$  is expressed in Kelvin. The molar volume expansibilities at infinite dilution,  $\phi_E^0 = [\partial\phi_v^0/\partial T]_p$ , calculated using expressions 4–15 for different salts in water and in 0.007 m and in

0.01 m SDS–water are also presented in Tables 1 and 2. It is evident from Tables 1 and 2 that the value of  $\phi_E^0$  decreases with increasing temperature for potassium chloride and potassium nitrate in water, but increases with increasing temperature for all the salts studied in 0.01 m aqueous SDS solution. The positive increase in  $\phi_E^0$  with increasing temperature for all the electrolytes may be due to the “caging effect” [38]. The variation of  $\phi_E^0$  with temperature for all electrolytes, in water as well as in 0.007 and 0.01 m aqueous SDS solutions, has been found to be linear. Representative plots are shown in Fig. 2. During the past few years, it has been emphasized by a number of workers that  $S_v$  is not the sole criterion for determining the structure making or breaking nature of any solute. Hepler [39] has developed a technique for examining the sign of various solutes in terms of long-range structure making or breaking capacities of the solutes in aqueous solutions using the general thermodynamic expression:  $[\partial C_p/\partial P]_T = [\partial\phi_v^0/\partial T]_p$ . On the basis of this relation, it has been deduced that structure maker solutes should have positive values whereas structure breaker solutes have negative values. In this study it is observed from Table 1 that  $[\partial\phi_v^0/\partial T]_p$  for the solutions of salts (mentioned along with the respective expression) in water are positive for magnesium chloride and magnesium nitrate but negative for potassium chloride and potassium nitrate, showing that magnesium chloride and magnesium nitrate are structure makers whereas potassium chloride and potassium nitrate are structure breakers. A significant increase in  $(\frac{\partial^2\phi_v^0}{\partial T^2})$  values with increasing temperature for potassium chloride and potassium nitrate was observed in the SDS solutions. The structure breaking effect of potassium chloride and potassium nitrate decreases due to its interaction with SDS molecules, and thus more water molecules are released to the bulk water in the presence of SDS and these contribute to the positive  $(\frac{\partial^2\phi_v^0}{\partial T^2})$  observed. In 0.01 m aqueous SDS solution all four electrolytes [KCl, KNO<sub>3</sub>, MgCl<sub>2</sub>, Mg(NO<sub>3</sub>)<sub>2</sub>] show positive  $[\partial\phi_v^0/\partial T]_p$  values, thereby showing that all the electrolytes act as structure makers. In other words, addition



**Fig. 2** Variation of limiting apparent molar volume expansibilities ( $\phi_E^0$ ) with temperature for some salts in 0.007 m SDS–water systems

of potassium chloride, potassium nitrate, magnesium chloride, and magnesium nitrate in 0.01 m aqueous SDS solution causes an increase in the structure of water.

## Experimental

Potassium chloride (KCl), potassium nitrate ( $\text{KNO}_3$ ), magnesium chloride ( $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ ), and magnesium nitrate [ $\text{Mg}(\text{NO}_3)_2 \cdot 7\text{H}_2\text{O}$ ] were used after drying over  $\text{P}_2\text{O}_5$  in a desiccator. The reagents were always placed in the desiccator over  $\text{P}_2\text{O}_5$  to keep them in dry atmosphere. Freshly distilled water (sp. cond.  $\sim 10^{-6} \Omega^{-1} \text{cm}^{-1}$ ) was used for preparing aqueous mixtures of SDS as well as the standard liquid. All the aqueous mixtures of SDS as well as the solutions of electrolytes were made by weight, and molalities (m) were converted into molarities (C) using the standard expression  $C = 1,000\rho / (1,000 + mM_2)$ , where  $\rho$  is the solution density and  $M_2$  is the molecular weight of an electrolyte.

Densities were measured with an Ostwald–Sprengel-type pycnometer having a bulb volume of  $10 \text{ cm}^3$ . The pycnometer was calibrated at 303.15, 308.15, 313.15, 318.15, and 323.15 K with double-distilled water. The pycnometer with the test solution was equilibrated in a water bath maintained within  $\pm 0.01$  K of the desired temperature by means of a mercury-in-glass thermoregulator, and the temperature was determined using a calibrated thermometer and a Muller bridge. The pycnometer was then removed from the thermostatic bath, properly dried, and weighed. The evaporation losses remained insignificant during the time of actual measurement. Average of triplicate measurements was taken into account. The uncertainty in the experimental data for density was estimated to be  $\pm 3 \times 10^{-5} \text{ g cm}^{-3}$ .

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