Volumetric Studies of Sodium Chloride in Aqueous and Aqueous Maltose Systems at Different Temperatures

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Densities of sodium chloride in the concentration range (0.010 to 0.090 \pm 0.001) mol·dm⁻³ have been determined in aqueous and aqueous maltose systems [(1.0, 3.0, 5.0, and 7.0) % w/v] at different temperatures [(298 to 323) K] with the interval of 5 K. Apparent molar volume (ϕ_{ν}), partial molar volume (ϕ_{ν}°) and the ion—ion interaction parameter (S_{ν}) have been calculated, using the Masson equation by applying linear regression analysis. Other parameters were also calculated, viz., transfer volume ($\phi_{\nu(tr)}^{\circ}$) and partial molar expansibility ($\phi_{\rm E}^{\circ}$). Values of $\phi_{\rm E}^{\circ}$ show the presence of caging or packing effects. The data obtained from volumetric studies have been used to investigate the ion—solvent interaction and ion—ion interaction. The structure-breaking capacity of sodium chloride has been inferred in aqueous and aqueous maltose systems from Hepler's criterion, i.e., ($\partial^2 \phi_{\nu}^{\circ} / \partial T^2$)_P second derivative of partial molar volume with respect to temperature at constant pressure.

Introduction

Carbohydrate solutions perform an important role in the biological and food industries. Sugars are often used in pharmaceuticals, foods, and biomedical applications to prepare a glassy matrix for long-term storage of biological materials.¹⁻⁴ Maltose a (disaccharide) is a water-soluble sugar used for immediate energy along with glucose, as it is a basic source for all living organisms. It is also used in a number of biological preparations as a stabilizing agent or osmolality regulator. Maltose plays a vital role in changing the effect by generating a more plasticizing effect than fructose.⁵ Therefore, it is very essential to study the interactions between electrolytes and maltose in water. The structure of α -D-maltose is



The behavior of electrolytes in aqueous carbohydrates and aqueous carbohydrates containing a small amount of ions which are present in body fluids has recently been a subject of great interest. Interactions of electrolytes with saccharides are very important in exploring the stability of polysaccharides in biological systems as well as in the chemical industry of saccharides. It is an essential component for maintaining cell viability, a natural cell-protecting agent, as well as an energy reservoir in many organisms.^{6,7}

The molecular interactions of sugars in dilute aqueous solution play an important role in governing the biological and medicinal

Table 1. Densities (ρ) of NaCl in the Aqueous and Aqueous Maltose Systems at Different Temperatures

$\rho/g \cdot cm^{-3}$ at temperature/K								
$[NaCl] \cdot 10^{2} / mol \cdot dm^{-3}$	298	303	308	313	318	323		
Aqueous System								
1.00	1.0052	1.0042	1.0032	1.0015	0.9994	0.9982		
3.00	1.0053	1.0046	1.0034	1.0018	0.9996	0.9984		
5.00	1.0056	1.0049	1.0040	1.0021	1.0003	0.9988		
7.00	1.0065	1.0058	1.0048	1.0029	1.0011	0.9996		
9.00	1.0076	1.0064	1.0061	1.0040	1.0022	1.0010		
1	.0 % (w/	v) Aqueo	ous Malte	ose				
1.00	1.0100	1.0094	1.0085	1.0056	1.0044	1.0025		
3.00	1.0101	1.0098	1.0086	1.0058	1.0046	1.0027		
5.00	1.0104	1.0100	1.0092	1.0060	1.0048	1.0037		
7.00	1.0115	1.0102	1.0102	1.0070	1.0060	1.0041		
9.00	1.0116	1.0103	1.0113	1.0080	1.0088	1.0053		
3	.0 % (w/	v) Aqueo	ous Malt	ose				
1.00	1.0174	1.0149	1.0140	1.0125	1.0110	1.0100		
3.00	1.0176	1.0152	1.0142	1.0127	1.0112	1.0102		
5.00	1.0179	1.0155	1.0146	1.0129	1.0114	1.0104		
7.00	1.0182	1.0157	1.0150	1.0131	1.0116	1.0106		
9.00	1.0183	1.0158	1.0155	1.0135	1.0118	1.0108		
5	5.0 % (w/	v) Aqueo	ous Malte	ose				
1.00	1.0250	1.0240	1.0224	1.0198	1.0170	1.0148		
3.00	1.0252	1.0242	1.0226	1.0200	1.0172	1.0150		
5.00	1.0254	1.0245	1.0230	1.0202	1.0174	1.0152		
7.00	1.0256	1.0248	1.0232	1.0204	1.0176	1.0154		
9.00	1.0260	1.0250	1.0234	1.0206	1.0178	1.0156		
7.0 % (w/v) Aqueous Maltose								
1.00	1.0315	1.0305	1.0294	1.0270	1.0250	1.0235		
3.00	1.0317	1.0307	1.0296	1.0272	1.0252	1.0237		
5.00	1.0320	1.0309	1.0298	1.0274	1.0254	1.0239		
7.00	1.0322	1.0311	1.0300	1.0276	1.0256	1.0241		
9.00	1.0324	1.0315	1.0302	1.0278	1.0260	1.0243		

mechanism of any system. The determination of apparent molar volume is used to study the structural properties and solute– solvent interactions of solutions.⁸ Nikam et al.⁹ have studied the density of sucrose and maltose in aqueous ammonium chloride solutions at different temperatures, and results were analyzed for solvent interactions in terms of molar volume. The aqueous solutions of sugars have been used by many workers^{4,8}

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Table 2. Apparent Molar Volumes (ϕ_v) of NaCl in the Aqueous and Aqueous Maltose Systems at Different Temperatures

	ϕ_{ν} 10	$)^{-1}/cm^{3} \cdot m$	ol ⁻¹ at ten	nperature/l	X	
NaCl] • 10 ² /						
mol•dm ⁻³	298	303	308	313	318	323
		Aque	ous Syster	n		
1.00	14.753	18.740	20.746	25.753	29.790	30.822
3.00	8.4590	8.7955	10.129	11.470	13.153	13.501
5.00	6.8084	7.0114	7.2160	8.6138	9.6326	9.6372
7.00	5.4465	5.3917	5.5322	6.6837	6.8376	7.4162
9.00	4.1579	4.8234	4.2743	5.2699	5.3958	5.5067
	1	.0 % (w/v)	Aqueous	Maltose		
1.00	15.671	19.631	21.625	27.628	30.632	40.600
3.00	8.7440	9.0792	10.735	12.413	13.418	16.743
5.00	6.9673	7.3644	7.5675	9.3708	9.9751	10.381
7.00	5.7804	6.6294	5.9269	6.9327	7.0808	8.5072
9.00	6.4398	6.3311	4.4715	5.5781	7.9005	6.5822
	3	.0 % (w/v)	Aqueous	Maltose		
1.00	17.518	20.529	28.381	33.333	43.204	51.097
3.00	9.0096	9.6851	12.637	14.291	17.583	20.215
5.00	7.1116	7.5206	9.0956	10.483	12.459	14.039
7.00	6.2981	6.7335	7.5775	8.8513	10.263	11.391
9.00	6.0644	6.4056	6.6248	7.7257	9.0434	9.9213
	5	.0 % (w/v)	Aqueous	Maltose		
1.00	20.305	22.271	30.094	35.044	48.799	56.709
3.00	9.9145	10.572	13.182	14.838	19.428	22.069
5.00	7.8363	8.0373	9.4096	10.797	13.553	15.141
7.00	6.9456	6.9509	8.0715	9.0658	11.036	12.171
9.00	6.2343	6.4557	7.3281	8.1036	9.6376	10.522
	7	.0 % (w/v)	Aqueous	Maltose		
1.00	22.109	25.030	30.854	37.704	52.283	57.196
3.00	10.495	11.471	13.412	15.704	20.561	22.204
5.00	7.9790	8.7592	9.9240	11.304	14.217	15.206
7.00	7.0388	7.5970	8.4290	9.4185	11.498	12.206
9.00	6.5165	6.7361	7.5984	8.3708	9.7721	10.540

in studying solute—solvent interactions in aqueous and mixed solvent systems. In the present study, disaccharides have been investigated because coverage of the disaccharides which can be formed by condensation can be useful to discuss the overall aspects of interactions measured by volumetric methods.^{10,11}

Solute-solvent interaction has great importance in biological chemistry, physical chemistry, surface chemistry, environmental chemistry, and geochemistry. To understand the processes occurring in living cells, the nature of ion hydration is prerequisite information. Density studies of aqueous solutions of salt are useful in understanding the nature of solute-solvent and ion-solvent interactions. Density data of aqueous solutions of salts are also required for molecular biology applications.¹² The ion-solvent interaction is also a very important tool for the many practical problems concerning energy transport, mass transport, and fluid flow.¹³

The purpose of the present study was to evaluate structural changes in terms of ion—ion and ion—solvent interactions of sodium chloride in aqueous and aqueous maltose systems. Different parameters like apparent molar volume, partial molar volume, partial molar expansibility, and $(\partial^2 \phi_{\nu}^{\rho} / \partial T^2)_P$ have been used to study the behavior of sodium chloride in aqueous and aqueous maltose systems at different temperatures.

Experimental Section

All glassware used was made of Pyrex A grade quality. Sodium chloride (Merck) and maltose of Anala R grade quality (BDH) with molecular weights of 58.44 g·mol⁻¹ and 360.32 g·mol⁻¹, respectively, were used. A stock solution of maltose was prepared by taking maltose in a known volume of double distilled water having a conductivity of $0.06 \,\mu\text{S} \cdot \text{cm}^{-1}$. Different



Figure 1. Plot of apparent molar volumes (ϕ_v) versus $C^{1/2}$ for the 1 % aqueous maltose system at different temperatures.



Figure 2. Plot of apparent molar volumes (ϕ_{ν}) versus $C^{1/2}$ for the aqueous and aqueous maltose system at 308 K.



Figure 3. Plot of partial molar volume (ϕ_{ν}°) versus temperature for the aqueous and aqueous maltose systems.

compositions of maltose ranging from (1.0, 3.0, 5.0, and 7.0) % (w/v) were prepared, and the concentration of sodium chloride in the aqueous maltose system was varied within the range of 0.010 to 0.090 \pm 0.001) mol·dm⁻³.

The densities of solvents and solutions were measured with the help of a relative density bottle having a capacity of 10 cm³ at different temperatures. Temperature was kept constant by keeping all solutions in a thermostatic water bath (circulator,

Table 3. Partial Molar Volumes (ϕ_{ν}°) of NaCl in the Aqueous and Aqueous Maltose Systems at Different Temperatures

$\phi_{\nu}^{\circ} \ 10^{-2} / \mathrm{cm}^3 \cdot \mathrm{mol}^{-1}$ at temperature/K						
% (w/v) aqueous maltose	298	303	308	313	318	323
0.00	$1.8761 (\pm 0.0001)$	$2.3252 (\pm 0.0002)$	$2.6595 (\pm 0.0002)$	$3.2898 (\pm 0.0001)$	$3.8056 (\pm 0.0001)$	3.9239 (± 0.0002)
1.00	2.1024 (± 0.0003)	2.3334 (± 0.0004)	2.7773 (± 0.0003)	3.4978 (± 0.0001)	3.7764 (± 0.0002)	5.1579 (± 0.0002)
3.00	2.1039 (± 0.0004)	2.4654 (± 0.0005)	3.5216 (± 0.0003)	4.1087 (± 0.0002)	5.3474 (± 0.0002)	6.3477 (± 0.0003)
5.00	$2.4590 (\pm 0.0002)$	$2.7130 (\pm 0.0003)$	3.7469 (± 0.0002)	4.3143 (± 0.0002)	6.0573 (± 0.0003)	$7.0596 (\pm 0.0003)$
7.00	2.6839 (± 0.0002)	$3.0585 (\pm 0.0001)$	$3.8265 (\pm 0.0003)$	$4.6523 (\pm 0.0003)$	$6.5119 (\pm 0.0003)$	6.4231 (± 0.0004)

Table 4. Experimental Slope (S_{ν}) of NaCl in the Aqueous and Aqueous Maltose Systems at Different Temperatures

$S_{\nu} 10^{-2}$ /cm ² ·dm ^{1/2} ·mol ^{-3/2} at temperature/K							
% (w/v) aqueous maltose	298	303	308	313	318	323	
0.00	-5.1051	-6.7371	-8.0164	-10.111	-11.822	-12.185	
	(± 0.0001)	(± 0.0002)	(± 0.0002)	(± 0.0002)	(± 0.0001)	(± 0.0002)	
1.00	-6.1999	-6.3730	-8.3425	-10.645	-11.290	-16.497	
	(± 0.0001)	(± 0.0003)	(± 0.0002)	(± 0.0002)	(± 0.0002)	(± 0.0003)	
3.00	-5.5774	-6.8218	-10.531	-12.320	-16.472	-19.855	
	(± 0.0002)	(± 0.0001)	(± 0.0003)	(± 0.0003)	(± 0.0003)	(± 0.0002)	
5.00	-6.7574	-7.6665	-10.974	-12.291	-18.884	-22.271	
	(± 0.0003)	(± 0.0002)	(± 0.0003)	(± 0.0004)	(± 0.0004)	(± 0.0003)	
7.00	-7.5432	-8.7940	-11.145	-14.144	-20.471	-19.769	
	(± 0.0003)	(± 0.0003)	(± 0.0002)	(± 0.0003)	(± 0.0004)	(± 0.0002)	

Table 5. Values of Transfer Volume $(\phi_{\gamma^{\circ}(tr)})$ for NaCl in theAqueous and Aqueous Maltose Systems at Different Temperatures

$\phi^{\circ}_{\nu(\mathrm{tr})} \ 10^{-2}/\mathrm{cm}^3 \cdot \mathrm{mol}^{-1}$ at temperature/K						
% (w/v) aqueous maltose	298	323				
1.00	0.2263	1.2340				
	(± 0.0003)	(± 0.0002)				
3.00	0.2278	2.4238				
	(± 0.0002)	(± 0.0003)				
5.00	0.5829	3.1357				
	(± 0.0001)	(± 0.0002)				
7.00	0.8078	2.4992				
	(± 0.0003)	(± 0.0003)				

model YCW-0.1, R. O. C. Taiwan) for about (10 to 15) min. A weighing balance (Sartorius, model No. BL 150S) was used for mass determination. The uncertainty in the experimental data for density was found to be \pm 0.001 g·mL⁻¹. Reproducibility of the results was checked by taking each measurement three times.

Results and Discussion

The densities of sodium chloride (NaCl) in aqueous and aqueous maltose systems ranging from (1.0 to 7.0) % (w/v) for concentrations (0.010 to 0.090) mol·dm⁻³ at different temperatures (298 to 323) K with a difference of 5 K are tabulated in Table 1. The results show that density increases with an increase in the concentration of sodium chloride and also with the percent composition of maltose and decreases with an increase in temperature.

Volumetric properties have been regarded as sensitive structural tools for understanding interactions in solutions.¹⁴ The respective values of apparent molar volumes " ϕ_{ν} " of sodium chloride were calculated from the density of the solutions using the equation

$$\phi_{\nu} = \frac{\mathrm{M}}{\rho^{\circ}} - \frac{1000(\rho - \rho^{\circ})}{C\rho^{\circ}} \tag{1}$$

where *M* is the molecular weight of solute; *C* is the concentration of the electrolyte solution; ρ is the density of the solution; and ρ° is the density of the solvent. Table 2 shows the values of

apparent molar volumes of sodium chloride in aqueous and aqueous maltose systems at different temperatures. The variation in partial molar properties with respect to concentration is expressed by the Masson equation¹⁵

$$\phi_{\nu} = \phi_{\nu}^{\circ} + S_{\nu} C^{1/2} \tag{2}$$

where ϕ_{ν}° is the limiting apparent molar volume that equals the standard partial molar volume of the solute related to ion–solvent interaction; *C* is the concentration; and S_{ν} is the experimental slope which is considered to be a volumetric pairwise interaction coefficient and can be related to solute–solute interactions. Representative plots of ϕ_{ν} versus $C^{1/2}$ are shown in Figures 1 and 2.

The standard partial molar volumes and their S_{ν} values are shown in Tables 3 and 4. The volumetric behavior of a solute at infinite dilution is satisfactorily represented by ϕ_{ν}° , which is independent of the solute-solute interaction and provides information concerning solute-solvent interactions. It was observed that ϕ_{ν}° values are positive for all the percent compositions of maltose at all temperatures suggesting the presence of strong solute-solvent interactions.¹⁶ The plots of ϕ_{ν} versus $C^{1/2}$ were linear using least-squares treatment, and from the intercept and slope, the values of ϕ_{ν}° and S_{ν} , respectively, can be obtained. The values of ϕ_{ν}° shown in Table 3 increased with an increase in temperature in the aqueous and aqueous maltose systems which indicate that the solvent molecules are loosely attached to solutes which expand with the increase of temperature, thus resulting in higher values of ϕ_{ν}° at higher temperatures.

The following contributions of $\phi_{\nu(ion)}^{\circ}$ are more instructive: (1) The ion has a definite intrinsic size, V_{int} , for which a cavity in the solvent must be provided. (2) The ion has a large electric field that exerts a strong compressive effect on the surrounding solvent, referred to as electrostriction, V_{el} . (3) Short-range interactions take place, in particular, where multivalent cations (donor-acceptor interactions) and anions (hydrogen bonding) are concerned that are manifested by a volume effect V_{cov} . (4) The volume of the solvent, V_{str} , changes due to its rearrangement

		$\phi_{\rm E}^{\circ}/{\rm cm}^3 \cdot {\rm m}^{\circ}$	$ol^{-1} \cdot K^{-1}$ at temperatu	ure/K		
% (w/v) aqueous maltose	298	303	308	313	318	323
1.00	-5.1776 (± 0.0002)	1.3164 (± 0.0002)	7.8104 (± 0.0002)	14.304 (± 0.0002)	20.798 (± 0.0003)	27.292 (± 0.0002)
3.00	10.398 (± 0.0003)	(± 0.0001)	16.004 (± 0.0002)	18.807 (± 0.0004)	(± 0.0002)	24.413 (± 0.0003)
7.00	(± 0.0004) (± 0.0004)	(± 0.0004) (± 0.0004)	(± 0.0003) (± 0.0003)	(± 0.0003) (± 0.0003)	(± 0.0002) (± 0.0002)	(± 0.0002) 20.744 (± 0.0002)
		$[\partial^2 \phi^{ m o}_{ u} / \partial T^2]$	$[P_{P}]_{P} 10^{-2}$ at temperatur	e/K		
% (w/v) aqueous maltose	298	303	308	313	318	323
1.00	-3.8704 (± 0.0002)	-3.9353 (± 0.0002)	-4.0003 (± 0.0002)	-4.0652 (± 0.0002)	-4.1301 (± 0.0003)	-4.1951 (± 0.0002)
3.00	-1.6705 (± 0.0003)	-1.6986 (± 0.0001)	-1.7266 (± 0.0002)	-1.7546 (± 0.0004)	-1.7827 (± 0.0002)	-1.8107 (± 0.0003)
7.00	-0.8725 (± 0.0004)	-0.8871 (± 0.0004)	-0.9018 (± 0.0003)	-0.9164 (± 0.0003)	-0.9311 (± 0.0002)	-0.9457 (± 0.0002)

Table 6. Partial Molar Expansibilities (ϕ_E^{α}) and $[\partial^2 \phi_{\mu}^{\alpha} / \partial T^2]_P$ of NaCl in the Aqueous Maltose System at Different Temperatures

around the ion as a result of the size, shape, electric field (beyond the effects of electrostriction), and short-range interactions of the ion and the size, shape, and structure of the solvent molecules. If these volume effects are chosen to be independent of each other (orthogonal), then the partial molar volume of the ion can be considered as their sum.¹⁷

$$\phi_{\nu(\text{ion})}^{\text{o}} = V_{\text{int}} + V_{\text{el}} + V_{\text{cov}} + V_{\text{str}}$$
(3)

A somewhat different expression was presented by Millero¹⁸ on the basis of the Frank and Wen model for aqueous ions.¹⁹

$$\phi_{\nu(\text{ion})}^{\circ} = V_{\text{int}} + V_{\text{el}} + V_{\text{dis}} + V_{\text{cag}}$$
(4)

where $V_{\rm dis}$ describes the volume effect of the broken (disordered) water structure around structure-breaking ions and $V_{\rm cag}$ describes the volume effect of "caged" water around hydrophobic ions with alkyl or phenyl substituents.

Since S_{ν} is a measure of ion—ion interactions, the S_{ν} values as shown in Table 4 are negative and decrease with an increase of temperature in the aqueous and aqueous maltose systems suggesting that less solute is accommodated in the void space left in the packing of the large associated solvent molecules. The results also indicate the presence of weak solute—solute interactions, and these interactions decrease with the increase in temperature. The values of S_{ν} decrease with the increase in percent composition of aqueous maltose showing weak solute—solute interactions. It can be said that the solvation of ions increases with the increase of maltose content in water.

The negative S_{ν} values are associated with hydrophobic solutes.²⁰ The results can be interpreted with the help of the Cosphere Overlap Model (COM) proposed by Friedman and Krishnan.²¹ According to the model, the effect of overlap of two cospheres is destructive. Further, Mishra et al.²² extended this model and observed that the overlapping of cospheres of two ionic species caused an increase in volume, whereas overlapping of hydrophilic-hydrophobic and hydrophobichydrophobic groups led to a decrease in volume. According to the structural hydration interaction model, the interactions between NaX and maltose can be classified as follows: (1) cation-hydrophobic (Na⁺-R, R represents alkyl groups); (2) anion-hydrophobic $(X^{-}-R)$; (3) cation-hydrophilic $(Na^{+}-O,$ O represents OH, C=O, and -O- groups); and (4) anion and hydrophilic $(X^{-}-O)$. Types (1), (2), and (4) contribute negative values to volume, whereas type (3) contributes a positive value to volume. It has been concluded that type (3) is predominant.⁷ So values of $\phi_{\nu(tr)}^{o}$ as shown in Table 5 are positive.

The thermodynamic transfer functions may be interpreted in terms of water structure forming or breaking ability of the solute, as has been postulated by Frank and Evans.²³ Thus, the transfer volume $\phi_{\nu(tr)}^{\circ}$ from aqueous to aqueous maltose solution was calculated using the relation

$$\phi^{\circ}_{\nu(\mathrm{tr})} = \phi^{\circ}_{\nu(\mathrm{aq.maltose})} - \phi^{\circ}_{\nu(\mathrm{aq})} \tag{5}$$

As shown in Table 5, it is found that the $\phi_{\nu(aq,maltose)}^{\circ}$ values are higher than $\phi_{\nu(aq)}^{\circ}$, resulting in positive transfer of volumes.

The variation of ϕ_{ν}° with temperature for sodium chloride in the aqueous and aqueous maltose solution systems, as shown in Figure 3, follows the polynomial equation.

$$\phi_{\nu}^{\circ} = \alpha_1 + \alpha_2 T + \alpha_3 T^2 \tag{6}$$

over the temperature range under investigation. The coefficients α 's are evaluated by the following relations

$$\phi_{\nu}^{\circ} = -8804.3 + 49.912T - 0.0663T^2 \tag{7}$$

(aqueous system)

$$\phi_{\nu}^{\circ} = +59441 - 392.22T + 0.6494T^2 \tag{8}$$

(1 % (w/v) aqueous maltose system)

$$\phi_{\nu}^{\circ} = +21997 - 156.66T + 0.2803T^2 \tag{9}$$

(3 % (w/v) aqueous maltose system)

$$\phi_{\nu}^{\circ} = +39741 - 272.57T + 0.4699T^2 \tag{10}$$

(5 % (w/v) aqueous maltose system)

$$\phi_{\nu}^{\circ} = +9253.1 - 73.83T + 0.1464T^2 \tag{11}$$

(7 % (w/v) aqueous maltose system)

The partial molar expansibilites

$$\phi_{\rm E}^{\circ} = \left(\frac{\partial \phi_{\nu}^{\circ}}{\partial T}\right)_{\rm P} = \alpha_2 + 2\alpha_3 T \tag{12}$$

calculated from eqs 7 to 11 are given in Table 6 and can be obtained by differentiating eq 6 with respect to temperature. It is evident that $\phi_{\rm E}^{\circ}$ increased in magnitude with the increase in temperature for NaCl in the aqueous and aqueous maltose systems, showing the presence of caging or packing effects.

During the past few years it has been emphasized by different works that S_{ν} is not the sole criterion for determining the structure-making or structure-breaking nature of any solute. Hepler²⁴ developed a technique of examining the sign of $(\partial^2 \phi_{\nu}^{o}/\partial T^2)_{\rm P}$ for various solutes in terms of long-range structure-making and structure-breaking capacity of solutes using the general thermodynamic expression

$$\left(\frac{\partial C_{\rm P}}{\partial P}\right)_T = -\left(\frac{\partial^2 \phi_\nu^o}{\partial T^2}\right)_{\rm P} = -2\alpha_3 T \tag{13}$$

On the basis of eq 13, it has been deduced that structure-making solutes should have positive values, whereas structure-breaking solutes have small positive or negative values. In the present system, it was observed that as shown in Table 6 $(\partial^2 \phi_{\nu}^{o} / \partial T^2)_P$ is negative, suggesting thereby that this salt behaves as a structure breaker.^{25,26} Several authors^{24,27} have also reported sodium chloride as a structure breaker in aqueous systems. Gupta et al.²⁸ studied the viscosities and densities of sodium chloride in aqueous and aqueous sucrose solutions and also found sodium chloride as a structure breaker.

Conclusion

The ionic interaction of sodium chloride in the aqueous and aqueous maltose systems was evaluated in terms of apparent molar volume by using the Masson equation. The molar volume increased with an increase in the percent composition of maltose and also with a rise in temperature. The values of partial molar expansibilities show the presence of caging or packing effects. On the basis of the Hepler criterion, sodium chloride behaves as a structure breaker in the aqueous and aqueous maltose systems.

Literature Cited

- Denise, P.; Alessandra, L. O.; Fernando, A. C. Modeling of Phase Equilibria for Aqueous Solutions of Sugars Using a Cubic Equation of State. J. Food Processing Eng. 2007, 30, 593–606.
- (2) Bordat, P.; Larbret, A.; Demaret, J.-P.; Affouard, F.; Descamps, M. Comparative Study of Trehalose, Sucrose and Maltose in Water Solutions. *Europhys. Lett.* **2004**, *65*, 41–47.
- (3) Comesana, J. F.; Correa, A.; Sereno, A. Measurements of Water Activity in "Sugar" + Sodium Chloride + Water Systems at 25 °C. *J. Chem. Eng. Data* **1999**, *44*, 1132–1134.
- (4) Gupta, R. R.; Singh, M. Apparent Molar Volumes of Mono- And Di-Saccharides in Water and in Aqueous Oxalic Acid Solutions at 293.15, 303.15, 313.15 And 323.15 K. J. Indian Chem. Soc. 2008, 85, 176– 181.
- (5) Villablanca, C. M.; Velasquez, N. R. Sugar-Lignocellulosic Composites: The Incorporation of Two Simple Saccharides into Moulding as Additives. J. Chil. Chem. Soc. 2003, 48, N 4.
- (6) Lomesh, S. K.; Jamwal, P.; Kumar, R. Molar Volume, Viscosity and Conductance Studies of Copper Sulphate in Some Multicomponent Solutions. J. Indian Chem. Soc. 2006, 83, 156–159.
- (7) Zhuo, K.; Liu, H.; Zhang, H.; Liu, Y.; Wang, J. Activity Coefficients and Volumetric Properties for the Nai + Maltose + Water System at 298.15 K. J. Chem. Eng. Data 2008, 53, 57–62.

- (8) Mathpal, R.; Joshi, B. K.; Kandpal, N. D. Intermolecular Forces of Sugars in Water. *Monatsh. Chem.* 2006, 137, 375–379.
- (9) Nikam, P. S.; Pawar, T. B.; Sawant, A. B.; Hasan, M. Limitimg Ionic Partial Molar Volumes of R₄N⁺ and Br⁻ in Aqueous Ethanol at 298.15 K. J. Mol. Liq. 2006, 126, 19–22.
- (10) Bouchard, A.; Hofland, G. W.; Witkamp, G.-J. Properties of Sugar, Polyol, and Polysaccharide Water-Ethanol Solutions. J. Chem. Eng. Data 2007, 52, 1838–1842.
- (11) Kant, S.; Kumar, K. Molar Volume, Viscosity and Conductance Studies of Nickel Sulfate in Water and Aqueous Mannitol. J. Indian Chem. Soc. 2008, 85, 1093–1101.
- (12) Kharat, S. J. Density and Viscosity studies of Aqueous Solutions of Cesium Troflouroacetate at Different Temperatures. J. Chem. Eng. Data 2008, 53, 1292–1294.
- (13) Ali, A.; Shahjahan. Interactions of Proline in Non-Aqueous Anionic, Cationic and Nonionic Surfactants at Different Temperatures. Acta Phys.-Chim. Sin. 2008, 24, 987–991.
- (14) Laxmi, V.; Singh, M. Viscometric and Thermodynamic Studies of Ion-Ion and Ion-Solvent Interactions in the Solutions of Uni-Valent and Bi-Valent Electrolytes in Purely Aqueous and Aqueous Thiourea Media at 293.15, 303.15 And 313.15 K. J. Indian Chem. Soc. 2008, 85, 184–191.
- (15) Masson, D. O. Solute Molecular Volumes in Relation to Solvation and Ionization. *Philos. Mag.* **1929**, *8*, 218–235.
- (16) Ali, A.; Sabir, S.; Tariq, M. Volumetric, Viscometric and Refractive Index Behaviors of α-Amino Acids in Aqueous Caffeine Solution at varying Temperatures. *Acta Phys.-Chim. Sin.* 2007, 23, 79–83.
- (17) Marcus, Y.; Hefter, G. Standard Partial Molar Volumes of Electrolytes and Ions in Nonaqueous Solvents. *Chem. Rev.* 2004, 104, 3405–3452.
- (18) Millero, F. J. Partial Molal Volume of Ions in Various Solvents. J. Phys. Chem. 1969, 73, 2417–2420.
- (19) Frank, H. S.; Wen, W. Y. Ion-Solvent Interaction. Structural Aspects of Ion-Solvent Interaction in Aqueous Solutions: A Suggested Picture of Water Structure. *Discuss. Faraday Soc.* **1957**, *24*, 133–140.
- (20) Iqbal, M.; Mateehullah, M. Partial Molar Volumes of Some Dipolar Ions in Water at 35°C. *Can. J. Chem.* **1990**, 68, 725–727.
- (21) Freidman, H. L.; Krishnan, C. V. Water-A comprehensive treatise; Franks, F., Ed.; Plenum Press: New York, 1973; Vol. 3, Chapter 1.
- (22) Mishra, A. K.; Prasad, K. P. Ahluwalia. Apparent Molar Volumes of Some Amino Acids, Peptides in Aqueous Urea Solutions. J. C. Biopolymers 1983, 22, 2397–2409.
- (23) Franks, H. S.; Evans, M. W. Free Volume and Entropy in Condensed System II. Entropy of Vaporization in Liquids and the Pictorial Theory of the Liquid State. J. Chem. Phys. 1945, 13, 493–507.
- (24) Hepler, L. G. Thermal Expansion and Structure in Water and Aqueous Solution. *Can. J. Chem.* **1969**, *47*, 4613–4617.
- (25) Roy, M. N.; Dakua, V. K.; Sinha, B. Partial Molar Volumes, Viscosity B- Coefficients and Adiabatic Compressibilities of Sodium Molybdate in Aqueous 1, 3-Dioxolane Mixtures from 303.15 to 323.15 K. *Int. J. Thermophys.* 2007, 28, 1275–1284.
- (26) Ali, A.; Sabir, S.; Nain, A. K.; Hyder, S.; Ahmad, S.; Patel, R. Volumetric, Viscometric and Refractive Indices Behavior of *dl*-valine, *l*-isoleucine and l-proline in Aqueous Dimethyl Sulfoxide at Different Temperatures. *J. Indian Chem. Soc.* **2006**, *83*, 581–587.
- (27) Fahimuddin, S. R. Study of the Effects of Concentration and Temperature on Electrolyte Binary System by Viscosity measurements. *Orient. J. Chem.* **1998**, *14*, 23–28.
- (28) Gupta, R.; Singh, M. Viscometric and Thermodynamic studies of Interactions in Ternary Solutions containing Sucrose and Aqueous Alkali Metal Halides at 293.15, 303.15 and 313.15 K. J. Chem. Sci. 2005, 117, 275–282.

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