Volumetric and Viscosity Properties of $MgSO_4/CuSO_4$ in Sucrose + Water Solutions at 298.15 K

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Apparent molar volumes $V_{\Phi,E}$ for $MgSO_4$, $CuSO_4$, Na_2SO_4, NaCl, $MgCl_2$, and $CuCl_2$ and viscosity *B*-coefficients for $MgSO_4/CuSO_4$ in sucrose + water solutions were determined from density and viscosity measurements at 298.15 K. Infinite-dilution apparent molar volumes $V^0_{\Phi,E}$ for Na_2SO_4, NaCl, $MgCl_2$, and $CuCl_2$ in sucrose + water solutions were evaluated. The $V^0_{\Phi,E}$ values for $MgSO_4$ and $CuSO_4$ were obtained by an additivity method. An empirical equation $V_{\Phi,E} = \sum_{i=0}^{n} \sum_{j=0}^{m} P_{ij}\, m^i{}_S m^{j/2}{}_E$ was used to relate the apparent molar volumes of $MgSO_4/CuSO_4$ to the molalities (m_E and m_S). Volumetric interaction parameters were also obtained from the transfer volumes of electrolytes. Activation energies $\Delta\mu^{0\neq}_E$ were also calculated from the viscosity *B*-coefficients. Results show that the values of standard transfer volumes, viscosity *B*-coefficients, and $\Delta\mu^{0\neq}_E$ are positive and increase usually with increasing sucrose content.

Introduction

Studies on the interactions of ions with saccharides can provide important information about physiological systems and can be used in the separation and purification processes for biomaterials. Therefore, a great deal of interest has developed in the studies of electrolytes in aqueous saccharide solutions. Morel and co-workers[1,2] have carried out a series of investigations on the association of cations and some saccharides with a specific stereochemical structure. Tian et al.[3] have used FT-IR to study the structure of crystalline galactaric acid and its K^+, $NH_4{}^+$, Ca^{2+}, Ba^{2+}, and La^{3+} complexes. In addition, the interactions of halide ions with ribose have been explored recently.[4]

Volumes and viscosities for electrolyte (E) + saccharide (S) + water (W) systems are required to understand the S−E, S−W, and E−W interactions. Banipal et al.[5] measured volumetric properties for saccharide + NaCl + H_2O systems. However, volumes and viscosities of electrolytes (especially 2:2 electrolytes) in disaccharide + water mixtures have been seldom reported.

Volumetric properties for sodium halide + monosaccharide + water systems have been investigated in our previous work. To explore further the interactions between electrolytes and saccharides, densities ρ and viscosities η of aqueous $MgSO_4/CuSO_4$ solutions are measured with and without sucrose at 298.15 K, together with densities of aqueous Na_2SO_4, NaCl, $MgCl_2$, and $CuCl_2$ solutions for obtaining accurate infinite-dilution apparent molar volumes of $MgSO_4$ and $CuSO_4$. Using these data, infinite-dilution apparent molar volumes, pair interaction parameters, viscosity *B*-coefficients, and activation free-energy parameters are also calculated. Results are discussed in terms of the structural hydration interaction model and the transition-state theory.

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Experimental Section

Chemicals. Sucrose (> 99.5 %, Sigma) was dried under a vacuum at room temperature to constant weight. NaCl (AR, > 99.0 %, Alfa) and Na_2SO_4 (AR, > 99.0 %, Beijing Chemical Co.) were dried under a vacuum at 333 K to constant weight. These dried reagents were stored over P_2O_5 in desiccators. The deionized water was doubly distilled over $KMnO_4$. The water with a conductivity of $(0.8\sim1.0)\cdot10^{-6}$ $S\cdot cm^{-1}$ was used throughout the experiments.

$MgSO_4$ and $CuSO_4$ (> 99.5 %, Alfa), $MgCl_2\cdot6H_2O$, and $CuCl_2\cdot2H_2O$ (AR, > 99.0 %, Beijing Chemical Co.) were dissolved in pure water, and then their molarities were determined by titration with EDTA.

Measurement of Densities and Viscosities. Solution densities were measured using a vibrating-tube digital densimeter (model DMA 60/602 Anton Paar Austria), which has been described elsewhere.[6–8] The temperature around the densimeter cell was controlled by circulating water from a constant-temperature bath (Schott, Germany). A CT-1450 temperature controller and a CK-100 ultracryostat were employed to maintain the bath temperature at (298.15 ± 0.005) K. The densimeter was calibrated with pure water (the value of density was taken to be 0.997046 $g\cdot cm^{-3}$ at 298.15 K[9,10]) and dry air. The uncertainty of molalities of monosaccharide and electrolytes is evaluated to be about ± 0.2 wt %. The uncertainty in density was estimated to be $\pm\ 3\cdot10^{-6}$ $g\cdot cm^{-3}$.

Solution viscosities were measured by a suspended level Ubbelohde viscometer, which was placed in a water thermostat (Schott, Germany), with a flow time of about 200 s for water at 298.15 K. The temperature of the water thermostat was controlled to be as precise as for the density measurements. The viscometer was calibrated at (298.15 and 308.15) K with water. Viscosities for water at different temperatures were taken from the literature.[11] Flow time measurements were performed by a Schott AVS310 photoelectric time unit with a resolution of 0.01 s. The estimated uncertainty of experimental viscosity

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is less than ± 0.2 %. Solution viscosity η is given by the following equation

$$\eta/\rho = Ct - K/t \quad (1)$$

where C and K are the cell constants and t is the flow time. The details of the experimental procedure were given elsewhere.[12]

Results and Discussion

Apparent Molar Volume. Densities of solutions are listed in Tables 1, 2, and 3. Apparent molar volumes of electrolytes, $V_{\Phi,E}$, were calculated from the equation[13]

$$V_{\Phi,E} = \frac{M_E}{\rho} - \frac{(1000 + m_S M_S)(\rho - \rho_1)}{m_E \rho \rho_1} \quad (2)$$

where M_S and M_E are the molar masses of sucrose and electrolytes; m_S and m_E are the molalities of sucrose and electrolytes; and ρ and ρ_1 are the densities of sucrose + electrolyte + water and sucrose + water solutions, respectively. The results are also included in Tables 1, 2, and 3. It has been observed that plots of $V_{\Phi,E}$ for the electrolytes studied versus $m_E^{1/2}$ are linear. Therefore, infinite-dilution apparent molar volumes ($V^0_{\Phi,E}$), which are equal in value to the standard partial molar volumes (V^0_E), were obtained by least-squares fitting experimental data to the following equation

$$V_{\Phi,E} = V^0_{\Phi,E} + S_E m_E^{1/2} \quad (3)$$

where S_E is the experimental slope. As $MgSO_4$/$CuSO_4$ forms ion pairs in aqueous solutions and aqueous sucrose solutions, their $V^0_{\Phi,E}$ values were determined by additivity

$$V^0_{\Phi,E}(MgSO_4) = V^0_{\Phi,I}(Mg^{2+}) + V^0_{\Phi,I}(SO_4^{2-}) = V^0_{\Phi,E}(MgCl_2) + V^0_{\Phi,E}(Na_2SO_4) - 2V^0_{\Phi,E}(NaCl) \quad (4)$$

$$V^0_{\Phi,E}(CuSO_4) = V^0_{\Phi,I}(Cu^{2+}) + V^0_{\Phi,I}(SO_4^{2-}) = V^0_{\Phi,E}(CuCl_2) + V^0_{\Phi,E}(Na_2SO_4) - 2V^0_{\Phi,E}(NaCl) \quad (5)$$

Resulting values are listed in Table 4. Values are in good agreement with literature data.[14–24]

The dependence of $V_{\Phi,E}$ on the molalities of sucrose and $MgSO_4$/$CuSO_4$ can be expressed as

$$V_{\Phi,E} = \sum_{i=0}^{n}\sum_{j=0}^{m} P_{ij} m_S^i m_E^{j/2} \quad (6)$$

Apparent molar volumes $V_{\Phi,E}$ in Table 1 and infinite-dilution apparent molar volumes $V^0_{\Phi,E}$ in Table 4 were fitted to eq 6 and

Table 1. Solution Densities ρ and Apparent Molar Volumes $V_{\Phi,E}$ for $MgSO_4$ and $CuSO_4$ in Water and in Sucrose + Water Solutions at 298.15 K

m_E / mol·kg^{-1}	ρ / g·cm^{-3}	$V_{\Phi,E}$ / cm^3·mol^{-1}	m_E / mol·kg^{-1}	ρ / g·cm^{-3}	$V_{\Phi,E}$ / cm^3·mol^{-1}	m_E / mol·kg^{-1}	ρ / g·cm^{-3}	$V_{\Phi,E}$ / cm^3·mol^{-1}
				$MgSO_4$ in water				
0.05000	1.003144	−1.93	0.20000	1.020830	1.08	0.40000	1.043794	3.02
0.10000	1.009130	−0.69	0.30000	1.032431	2.01	0.50000	1.055112	3.69
				$CuSO_4$ in water				
0.05000	1.005220	−4.68	0.20000	1.029162	−1.41	0.40000	1.060401	0.70
0.10000	1.013293	−3.25	0.30000	1.044868	−0.26	0.50000	1.075777	1.56
				$MgSO_4$ in Sucrose Solutions				
m_S/mol·kg^{-1} = 0.20000			m_S/mol·kg^{-1} = 0.40000			m_S/mol·kg^{-1} = 0.60000		
0	1.022166		0	1.045255		0	1.066440	
0.05000	1.027947	−0.47	0.05000	1.050710	1.62	0.05000	1.071667	2.06
0.10000	1.033635	0.47	0.10000	1.056118	2.10	0.10000	1.076823	2.80
0.20017	1.044810	2.05	0.20000	1.066726	3.38	0.20000	1.086955	4.08
0.30000	1.055807	2.99	0.30000	1.077188	4.26	0.30000	1.096940	4.98
0.40000	1.066581	4.03	0.40000	1.087514	5.02	0.40807	1.107711	5.48
0.5000	1.077327	4.69	0.5000	1.097699	5.72	0.5000	1.116492	6.47
m_S/mol·kg^{-1} = 0.80000			m_S/mol·kg^{-1} = 1.0000			m_S/mol·kg^{-1} = 1.2000		
0	1.086042		0	1.104198		0	1.121030	
0.05000	1.091030	3.08	0.05001	1.108951	4.34	0.05000	1.125591	4.95
0.10000	1.095957	3.72	0.10003	1.113672	4.67	0.10000	1.130117	5.32
0.20000	1.105632	4.96	0.20000	1.122922	5.84	0.20000	1.138981	6.51
0.30000	1.115159	5.86	0.30000	1.132050	6.63	0.30000	1.147724	7.31
0.40000	1.124516	6.72	0.40000	1.141066	7.30	0.40000	1.156363	7.96
0.50000	1.133862	7.22	0.50000	1.149949	7.95	0.50000	1.164888	8.57
				$CuSO_4$ in Sucrose Solutions				
m_S/mol·kg^{-1} = 0.20000			m_S/mol·kg^{-1} = 0.40000			m_S/mol·kg^{-1} = 0.60000		
0.05000	1.02994	−2.92	0.05000	1.05266	−1.33	0.05000	1.07356	−1.20
0.10000	1.03764	−2.09	0.10000	1.05998	−0.51	0.10000	1.08055	0.11
0.20000	1.05279	−0.41	0.20000	1.07446	0.74	0.20000	1.09440	1.48
0.30000	1.06778	0.63	0.30000	1.08870	1.92	0.30000	1.10802	2.67
0.40000	1.08253	1.73	0.40000	1.10285	2.69	0.40000	1.12154	3.48
0.50000	1.09726	2.37	0.50000	1.11682	3.50	0.50000	1.13491	4.24
m_S/mol·kg^{-1} = 0.80000			m_S/mol·kg^{-1} = 1.0000			m_S/mol·kg^{-1} = 1.2000		
0.05000	1.092791	1.17	0.0500	1.11068	1.78	0.04996	1.127267	2.33
0.10000	1.099534	1.23	0.1000	1.11713	2.19	0.10000	1.133462	2.78
0.20000	1.112806	2.37	0.2000	1.12983	3.37	0.20000	1.145658	4.05
0.30000	1.125863	3.47	0.3000	1.14239	4.25	0.30000	1.157721	4.91
0.40000	1.138820	4.25	0.4000	1.15481	5.02	0.40000	1.169665	5.63
0.50000	1.151628	4.99	0.5000	1.16711	5.70	0.50000	1.181475	6.32

Table 2. Solution Densities ρ and Apparent Molar Volumes $V_{\Phi,E}$ for Na_2SO_4 and NaCl in Water and in Sucrose + Water Solutions at 298.15 K

m_E / mol·kg^{-1}	ρ / g·cm^{-3}	$V_{\Phi,E}$ / cm^3·mol^{-1}	m_E / mol·kg^{-1}	ρ / g·cm^{-3}	$V_{\Phi,E}$ / cm^3·mol^{-1}	m_E / mol·kg^{-1}	ρ / g·cm^{-3}	$V_{\Phi,E}$ / cm^3·mol^{-1}
Na_2SO_4 in Sucrose Solutions								
m_S/mol·kg^{-1} = 0			m_S/mol·kg^{-1} = 0.20000			m_S/mol·kg^{-1} = 0.60000		
0.09205	1.00869	15.06	0.09926	1.03402	16.66	0.05146	1.07201	18.39
0.20010	1.02199	16.65	0.20024	1.04575	18.12	0.10261	1.07745	19.25
0.30003	1.03401	17.87	0.30001	1.05711	19.18	0.20105	1.08774	20.47
0.39992	1.04581	18.88	0.40380	1.06865	20.31	0.40222	1.10816	22.38
0.50013	1.05744	19.80	0.50126	1.07940	21.01	0.49922	1.11776	23.11
m_S/mol·kg^{-1} = 1.0000			m_S/mol·kg^{-1} = 1.2000					
0.09997	1.11389	21.72	0.10116	1.13042	22.31			
0.20014	1.12338	22.74	0.20223	1.13958	23.36			
0.29836	1.13251	23.55	0.30037	1.14830	24.21			
0.40149	1.14195	24.30	0.40041	1.15706	24.88			
0.49912	1.15073	24.94	0.49902	1.16555	25.53			
NaCl in Sucrose Solutions								
m_S/mol·kg^{-1} = 0			m_S/mol·kg^{-1} = 0.20000			m_S/mol·kg^{-1} = 0.60000		
0.04999	0.99911	17.01	0.10081	1.02605	17.74	0.05273	1.06825	18.47
0.09999	1.00116	17.17	0.20064	1.02984	17.95	0.21730	1.07380	18.76
0.19989	1.00520	17.46	0.29928	1.03354	18.11	0.30381	1.07669	18.85
0.29987	1.00920	17.64	0.40112	1.03733	18.24	0.39968	1.07986	18.97
0.40021	1.01317	17.80	0.50036	1.04101	18.33	0.49891	1.08310	19.11
m_S/mol·kg^{-1} = 1.0000			m_S/mol·kg^{-1} = 1.2000					
0.25359	1.11187	19.49	0.10847	1.12422	19.12			
0.34546	1.11460	19.58	0.20200	1.12690	19.43			
0.46797	1.11821	19.70	0.30667	1.12987	19.64			
0.53922	1.12030	19.77	0.39566	1.13237	19.76			
0.58212	1.12154	19.81	0.49183	1.13505	19.89			

Table 3. Solution Densities ρ and Apparent Molar Volumes $V_{\Phi,E}$ for $MgCl_2$ and $CuCl_2$ in Water and in Sucrose + Water Solutions at 298.15 K

m_E / mol·kg^{-1}	ρ / g·cm^{-3}	$V_{\Phi,E}$ / cm^3·mol^{-1}	m_E / mol·kg^{-1}	ρ / g·cm^{-3}	$V_{\Phi,E}$ / cm^3·mol^{-1}	m_E / mol·kg^{-1}	ρ / g·cm^{-3}	$V_{\Phi,E}$ / cm^3·mol^{-1}
$MgCl_2$ in Sucrose Solutions								
m_S/mol·kg^{-1} = 0			m_S/mol·kg^{-1} = 0.20000			m_S/mol·kg^{-1} = 0.60000		
0.09998	1.00488	16.56	0.04971	1.02587	16.86	0.10329	1.07333	18.48
0.20005	1.01254	17.33	0.10137	1.02967	17.30	0.20141	1.07974	19.05
0.30005	1.02007	17.89	0.19989	1.03682	17.91	0.30052	1.08612	19.51
0.40017	1.02751	18.36	0.40130	1.05108	18.93	0.40185	1.09255	19.93
0.49999	1.03483	18.76	0.50100	1.05801	19.31	0.49842	1.09860	20.28
m_S/mol·kg^{-1} = 1.0000			m_S/mol·kg^{-1} = 1.2000					
0.10085	1.11029	19.63	0.05036	1.12395	19.79			
0.20006	1.11619	20.03	0.20613	1.13282	20.49			
0.29849	1.12195	20.43	0.31372	1.13883	20.92			
0.40204	1.12792	20.81	0.41441	1.14438	21.23			
0.49933	1.13345	21.17	0.51123	1.14966	21.52			
$CuCl_2$ in Sucrose Solutions								
m_S/mol·kg^{-1} = 0			m_S/mol·kg^{-1} = 0.20000			m_S/mol·kg^{-1} = 0.60000		
0.04980	1.00312	12.13	0.05198	1.02816	13.54	0.10161	1.07702	15.60
0.09962	1.00910	12.95	0.09941	1.03357	14.12	0.20250	1.08734	16.35
0.19919	1.02092	13.96	0.19982	1.04485	15.13	0.29948	1.09712	17.00
0.29880	1.03258	14.71	0.29886	1.05584	15.81	0.40248	1.10739	17.55
0.49805	1.05547	15.92	0.50053	1.07778	16.99	0.50156	1.11714	18.09
m_S/mol·kg^{-1} = 1.0000			m_S/mol·kg^{-1} = 1.2000					
0.04905	1.10889	16.33	0.05294	1.12590	16.57			
0.09986	1.11371	16.73	0.20886	1.13997	17.82			
0.29866	1.13221	18.04	0.30274	1.14829	18.40			
0.40433	1.14185	18.61	0.40348	1.15713	18.90			
0.49932	1.15042	19.05	0.51254	1.16654	19.46			

showed that when $n = 2$ and $m = 3$ eq 6 can work well for the studied systems. The P_{ij} values obtained are given in Table 5, along with the estimated standard deviations of the fits. Using eq 6 and values of P_{ij} in Table 5, apparent molar volumes in the experimental concentration range can be evaluated, as well as infinite-dilution apparent molar volumes.

Plots of $V^0_{\Phi,E}$ versus m_S are represented in Figure 1, indicating that (1) values of $V^0_{\Phi,E}$ for Na_2SO_4, NaCl, $MgCl_2$, and $CuCl_2$ are positive, whereas those for $MgSO_4$ and $CuSO_4$ are negative except $MgSO_4$ at $m_S = 1.2$ mol·kg^{-1}; (2) values of $V^0_{\Phi,E}$ for all six electrolytes increase with increasing m_S except NaCl at $m_S = 1.2$ mol·kg^{-1}; and (3) the $V^0_{\Phi,CuSO_4}$ values are more negative than $V^0_{\Phi,MgSO_4}$.

Table 4. Infinite-Dilution Apparent Molar Volumes for Electrolytes in Water and in Sucrose + Water Solutions at 298.15 K

m_S / mol·kg^{-1}	V^0_{Φ,Na_2SO_4} / cm^3·mol^{-1}	$V^0_{\Phi,NaCl}$ / cm^3·mol^{-1}	$V^0_{\Phi,MgCl_2}$ / cm^3·mol^{-1}	$V^0_{\Phi,CuCl_2}$ / cm^3·mol^{-1}	$V^0_{\Phi,MgSO_4}$ / cm^3·mol^{-1}	$V^0_{\Phi,CuSO_4}$ / cm^3·mol^{-1}
0	11.46 ± 0.08	16.57 ± 0.02	14.80 ± 0.03	10.45 ± 0.06	−6.89	−11.25
	11.56[a]	16.62[a]	14.49[a]	9.79[i]		
	11.72[b]	16.61[e,f]	14.52[d,f]	10.14[j]		
	11.62[c]	16.65[g]	14.51[h]	10.1[k]		
0.20000	13.12 ± 0.11	17.26 ± 0.02	15.69 ± 0.05	11.88 ± 0.04	−5.72	−9.53
0.60000	16.10 ± 0.06	18.15 ± 0.04	16.96 ± 0.03	13.52 ± 0.08	−3.24	−6.68
1.0000	19.08 ± 0.07	18.86 ± 0.02	18.31 ± 0.11	15.01 ± 0.09	−0.32	−3.63
1.2000	19.66 ± 0.04	18.48 ± 0.07	18.96 ± 0.08	15.18 ± 0.08	1.67	−2.12

[a] Ref 14. [b] Ref 15. [c] Ref 16. [d] Ref 17. [e] Ref 18. [f] Ref 19. [g] Ref 20. [h] Ref 21. [i] Ref 22. [j] Ref 23. [k] Ref 24.

Table 5. Coefficients of Equation 8 and the Standard Deviations of the Fit σ

P_{ij}[a]	$MgSO_4$−sucrose	$CuSO_4$−sucrose
P_{00}	−6.825	−11.165
P_{10}	5.013	7.901
P_{20}	1.679	−0.292
P_{01}	28.029	38.538
P_{11}	29.847	9.678
P_{21}	−31.434	−15.615
P_{02}	−32.099	−51.834
P_{12}	−95.895	−53.958
P_{22}	84.818	49.123
P_{03}	19.264	32.237
P_{13}	76.724	49.622
P_{23}	−64.768	−40.440
σ/cm^3·mol^{-1}	0.221	0.270

[a] Units of P_{ij}: cm^3·mol^{-1}·(mol·kg^{-1})$^{-(i+j)}$.

The infinite-dilution apparent molar volume of an electrolyte ($V^0_{\Phi,E}$) is the sum of individual ionic volumes ($V^0_{\Phi,I}$). The values of $V^0_{\Phi,I}$ can be expressed as

$$V^0_{\Phi,I} = V_{int} + \Delta V_e \quad (7)$$

where V_{int} is the intrinsic volume and is a positive value, and ΔV_e is the apparent electrostriction volume, which arises mainly from the solvent−structure reaction volume (V_r) and the electrostriction volume (V_e) due to the electrostatic compression of the dielectric solvent around the ion by the ionic field and field gradient. Normally, ΔV_e is a negative quantity. The anions (Cl^-/SO_4^{2-}) have relatively large ion radii, and hence ΔV_e have relatively small negative values; whereas monatomic cations, particularly high charged cations (Cu^{2+}/Mg^{2+}), have relatively small ion radii, and hence ΔV_e have large negative values. This is a reason why the $V^0_{\Phi,E}$ values for $MgSO_4$ and $CuSO_4$ are negative.

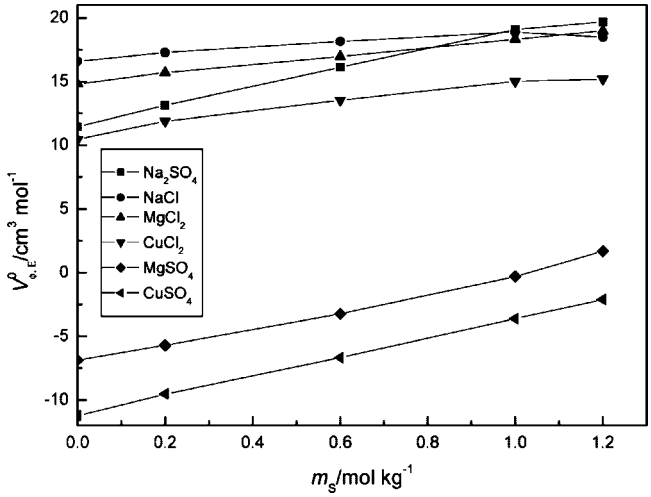

Figure 1. Infinite-dilution apparent molar volumes for electrolytes in sucrose + water solutions as a function of m_S at 298.15 K.

Table 6. Volumetric Interaction Parameters for Electrolyte + Sucrose + Water Solutions at 298.15 K

electrolyte	$2v\upsilon_{ES}$ / cm^3·mol^{-2}·kg	$3v\upsilon_{ESS}$ / cm^3·mol^{-3}·kg^2	σ / cm^3·mol^{-1}
Na_2SO_4	8.568 ± 0.301	−1.259 ± 0.357	0.275
NaCl	3.754 ± 0.220	−1.694 ± 0.261	0.200
$MgCl_2$	4.412 ± 0.279	−0.891 ± 0.331	0.254
$CuCl_2$	7.480 ± 0.483	−3.041 ± 0.573	0.440
$MgSO_4$	5.472 ± 0.226	1.239 ± 0.268	0.206
$CuSO_4$	8.540 ± 0.366	−0.911 ± 0.435	0.334

With increasing m_S, the dehydration effect of the ions increases, and then the negative contribution from ΔV_e decreases. Therefore, the $V^0_{\Phi,E}$ values increase.

Both Mg^{2+} and Cu^{2+} have two net positive charges and have almost the same ionic radii [$r_p(Mg^{2+}) = 0.65$ Å, $r_p(Cu^{2+}) = 0.72$ Å, $r_G(Mg^{2+}) = 0.78$ Å, $r_G(Cu^{2+}) = 0.72$Å[25]]; however, Cu^{2+} has a larger nuclear charge ($Z = 29$) than Mg^{2+} ($Z = 12$), and the 3d electrons of Cu^{2+} have a poor screening effect of the atomic nucleus. Thus, the Cu^{2+} attracts more strongly the O atoms of water molecules in the hydration shell around Cu^{2+} than Mg^{2+}. This is a reason why the ΔV_e values of Cu^{2+} are more negative than Mg^{2+}.

McMillan and Mayer[26] proposed a theory of solution that permits the formal separation of the interactions between two or more solute molecules. According to this treatment, the transfer apparent molar volume of an electrolyte from water to sucrose + water solutions ($\Delta_t V_{\Phi,E}$) can be expressed as

$$\Delta_t V_{\Phi,E} = V_{\Phi,E}(m_E,m_S) - V_{\Phi,E}(m_E) = 2v\upsilon_{ES}m_S + 3v^2\upsilon_{EES}m_Em_S + 3v\upsilon_{ESS}m_S^2 + \ldots \quad (8)$$

where υ is the number of ions into which the electrolyte dissociates and υ_{ES}, υ_{EES}, and υ_{ESS} are pair and triplet interaction parameters, respectively. Equation 8 can be rearranged as follows when $m_E = 0$

$$\Delta_t V^0_{\Phi,E}/m_S = 2v\upsilon_{ES} + 3v\upsilon_{ESS}m_S + \ldots \quad (9)$$

These interaction parameters were obtained using least-squares and are included in Table 6, together with their standard deviations.

Positive υ_{ES} values indicate that the interactions between electrolytes and sucrose contribute a positive value to volume. This is due to the dehydration of ions, which contributes a positive volume. It is noticed that $\upsilon_{ES}(CuSO_4) > \upsilon_{ES}(MgSO_4)$, i.e., $\upsilon_{Cu^{2+}\text{-}S} > \upsilon_{Mg^{2+}\text{-}S}$. Since $\Delta V_e(Cu^{2+})$ is more negative than $\Delta V_e(Mg^{2+})$, the dehydration of Cu^{2+} contributes a more positive volume to υ_{ES}. Hence the pair interaction parameter (υ_{ES}) for $CuSO_4$ is larger than that for $MgSO_4$.

Table 7. Viscosities η of the Electrolyte + Water and Electrolyte + Sucrose + Water Solutions at 298.15 K

c^a / mol·cm^{-3}	η / mPa·s	c^a / mol·cm^{-3}	η / mPa·s	c^a / mol·cm^{-3}	η / mPa·s	c^a / mol·cm^{-3}	η / mPa·s
			$MgSO_4$				
m_S/mol·kg^{-1} = 0		m_S/mol·kg^{-1} = 0.20000		m_S/mol·kg^{-1} = 0.40000		m_S/mol·kg^{-1} = 0.60000	
0	0.8904[b]	0	1.0641	0	1.2769	0	1.5326
0.04787	0.9216	0.04783	1.1047	0.04642	1.3274	0.04510	1.5948
0.09971	0.9527	0.09566	1.1420	0.09192	1.3722	0.08845	1.6511
0.19937	1.0158	0.19128	1.2216	0.18376	1.4695	0.17682	1.7732
0.29893	1.0831	0.28676	1.3048	0.27549	1.5815	0.26507	1.9008
0.39834	1.1552	0.38208	1.3946	0.36707	1.6864	0.35321	2.0411
0.49761	1.2336	0.47727	1.4919	0.45848	1.8081	0.44110	2.1912
m_S/mol·kg^{-1} = 0.80000		m_S/mol·kg^{-1} = 1.0000		m_S/mol·kg^{-1} = 1.2000			
0	1.8425	0	2.2411	0	2.6382		
0.04262	1.9176	0.04112	2.2860	0.03972	2.7479		
0.08523	1.9878	0.08223	2.3733	0.07943	2.8544		
0.17037	2.1368	0.16437	2.5534	0.15876	3.0782		
0.25539	2.2990	0.24638	2.7498	0.23797	3.3204		
0.34025	2.4683	0.32826	2.9582	0.31705	3.5813		
0.42545	2.6606	0.41273	3.1981	0.39597	3.8608		
			$CuSO_4$				
m_S/mol·kg^{-1} = 0		m_S/mol·kg^{-1} = 0.20000		m_S/mol·kg^{-1} = 0.40000		m_S/mol·kg^{-1} = 0.60000	
0.04986	0.9222	0.04784	1.1031	0.04597	1.3236	0.04424	1.5914
0.09974	0.9516	0.09569	1.1394	0.09194	1.3696	0.08847	1.6462
0.19947	1.0128	0.19135	1.2166	0.18385	1.4641	0.17690	1.7640
0.29914	1.0827	0.28695	1.3031	0.27567	1.5700	0.26523	1.8971
0.39871	1.1473	0.38242	1.3844	0.36739	1.6847	0.35346	2.0188
0.49814	1.2225	0.47779	1.4761	0.45895	1.7857	0.44154	2.1584
m_S/mol·kg^{-1} = 0.80000		m_S/mol·kg^{-1} = 1.0000		m_S/mol·kg^{-1} = 1.2000			
0.04220	1.9132	0.04113	2.3023	0.03973	2.7449		
0.08525	1.9827	0.08225	2.3647	0.07945	2.8468		
0.17045	2.1260	0.16443	2.5370	0.15882	3.0599		
0.25554	2.2894	0.24653	2.7245	0.23811	3.3035		
0.34054	2.4482	0.32850	2.9317	0.31728	3.5432		
0.42769	2.6240	0.41035	3.1304	0.39632	3.7969		

[a] c molarity of electrolytes (in mol·dm^{-3}). [b] Ref 11.

Viscosity B-Coefficient. The experimental viscosity data for the systems studied are collected in Table 7. The relative viscosity η_r can be analyzed using the Jones−Dole equation[27]

$$\eta_r = \eta/\eta_1 = 1 + Ac^{1/2} + Bc + Dc^2 \qquad (10)$$

where η and η_1 are, respectively, the viscosity of the electrolyte solutions and the solvent (water or sucrose + water mixed solvent); c (mol·dm^{-3}) is the molarity of the electrolyte; and A, B, and D are empirical constants known as the viscosity A-, B-, and D-coefficients. Equation 10 can be rearranged as

$$(\eta_r - 1)/c^{1/2} = A + Bc^{1/2} + Dc^{3/2} \qquad (11)$$

Values of A, B, and D were obtained by the fit of experimental data to the equation and are given in Table 8, together with correlation coefficients. Using theoretical values of A (A can be calculated by the physical properties of the solvent and the limiting equivalent conductances[28]), values of B were also obtained by fit to eq 11 and are also collected in Table 8. Thus obtained values are in good agreement with the literature data[29] listed in Table 8.

The A-coefficient represents the contribution from interionic electrostatic forces. The B-coefficient represents the order or disorder of the solvent molecules in the solvation shell of the ions except the size and shape of the ions. In other words, the B-coefficient is connected with the ion−solvent interactions. The A-coefficients obtained by the fit are small positive values and are in reasonable agreement with theoretically evaluated values (see Table 8).

The B-coefficients for $MgSO_4$ and $CuSO_4$ exhibit positive values and increase with increasing molalities of sucrose except those at m_S = 1.0 mol·kg^{-1} (Figure 2). The rather pronounced deviation of the B-coefficient in 1.0 mol·kg^{-1} should not result from some experimental problems because the measurements were remade twice at this concentration and the same results were obtained. To understand the specialty of the B-coefficients at m_S = 1.0 mol·kg^{-1}, it is necessary to carry out more work both experimentally and theoretically. This shows that $MgSO_4$ and $CuSO_4$ are "structure makers". Given that SO_4^{2-} is a weak "structure breaker",[30] the "structure making" behavior of the two electrolytes can be attributed mainly to M^{2+} (Cu^{2+}/Mg^{2+}). The structure making behavior of M^{2+} enhances as the sucrose concentration increases, confirming that M^{2+} is solvated preferentially by sucrose molecules. At a given molality of sucrose, the B-coefficients are in the order: $CuSO_4$ > $MgSO_4$, indicating that Cu^{2+} is a stronger structure maker than Mg^{2+}.

Activation Parameters for Viscous Flow. The viscosity data have also been analyzed on the basis of transition-state theory of the relative viscosity of electrolyte solutions suggested by Feakins et al.[31]

$$B = (V_{\Phi,1} - V^0_{\Phi,E})/1000 + (V_{\Phi,1}/1000)(\Delta\mu^{0\ddagger}_E - \Delta\mu^{\ddagger}_1)/(RT) \qquad (12)$$

where $V_{\Phi,1}$ is the molar volume of the solvent. When a binary solvent is used, $V_{\Phi,1}$ is the molar volume of the mixed solvent, which equals in value the molar mass of the mixed solvent

Table 8. Viscosity *A*-, *B*-, and *D*-Coefficients of Electrolytes in Water and in Sucrose + Water Solutions at 298.15 K

m_S / mol·kg^{-1}	A / dm$^{3/2}$·mol$^{-1/2}$	B / dm^3·mol^{-1}	D / dm^6·mol^{-2}	R[e]
		$MgSO_4$		
0	0.0316 ± 0.0015	0.571 ± 0.0054	0.318 ± 0.0076	0.99999
	0.0228[a]	0.601 ± 0.0041[b]	0.279 ± 0.0109	0.99994
	0.0228[a]	0.591[c], 0.585[c], 0.59[d]		
0.20000	0.0333 ± 0.0032	0.628 ± 0.011	0.346 ± 0.017	0.99998
0.40000	0.0270 ± 0.0147	0.699 ± 0.053	0.368 ± 0.081	0.99966
0.60000	0.0323 ± 0.0036	0.728 ± 0.014	0.447 ± 0.021	0.99998
0.80000	0.0354 ± 0.0051	0.759 ± 0.019	0.536 ± 0.032	0.99996
1.0000	0.0695 ± 0.0032	0.745 ± 0.012	0.648 ± 0.021	0.99998
1.2000	0.0277 ± 0.0004	0.884 ± 0.002	0.611 ± 0.003	0.99999
		$CuSO_4$		
0	0.0216 ± 0.0119	0.602 ± 0.042	0.232 ± 0.058	0.99969
	0.0230[a]	0.597 ± 0.009[b]	0.239 ± 0.024	0.99969
	0.0230[a]	0.582[c], 0.594[e], 0.568[d]		
0.20000	0.0160 ± 0.0115	0.673 ± 0.041	0.240 ± 0.060	0.99975
0.40000	0.0050 ± 0.0187	0.752 ± 0.068	0.254 ± 0.104	0.99942
0.60000	0.0124 ± 0.0156	0.783 ± 0.058	0.279 ± 0.092	0.99961
0.80000	0.0134 ± 0.0113	0.820 ± 0.043	0.358 ± 0.070	0.99982
1.0000	0.0592 ± 0.0131	0.751 ± 0.050	0.526 ± 0.086	0.99976
1.2000	0.0170 ± 0.0128	0.904 ± 0.050	0.454 ± 0.088	0.99980

[a] Theoretical values.[28] [b] Obtained using the theoretical values of *A*. [c] Selected by Donald, Jenkins, and Marcus.[28] [d] Ref 29. [e] *R* = Correlation coefficient.

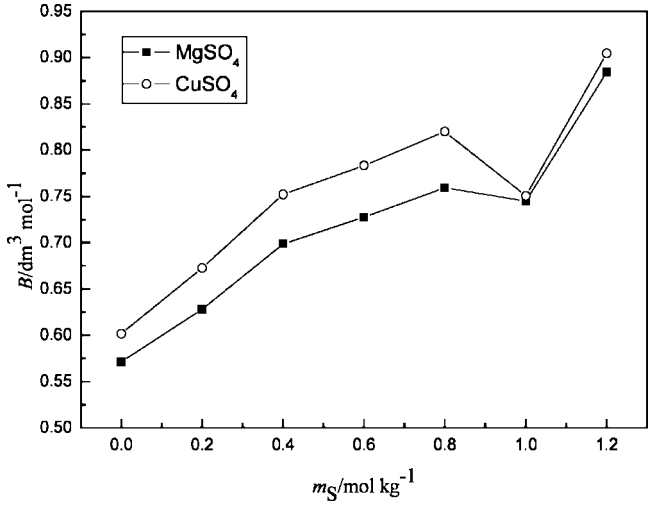

Figure 2. Viscosity *B*-coefficients of electrolytes in water and in sucrose + water solutions as a function of molality of sucrose at 298.15 K.

divided by its density. $V^0_{\Phi,E}$ is the infinite-dilution apparent molar volume of the electrolyte. $\Delta\mu_1^{\neq}$ is the free energy of activation per mole of solvent and is given by

$$\Delta\mu_1^{\neq} = RT\ln(\eta_1 V_{\Phi,1}/hN_A) \quad (13)$$

where h is Planck's constant; N_A is the Avogadro constant; η_1 is the viscosity of the solvent; and $\Delta\mu_E^{0\neq}$ is the contribution per mole of solute (electrolyte) to the free energy of activation for viscous flow of the solution at infinite dilution. Hence, eq 13 can be rearranged as follows

$$\Delta\mu_E^{0\neq} = \Delta\mu_1^{\neq} + (RT/V_{\Phi,1})[1000B - (V_{\Phi,1} - V^0_{\Phi,E})] \quad (14)$$

The $\Delta\mu_E^{0\neq}$ values in water and in sucrose + water mixed solvents were calculated and are recorded in Table 9.

The trends in $\Delta\mu_E^{0\neq}$ for $MgSO_4$ and $CuSO_4$ with addition of sucrose are almost the same as those in *B*-coefficients. The $\Delta\mu_E^{0\neq}$ values in Table 9 are positive and increase with increasing sucrose content. This suggests that the formation of the transition state is less favored in the presence of ions and accompanied by the breaking of attractive interactions between ions and solvents. Addition of sucrose strengthens the interactions of ions with the mixed solvent. It is also found that values of $\Delta\mu_E^{0\neq}$ are in the order: $CuSO_4 > MgSO_4$, meaning that it is more difficult to form the transition state for Cu^{2+} than for Mg^{2+}. This can be ascribed to the fact that the solvation effect for Cu^{2+} is stronger than Mg^{2+} and is identical to the conclusion from the volumetric properties discussed above.

Rearrangement of eq 12 yields

$$B = \left(\frac{V_{\Phi,1}}{1000} - \frac{\Delta\mu^{\neq}_{\Phi,1}V_{\Phi,1}}{1000RT}\right) + \left(\frac{V_{\Phi,1}\Delta\mu^{0\neq}_{\Phi,E}}{1000RT} - \frac{\Delta\mu^{0\neq}_{\Phi,E}}{1000}\right) \quad (15a)$$

$$B_1 = \left(\frac{V_{\Phi,1}}{1000} - \frac{\Delta\mu^{\neq}_{\Phi,1}V_{\Phi,1}}{1000RT}\right) \quad (15b)$$

Table 9. Activation Free Energy of Binary Sucrose + Water Solvents $\Delta\mu_1^{\neq}$ and of $MgSO_4$ and $CuSO_4$ ($\Delta\mu_E^{0\neq}$) in Binary Sucrose + Water Solvents at Infinite-Dilution and B_1, B_2 Values at 298.15 K

m_S / mol·kg^{-1}	$\Delta\mu_1^{\neq}$ / kJ·mol^{-1}	B_1 / dm^3·mol^{-1}	$\mu_E^{0\neq}$ / kJ·mol^{-1}	B_2 / dm^3·mol^{-1}	$\Delta\mu_E^{0\neq}$ / kJ·mol^{-1}	B_2 / dm^3·mol^{-1}
	Sucrose + Water		$MgSO_4$		$CuSO_4$	
0	9.2	−0.049	84.1	0.620	87.7	0.651
0.20000	9.7	−0.055	89.4	0.683	94.9	0.728
0.40000	10.2	−0.061	96.3	0.760	102.6	0.813
0.60000	10.8	−0.067	97.5	0.795	103.9	0.850
0.80000	11.3	−0.074	99.0	0.833	105.8	0.894
1.0000	11.9	−0.082	95.2	0.827	95.5	0.833
1.2000	12.4	−0.089	108.8	0.973	110.6	0.993

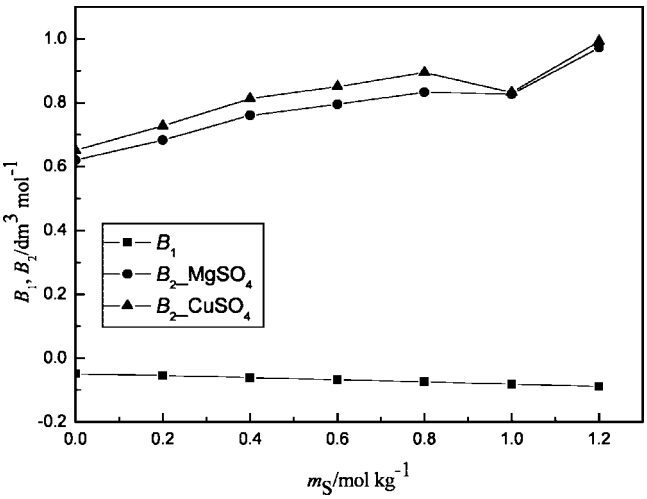

Figure 3. B_1 and B_2 values for electrolyte + sucrose + water systems as a function of molality of sucrose at 298.15 K.

$$B_2 = \left(\frac{V_{\Phi,1} \Delta\mu^{0\pm}_{\Phi,E}}{1000RT} - \frac{\Delta\mu^{0\pm}_{\Phi,E}}{1000} \right) \tag{15c}$$

where B_1 and B_2 are, respectively, the contributions of the solvent properties ($V_{\Phi,1}$ and $\Delta\mu_1^{\pm}$) and the electrolyte−solvent interactions to the B value (listed in Table 9). Figure 3 shows that the B_1 values are small and negative and get more negative with increasing m_S. B_2 values are relatively larger and positive and increase with increasing m_S. So the contributions of electrolyte−solvent interactions dominate. The B_2 values are in the order: B_2 ($CuSO_4$) > B_2 ($MgSO_4$), confirming that the interaction between Cu^{2+} and the solvent is stronger than Mg^{2+}.

Supporting Information Available:

Figures S1 and S2 show variation of apparent molar volumes $V_{\Phi,E}$ for $MgSO_4$ and $CuSO_4$ in sucrose + water solutions with molalities of $MgSO_4$ and sucrose at 298.15 K. This material is available free of charge via the Internet at http://pubs.acs.org.

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