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Enthalpic Interactions of Formamide with D-Mannitol and D-Sorbitol in Aqueous Sodium Chloride Solutions at 298.15 K[†]

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The enthalpies of mixing of formamide with D-mannitol and D-sorbitol and their respective enthalpies of dilution in aqueous sodium chloride solution have been determined by using flow-mix-isothermal microcalorimetry at 298.15 K. These experimental results have been used to determine the heterotactic enthalpic interaction coefficients (h_{xy}, h_{xxy}, and h_{xyy}) according to the McMillan−Mayer theory. It has been found that the heterotactic enthalpic pairwise interaction coefficients (h_{xy}) between formamide and D-mannitol in aqueous sodium chloride solution are positive and become more positive with an increase in the molality of sodium chloride. In contrast, the h_{xy} between formamide and D-sorbitol varies from a negative value to a positive one and increases with the elevated molality of sodium chloride. The results are discussed in terms of solute−solute interaction and solute−solvent interaction.

Introduction

Interactions between the solvents and various functional groups on the protein, along with the various noncovalent bonding interactions among protein constituent groups, are very important factors that determine the folded conformation of a globular protein.[1] As proteins are large complex molecules, small solutes that incorporate some of the structural features found in proteins have been used as models for specific aspects of proteins in aqueous solution.[2−4] Amides are the simplest molecules containing a peptide linkage and are considered to be one of the important model compounds of protein molecules.[5,6]

Many investigations have shown that polyalcohol can increase the thermal stability of globular proteins or reduce the extent of denaturation by other reagents.[7−9] D-Mannitol, clinically used as a hyperosmolar solution in the treatment of elevated intracranial pressure in brain trauma, can reduce brain water content by establishing an osmotic gradient.[10−12] It is also used as a diuretic agent.[13] As an important isomer of D-mannitol, D-sorbitol, is derived from glucose by the enzyme aldose reductase in many cells of the human and animal body.[14,15] Its function and clinic application are similar to those of D-mannitol. On the other hand, sodium chloride is an electrolyte that bears an extraordinary important function in biological systems. Studies on the interactions of acylamide with polyalcohol in aqueous sodium chloride solutions will be helpful to understand the stabilizing mechanism of proteins in the biological systems. As an extension to our previous study,[16] the present work is aimed at measuring the mixing enthalpies of formamide with D-mannitol and D-sorbitol along with their respective dilution enthalpies in aqueous sodium chloride solutions. By analyzing the results, the heterotactic enthalpic interaction coefficients of formamide with D-mannitol and D-sorbitol in aqueous sodium chloride solutions with different molalities are obtained.

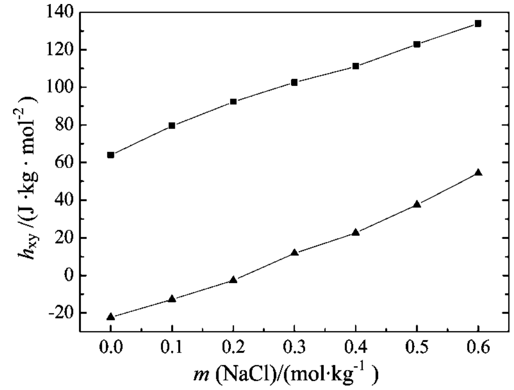

Figure 1. Enthalpic pair interaction coefficients (h_{xy}) of formamide with D-mannitol and D-sorbitol versus the molality m of sodium chloride in aqueous solutions at 298.15 K: ■, D-mannitol; ▲, D-sorbitol.

Experimental

Materials. Formamide, D-mannitol, and D-sorbitol were all purchased from Aldrich, and the purity is better than 99 %. Both D-mannitol and D-sorbitol were dried under reduced pressure at 323 K before being used. Sodium chloride (analytical reagent, mass fraction > 99 %, from the Shanghai Chem. Co.) was recrystallized from distilled water and dried under reduced pressure at 393 K. All the reagents were stored over P_2O_5 in a vacuum desiccator for 72 h at room temperature prior to use.

Twice distilled water was deionized by passing through a quartz sub-boiling purifier before use in the preparation of solutions. All the solutions were prepared by mass using a Mettler AG 135 balance with precision to ± 0.00001 g. The molality range of aqueous sodium chloride solutions was (0 to 0.60) mol·kg^{-1}. The molality ranges of aqueous formamide, D-mannitol, and D-sorbitol were all (0.10 to 0.40) mol·kg^{-1}. All the solutions were degassed with ultrasonic waves and used within 12 h of preparation.

Apparatus and Procedure. The enthalpies of dilution and mixing were determined with a 2277-204 Measuring Cylinder

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Table 1. Enthalpies of Mixing of Formamide and D-Mannitol along with Those of Their Dilution in Water and Aqueous Sodium Chloride Solutions at 298.15 K

$m(\text{NaCl})$ / mol·kg^{-1}	$m_{x,\text{i}}$ / mol·kg^{-1}	$m_{y,\text{i}}$ / mol·kg^{-1}	m_x / mol·kg^{-1}	m_y / mol·kg^{-1}	$\Delta H_{\text{dil}(x)}$ / J·kg^{-1}	$\Delta H_{\text{dil}(y)}$ / J·kg^{-1}	ΔH_{mix} / J·kg^{-1}	ΔH^* / J·kg^{-1}
0.0000	0.1000	0.1000	0.0571	0.0495	3.81	−0.25	0.30	−3.25
	0.1500	0.1500	0.0859	0.0740	4.16	−0.56	0.72	−2.88
	0.1800	0.1800	0.1028	0.0886	4.55	−0.80	1.15	−2.6
	0.2000	0.2000	0.1141	0.0983	4.77	−0.99	1.48	−2.3
	0.2200	0.2200	0.1245	0.1081	5.10	−1.19	1.86	−2.05
	0.2500	0.2500	0.1419	0.1226	5.51	−1.52	2.34	−1.65
	0.2800	0.2800	0.1593	0.1373	6.05	−1.90	2.92	−1.22
	0.3000	0.3000	0.1722	0.1467	6.39	−2.18	3.39	−0.82
	0.3200	0.3200	0.1827	0.1564	6.83	−2.47	3.83	−0.53
	0.3500	0.3500	0.1976	0.1707	7.51	−2.95	4.53	−0.03
	0.3800	0.3800	0.2161	0.1852	8.18	−3.47	5.26	0.55
	0.4000	0.4000	0.2270	0.1947	8.64	−3.84	5.83	0.97
0.1000	0.1000	0.1000	0.0566	0.0490	3.83	−0.27	0.32	−3.24
	0.1500	0.1500	0.0852	0.0732	4.25	−0.59	0.89	−2.76
	0.1800	0.1800	0.1020	0.0877	4.57	−0.84	1.38	−2.35
	0.2000	0.2000	0.1132	0.0972	4.82	−1.03	1.66	−2.14
	0.2200	0.2200	0.1235	0.1069	5.13	−1.23	2.08	−1.82
	0.2500	0.2500	0.1407	0.1212	5.56	−1.57	2.53	−1.45
	0.2800	0.2800	0.1580	0.1358	6.07	−1.95	3.21	−0.91
	0.3000	0.3000	0.1709	0.1451	6.43	−2.23	3.70	−0.50
	0.3200	0.3200	0.1811	0.1547	6.84	−2.52	4.10	−0.22
	0.3500	0.3500	0.1959	0.1688	7.49	−2.99	4.80	0.30
	0.3800	0.3800	0.2142	0.1831	8.19	−3.52	5.66	1.00
	0.4000	0.4000	0.2252	0.1925	8.66	−3.92	6.04	1.30
0.2000	0.1000	0.1000	0.0556	0.0494	3.85	−0.29	−0.72	−3.30
	0.1500	0.1500	0.0833	0.0737	4.23	−0.64	−0.13	−3.10
	0.1800	0.1800	0.0999	0.0883	4.54	−0.90	0.33	−2.99
	0.2000	0.2000	0.1110	0.0980	4.78	−1.10	0.70	−2.76
	0.2200	0.2200	0.1224	0.1076	5.04	−1.32	1.10	−3.72
	0.2500	0.2500	0.1390	0.1219	5.47	−1.69	1.76	−1.56
	0.2800	0.2800	0.1549	0.1364	5.97	−2.09	2.47	−0.95
	0.3000	0.3000	0.1665	0.1464	6.34	−2.38	3.04	−0.64
	0.3200	0.3200	0.1773	0.1559	6.70	−2.69	3.57	−4.01
	0.3500	0.3500	0.1939	0.1703	7.30	−3.19	4.44	0.31
	0.3800	0.3800	0.2104	0.1844	7.97	−3.76	5.26	−4.22
	0.4000	0.4000	0.2213	0.1940	8.43	−4.18	5.91	1.67
0.3000	0.1000	0.1000	0.0540	0.0491	3.92	−0.32	−0.05	−3.65
	0.1500	0.1500	0.0804	0.0735	4.28	−0.69	0.44	−3.15
	0.1800	0.1800	0.0961	0.0879	4.56	−0.98	0.97	−2.61
	0.2000	0.2000	0.1072	0.0975	4.77	−1.19	1.33	−2.25
	0.2200	0.2200	0.1175	0.1072	5.01	−1.43	1.71	−1.87
	0.2500	0.2500	0.1332	0.1216	5.40	−1.82	2.32	−1.26
	0.2800	0.2800	0.1483	0.1359	5.87	−2.27	3.00	−0.61
	0.3000	0.3000	0.1619	0.1456	6.22	−2.59	3.66	0.03
	0.3200	0.3200	0.1716	0.1550	6.55	−2.92	4.12	0.50
	0.3500	0.3500	0.1868	0.1692	7.09	−3.47	4.91	1.29
	0.3800	0.3800	0.2043	0.1834	7.74	−4.08	5.94	2.28
	0.4000	0.4000	0.2124	0.1931	8.10	−4.51	6.31	2.72
0.4000	0.1000	0.1000	0.0541	0.0495	4.15	−0.34	−0.85	−4.66
	0.1500	0.1500	0.0814	0.0740	4.96	−0.78	0.14	−4.04
	0.1800	0.1800	0.0972	0.0886	5.58	−1.08	0.85	−3.65
	0.2000	0.2000	0.1079	0.1004	6.00	−1.37	1.33	−3.30
	0.2200	0.2200	0.1189	0.1082	6.39	−1.62	1.72	−3.05
	0.2500	0.2500	0.1350	0.1227	7.05	−2.07	2.43	−2.55
	0.2800	0.2800	0.1510	0.1371	7.80	−2.59	3.11	−2.10
	0.3000	0.3000	0.1634	0.1466	8.21	−2.98	3.49	−1.74
	0.3200	0.3200	0.1728	0.1562	8.84	−3.33	4.05	−1.46
	0.3500	0.3500	0.1858	0.1702	9.91	−4.04	4.85	−1.02
	0.3800	0.3800	0.2017	0.1845	10.88	−4.76	5.49	−0.63
	0.4000	0.4000	0.2152	0.1936	11.38	−5.24	5.92	−0.22
0.5000	0.1000	0.1000	0.0543	0.0491	4.10	−0.36	0.08	−3.66
	0.1500	0.1500	0.0818	0.0735	4.55	−0.80	0.74	−3.00
	0.1800	0.1800	0.0976	0.0880	4.92	−1.14	1.24	−2.54
	0.2000	0.2000	0.1084	0.0977	5.20	−1.39	1.60	−2.21
	0.2200	0.2200	0.1193	0.1073	5.46	−1.67	1.94	−1.85
	0.2500	0.2500	0.1353	0.1218	5.85	−2.14	2.42	−1.29
	0.2800	0.2800	0.1521	0.1359	6.35	−2.66	3.02	−0.68
	0.3000	0.3000	0.1621	0.1455	6.78	−3.03	3.43	−0.32
	0.3200	0.3200	0.1735	0.1549	7.10	−3.43	3.78	0.11
	0.3500	0.3500	0.1889	0.1694	7.75	−4.08	4.33	0.66
	0.3800	0.3800	0.2047	0.1833	8.40	−4.77	4.87	1.24
	0.4000	0.4000	0.2156	0.1927	8.79	−5.26	5.15	1.63
0.6000	0.1000	0.1000	0.0559	0.0499	3.62	−0.38	−0.61	−3.85
	0.1500	0.1500	0.0833	0.0746	4.02	−0.84	−0.06	−3.25
	0.1800	0.1800	0.0999	0.0892	4.24	−1.19	0.31	−2.74
	0.2000	0.2000	0.1114	0.0991	4.33	−1.46	0.53	−2.34
	0.2200	0.2200	0.1222	0.1089	4.64	−1.76	0.94	−1.94
	0.2500	0.2500	0.1391	0.1234	4.97	−2.24	1.46	−1.27

Table 1. Continued

$m(\text{NaCl})$ / $\text{mol}\cdot\text{kg}^{-1}$	$m_{x,\text{i}}$ / $\text{mol}\cdot\text{kg}^{-1}$	$m_{y,\text{i}}$ / $\text{mol}\cdot\text{kg}^{-1}$	m_x / $\text{mol}\cdot\text{kg}^{-1}$	m_y / $\text{mol}\cdot\text{kg}^{-1}$	$\Delta H_{\text{dil}(x)}$ / $\text{J}\cdot\text{kg}^{-1}$	$\Delta H_{\text{dil}(y)}$ / $\text{J}\cdot\text{kg}^{-1}$	ΔH_{mix} / $\text{J}\cdot\text{kg}^{-1}$	ΔH^* / $\text{J}\cdot\text{kg}^{-1}$
	0.2800	0.2800	0.1553	0.1379	5.38	−2.79	1.89	−0.70
	0.3000	0.3000	0.1664	0.1475	5.67	−3.19	2.14	−0.34
	0.3200	0.3200	0.1772	0.1571	6.02	−3.60	2.52	0.10
	0.3500	0.3500	0.1937	0.1714	6.57	−4.29	3.03	0.75
	0.3800	0.3800	0.2108	0.1857	7.04	−5.03	3.46	1.45
	0.4000	0.4000	0.2211	0.1949	7.49	−5.55	3.69	1.75

supported by a Thermometric 2277 Thermal Activity Monitor (Thermometric, Sweden) at 298.15 K. The baseline stability (over a period of 24 h) of the Thermometric 2277 Thermal Activity Monitor is 0.2 μW. The solutions were pumped through the mixing-flow vessel of the calorimeter using VS2-10R MIDI dual channel pumps. The flow rates were determined from the mass of the samples delivered in 6 min. The variation of flow rates was less than 0.1 % both before and after a complete dilution experiment. The relative mean deviation in weighing was 0.01 %. The relative mean deviation of the thermal power determined was 0.3 %, and at last, the relative mean deviation of the enthalpies of dilution and mixing was less than 1 %. The details of this apparatus, associated equipment, and the experimental procedure have been reported elsewhere.[17−20]

The dilution enthalpies ΔH_{dil} are determined by measuring the thermal power P and the flow rates of the solution and the solvent (f_{A} and f_{B})

$$\Delta H_{\text{dil}} = P/(f_{\text{A}} + f_{\text{B}} - m_{x,\text{i}} M_x f_{\text{A}}) \tag{1}$$

where $m_{x,\text{i}}$ is the initial molality of the solution before dilution and M_x is the molar mass of the solute.

The final molality $m_{x,\text{f}}$ may be calculated from the equation

$$m_{x,\text{f}} = m_{x,\text{i}} f_{\text{A}}/[f_{\text{B}}(m_{x,\text{i}} M_x + 1) + f_{\text{A}}] \tag{2}$$

The enthalpy of mixing ΔH_{mix} of an aqueous x solution and an aqueous y solution is calculated from the equation

$$\Delta H_{\text{mix}} = P_{\text{mix}}/(f_x + f_y - m_{x,\text{i}} M_x f_x - m_{y,\text{i}} M_y f_y) \tag{3}$$

in which P_{mix} is the mixing thermal power and f_x, f_y are the flow rates of solutions x and y, respectively, and $m_{x,\text{i}}$, $m_{y,\text{i}}$ are the initial molalities of solutions x and y before mixing.

The treatment of the experimental data concerning the mixing experiments for the aqueous solutions is based on the excess enthalpy expression.[21−23]

$$\begin{aligned} H^{\text{E}}(m_x, m_y)/w_1 &= H(m_x, m_y)/w_1 - H^* - H^{\infty}_{x,\text{m}} - H^{\infty}_{y,\text{m}} \\ &= h_{xx} m_x^2 + 2h_{xy} m_x m_y + h_{yy} m_y^2 + h_{xxx} m_x^3 + \\ &\quad 3h_{xxy} m_x^2 m_y + 3h_{xyy} m_x m_y^2 + h_{yyy} m_y^3 + \cdots \end{aligned} \tag{4}$$

where $H^{\text{E}}(m_x, m_y)/w_1$ and $H(m_x, m_y)/w_1$ represent the excess and the absolute enthalpy, respectively, of a solution containing 1 kg of solvent; m_x is mol of x and m_y mol of y; H^* is the standard enthalpy of 1 kg of pure solvent; and $H^{\infty}_{x,\text{m}}$ and $H^{\infty}_{y,\text{m}}$ are the limiting partial molar enthalpies of species x and y, respectively. The h_{ij} and h_{ijk} terms are the enthalpic virial coefficients characterizing the pairwise and triplet interactions between the subscripted species. m_x and m_y are the molalities of the solutes x and y, respectively. $\Delta H_{\text{dil}(x)}$, $\Delta H_{\text{dil}(y)}$, and ΔH_{mix} have been determined. To facilitate the calculation, an auxiliary function ΔH^* is introduced

$$\begin{aligned} \Delta H^* &= \Delta H_{\text{mix}} - \Delta H_{\text{dil}(x)} - \Delta H_{\text{dil}(y)} \\ &= H^{\text{E}}(m_x, m_y) - H^{\text{E}}(m_x) - H^{\text{E}}(m_y) \end{aligned} \tag{5}$$

and combining eqs 4 and 5, it follows that

$$\Delta H^*/w_1 = 2h_{xy} m_x m_y + 3h_{xxy} m_x^2 m_y + 3h_{xyy} m_x m_y^2 + \cdots \tag{6}$$

Results and Discussion

The experimental values of enthalpies of dilution and mixing of formamide (x) with D-mannitol and D-sorbitol (y) in water and aqueous sodium chloride solutions are given in Table 1 and Table 2, respectively, together with those of ΔH^*. The data were fitted by eq 6 using a least-squares procedure to obtain the heterotactic enthalpic interaction coefficients (Table 3 and Table 4 for formamide−mannitol and formamide−sorbitol systems, respectively).

The enthalpic pairwise interaction coefficients are regarded as a measure of the heat effects when two solute species approach each other. This process is accompanied by overlapping of the solvation cospheres of the solute molecules, resulting in a partial reorganization of the solvation cospheres and a change of the solute−solvent interactions. Therefore, the enthalpic pairwise interaction coefficients h_{xy} are the results of solvation effects and direct solute−solute interaction effects.[24]

In Tables 3 and 4, some higher-order h coefficients have higher standard errors. This may be due to the covariance in the multiple linear regression being too high and must be taken into account in the error calculation. Since it is difficult to interpret the higher-order h coefficients, only the enthalpic pairwise coefficients h_{xy} are discussed here. Figure 1 shows the h_{xy} of formamide with D-mannitol and D-sorbitol versus the molality of sodium chloride in aqueous solutions.

From Figure 1, it can be seen that the h_{xy} values between formamide and D-mannitol are all positive over the whole molality range of the aqueous salt solutions investigated, while the h_{xy} values for D-sorbitol vary from a negative value to a positive one. This could be attributed to the cooperative effects of partial dehydration of the hydration shell (positive contribution to h_{xy}), solvent reorganization in the neighborhood of the hydrophobic groups (nagative contribution to h_{xy}[25]), and direct interaction between formamide molecules and polyalcohol molecules. The discrepancies of h_{xy} between the formamide−manitol system and formamide−sorbitol are mainly dependent on the differences in the structure of D-mannitol and D-sorbitol.[26] There may be more opportunities for D-mannitol molecules to form an intermolecular hydrogen bond with neighboring water molecules because all four secondary hydroxyl groups (−OH) stretch to different directions while 2- and 3-OH in the D-sorbitol molecule can form an intramolecule hydrogen bond. So partial dehydration of the hydration shell of the D-mannitol molecules needs more energy than that of D-sorbitol molecules. Indeed, partial dehydration of the hydration shell of the D-mannitol

Table 2. Enthalpies of Mixing of Formamide and D-Sorbitol along with Those of Their Dilution in Water and Aqueous Sodium Chloride Solutions at 298.15 K

$m(\mathrm{NaCl})$ / $\mathrm{mol \cdot kg^{-1}}$	$m_{x,\mathrm{i}}$ / $\mathrm{mol \cdot kg^{-1}}$	$m_{y,\mathrm{i}}$ / $\mathrm{mol \cdot kg^{-1}}$	m_x / $\mathrm{mol \cdot kg^{-1}}$	m_y / $\mathrm{mol \cdot kg^{-1}}$	$\Delta H_{\mathrm{dil}(x)}$ / $\mathrm{J \cdot kg^{-1}}$	$\Delta H_{\mathrm{dil}(y)}$ / $\mathrm{J \cdot kg^{-1}}$	ΔH_{mix} / $\mathrm{J \cdot kg^{-1}}$	ΔH^* / $\mathrm{J \cdot kg^{-1}}$
0.0000	0.1000	0.1000	0.0571	0.0497	3.81	0.09	−0.32	−4.22
	0.1500	0.1500	0.0859	0.0746	4.16	0.08	−0.13	−4.37
	0.1800	0.1800	0.1028	0.0895	4.55	0.07	0.13	−4.49
	0.2000	0.2000	0.1141	0.0994	4.77	0.07	0.25	−4.59
	0.2200	0.2200	0.1245	0.1090	5.10	0.06	0.48	−4.68
	0.2500	0.2500	0.1419	0.1236	5.51	0.05	0.74	−4.82
	0.2800	0.2800	0.1593	0.1384	6.05	0.04	1.08	−5.01
	0.3000	0.3000	0.1722	0.1478	6.39	0.03	1.28	−5.14
	0.3200	0.3200	0.1827	0.1576	6.83	0.01	1.59	−5.25
	0.3500	0.3500	0.1976	0.1721	7.51	−0.01	2.05	−5.45
	0.3800	0.3800	0.2161	0.1864	8.18	−0.04	2.43	−5.71
	0.4000	0.4000	0.2270	0.1966	8.70	−0.07	2.77	−5.86
0.1000	0.1000	0.1000	0.0566	0.0492	3.83	0.05	−0.42	−4.30
	0.1500	0.1500	0.0852	0.0738	4.25	0.02	−0.14	−4.41
	0.1800	0.1800	0.1020	0.0885	4.57	−0.02	0.07	−4.48
	0.2000	0.2000	0.1132	0.0983	4.82	−0.05	0.23	−4.54
	0.2200	0.2200	0.1235	0.1079	5.13	−0.09	0.42	−4.62
	0.2500	0.2500	0.1407	0.1222	5.56	−0.16	0.68	−4.72
	0.2800	0.2800	0.1580	0.1369	6.07	−0.24	0.97	−4.86
	0.3000	0.3000	0.1709	0.1462	6.43	−0.31	1.16	−4.96
	0.3200	0.3200	0.1811	0.1559	6.84	−0.38	1.41	−5.05
	0.3500	0.3500	0.1959	0.1702	7.49	−0.49	1.79	−5.21
	0.3800	0.3800	0.2142	0.1844	8.19	−0.63	2.14	−5.42
	0.4000	0.4000	0.2252	0.1944	8.66	−0.73	2.37	−5.56
0.2000	0.1000	0.1000	0.0556	0.0496	3.85	−0.01	−0.37	−4.21
	0.1500	0.1500	0.0833	0.0743	4.23	−0.10	−0.11	−4.24
	0.1800	0.1800	0.0999	0.0891	4.54	−0.17	0.10	−4.27
	0.2000	0.2000	0.1110	0.0990	4.78	−0.23	0.26	−4.29
	0.2200	0.2200	0.1224	0.1086	5.04	−0.30	0.43	−4.31
	0.2500	0.2500	0.1390	0.1229	5.47	−0.42	0.70	−4.35
	0.2800	0.2800	0.1549	0.1374	5.97	−0.56	1.02	−4.39
	0.3000	0.3000	0.1665	0.1473	6.34	−0.66	1.25	−4.43
	0.3200	0.3200	0.1773	0.1570	6.70	−0.77	1.46	−4.47
	0.3500	0.3500	0.1939	0.1717	7.30	−0.96	1.80	−4.54
	0.3800	0.3800	0.2104	0.1856	7.97	−1.17	2.18	−4.62
	0.4000	0.4000	0.2213	0.1955	8.43	−1.31	2.44	−4.68
0.3000	0.1000	0.1000	0.0540	0.0494	3.92	−0.08	−0.31	−4.15
	0.1500	0.1500	0.0804	0.0740	4.28	−0.22	−0.03	−4.09
	0.1800	0.1800	0.0961	0.0887	4.56	−0.33	0.19	−4.04
	0.2000	0.2000	0.1072	0.0986	4.77	−0.42	0.35	−4.00
	0.2200	0.2200	0.1175	0.1082	5.01	−0.52	0.54	−3.95
	0.2500	0.2500	0.1332	0.1226	5.40	−0.69	0.83	−3.88
	0.2800	0.2800	0.1483	0.1370	5.87	−0.88	1.18	−3.81
	0.3000	0.3000	0.1619	0.1465	6.22	−1.02	1.43	−3.77
	0.3200	0.3200	0.1716	0.1562	6.55	−1.18	1.66	−3.71
	0.3500	0.3500	0.1868	0.1706	7.09	−1.43	2.02	−3.64
	0.3800	0.3800	0.2043	0.1846	7.74	−1.72	2.47	−3.55
	0.4000	0.4000	0.2124	0.1947	8.10	−1.91	2.71	−3.48
0.4000	0.1000	0.1000	0.0541	0.0497	4.15	−0.12	−0.32	−4.35
	0.1500	0.1500	0.0814	0.0745	4.96	−0.30	0.29	−4.37
	0.1800	0.1800	0.0972	0.0894	5.58	−0.45	0.73	−4.40
	0.2000	0.2000	0.1079	0.0995	6.00	−0.56	0.99	−4.45
	0.2200	0.2200	0.1189	0.1091	6.39	−0.68	1.18	−4.53
	0.2500	0.2500	0.1350	0.1236	7.05	−0.90	1.46	−4.69
	0.2800	0.2800	0.1510	0.1381	7.80	−1.14	1.75	−4.91
	0.3000	0.3000	0.1634	0.1476	8.21	−1.32	1.77	−5.12
	0.3200	0.3200	0.1728	0.1573	8.84	−1.52	1.99	−5.33
	0.3500	0.3500	0.1858	0.1717	9.91	−1.83	2.40	−5.68
	0.3800	0.3800	0.2017	0.1857	10.88	−2.19	2.52	−6.17
	0.4000	0.4000	0.2152	0.1955	11.38	−2.43	2.29	−6.66
0.5000	0.1000	0.1000	0.0543	0.0494	4.10	−0.16	−0.39	−4.33
	0.1500	0.1500	0.0818	0.0740	4.55	−0.39	0.01	−4.15
	0.1800	0.1800	0.0976	0.0887	4.92	−0.57	0.32	−4.03
	0.2000	0.2000	0.1084	0.0986	5.20	−0.71	0.54	−3.95
	0.2200	0.2200	0.1193	0.1082	5.46	−0.86	0.72	−3.88
	0.2500	0.2500	0.1353	0.1227	5.85	−1.12	0.97	−3.76
	0.2800	0.2800	0.1521	0.1370	6.35	−1.42	1.26	−3.67
	0.3000	0.3000	0.1621	0.1464	6.78	−1.64	1.53	−3.61
	0.3200	0.3200	0.1735	0.1560	7.10	−1.88	1.65	−3.57
	0.3500	0.3500	0.1889	0.1706	7.75	−2.25	1.99	−3.51
	0.3800	0.3800	0.2047	0.1846	8.40	−2.69	2.23	−3.48
	0.4000	0.4000	0.2156	0.1946	8.79	−2.97	2.37	−3.45
0.6000	0.1000	0.1000	0.0559	0.0502	3.62	−0.34	−0.21	−3.49
	0.1500	0.1500	0.0833	0.0752	4.02	−0.78	0.02	−3.22
	0.1800	0.1800	0.0999	0.0901	4.24	−1.12	0.18	−2.94
	0.2000	0.2000	0.1114	0.1001	4.33	−1.39	0.22	−2.72
	0.2200	0.2200	0.1222	0.1099	4.64	−1.68	0.38	−2.58
	0.2500	0.2500	0.1391	0.1245	4.97	−2.15	0.54	−2.28

Table 2. Continued

m(NaCl) mol·kg^{-1}	$m_{x,\mathrm{i}}$ mol·kg^{-1}	$m_{y,\mathrm{i}}$ mol·kg^{-1}	m_x mol·kg^{-1}	m_y mol·kg^{-1}	$\Delta H_{\mathrm{dil}(x)}$ J·kg^{-1}	$\Delta H_{\mathrm{dil}(y)}$ J·kg^{-1}	ΔH_{mix} J·kg^{-1}	ΔH^* J·kg^{-1}
	0.2800	0.2800	0.1553	0.1390	5.38	−2.66	0.75	−1.97
	0.3000	0.3000	0.1664	0.1486	5.67	−3.01	0.91	−1.75
	0.3200	0.3200	0.1772	0.1584	6.02	−3.36	1.14	−1.52
	0.3500	0.3500	0.1937	0.1730	6.57	−3.85	1.55	−1.17
	0.3800	0.3800	0.2108	0.1870	7.04	−4.33	1.88	−0.83
	0.4000	0.4000	0.2211	0.1968	7.49	−4.60	2.31	−0.58

Table 3. Enthalpic Interaction Coefficients of Formamide with D-Mannitol in Water and Aqueous Sodium Chloride Solutions at 298.15 K

m(NaCl) mol·kg^{-1}	h_{xy} J·kg·mol^{-2}	h_{xxy} J·kg^2·mol^{-3}	h_{xyy} J·kg^3·mol^{-4}	SD J·kg^{-1}
0.0000	64.0 ± 2.4[a]	67.1 ± 151.5[a]	−120.2 ± 177.9[a]	0.03
0.1000	79.4 ± 3.4[a]	195.2 ± 215.4[a]	−305.2 ± 253.4[a]	0.04
0.2000	92.3 ± 3.3[a]	268.4 ± 238.3[a]	−365.9 ± 279.5[a]	0.03
0.3000	102.5 ± 2.6[a]	297.6 ± 109.3[a]	−389.5 ± 121.2[a]	0.03
0.4000	111.1 ± 2.5[a]	35.4 ± 72.9[a]	−219.4 ± 81.4[a]	0.03
0.5000	122.8 ± 0.3[a]	326.0 ± 45.9[a]	−545.3 ± 51.5[a]	0.01
0.6000	133.9 ± 6.3[a]	993.5 ± 688.2[a]	−1333.7 ± 797.7[a]	0.04

[a] The values are the standard errors, which are given by the computer during the multiple linear regression analysis. SD = standard derivation.

Table 4. Enthalpic Interaction Coefficients of Formamide with D-Sorbitol in Water and Aqueous Sodium Chloride Solutions at 298.15 K

m(NaCl) mol·kg^{-1}	h_{xy} J·kg·mol^{-2}	h_{xxy} J·kg^2·mol^{-3}	h_{xyy} J·kg^3·mol^{-4}	SD J·kg^{-1}
0.0000	−22.3 ± 0.9	−30.3 ± 51.2	44.0 ± 59.3	0.01
0.1000	−12.7 ± 0.7	−17.7 ± 37.8	12.3 ± 43.9	0.01
0.2000	−2.6 ± 0.4	−48.3 ± 67.4	44.7 ± 77.1	0.01
0.3000	11.8 ± 0.6	−58.4 ± 20.7	53.6 ± 22.8	0.01
0.4000	22.7 ± 0.4	−161.9 ± 14.0	9.8 ± 15.4	0.01
0.5000	37.5 ± 0.7	−311.6 ± 113.2	258.6 ± 125.5	0.01
0.6000	54.3 ± 2.3	−140.7 ± 212.0	98.5 ± 243.1	0.02

molecules surpasses the effect of direct interaction between formamide molecules and D-mannitol molecules,[27] which leads to the h_{xy} values for the formamide−mannitol system all being positive over the whole molality range of the aqueous salt solutions investigated.

On the other hand, the values of h_{xy} for both the formamide−mannitol system and the formamide−sorbitol system increase positively with elevation of molality of sodium chloride solutions. Even more obviously, the h_{xy} between formamide and D-sorbitol vary from a negative value to a positive one when the salt molality increases. This variation trend is the result of the influence of salt on the interaction of the formamide molecule and polyalcohol molecules. The larger the molality of sodium chloride is, the more difficultly the water molecules depart from the ion or solute molecule and the more positive the contribution to the enthalpy will be. Consequently, enthalpic interaction coefficients h_2 of investigated systems become more positive with the elevated molality of sodium chloride.

Conclusion

(1) The heterotactic enthalpic pairwise interaction coefficients h_{xy} between formamide and D-mannitol in water and aqueous sodium chloride solution of different molality are all positive. In contrast, the h_{xy} between formamide and D-sorbitol varies from a negative value to a positive one. This could be attributed to the cooperative effects of partial dehydration of the hydration shell, solvent reorganization in the neighborhood of the hydrophobic groups, and direct interaction between formamide molecules and polyalcohol molecules.

(2) The value of h_{xy} for the formamide−mannitol system is larger than that for the formamide−sorbitol system at the same molality of sodium chloride. The discrepancy is mainly attributed to the differences in the structure of D-mannitol and D-sorbitol.

(3) In aqueous sodium chloride solution of different molality, the values of h_{xy} increase with the elevated molality of sodium chloride. This mainly is due to the increase of dehydration effects of solute molecules caused by the increase of the molality of sodium chloride.

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