Enthalpies of Interaction of (2*R*,3*S*,4*S*,5*S*)-Hexane-1,2,3,4,5,6-hexol with Acetamide and *N*,*N*-Dimethylformamide in Aqueous Sodium Chloride Solutions at 298.15 K†

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The enthalpies of mixing of (2*R*,3*S*,4*S*,5*S*)-hexane-1,2,3,4,5,6-hexol with acetamide and *N*,*N*-dimethylamide in aqueous sodium chloride solutions 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}) for (2*R*,3*S*,4*S*,5*S*)-hexane-1,2,3,4,5,6-hexol−acetamide and (2*R*,3*S*,4*S*,5*S*)-hexane-1,2,3,4,5,6-hexol−*N*,*N*-dimethylamide systems in aqueous sodium chloride solutions are both positive and become more positive with an increase in the molality of sodium chloride. The results are discussed in terms of solute−solute interaction and solute−solvent interaction.

Introduction

Globular proteins in the human body are usually surrounded by a complex mixture of different types of molecules, including water, salts, sugars, polyols, lipids, etc. Many of these molecules can interact either directly or indirectly with the proteins to alter their functional properties, e.g., catalytic activity, thermostability, surface activity, and structure formation.[1−3] Among these molecules, sodium chloride bears an extraordinary important function in biological systems.[4] On the other hand, it is well-known that polyhydroxy compounds help in stabilizing the native conformation of globular proteins.[5−7] (2*R*,3*S*,4*S*,5*S*)-Hexane-1,2,3,4,5,6-hexol (D-sorbitol), a polylol derived from glucose by the enzyme aldose reductase, is a common organic solute in many cells of the human body.[8] It can be used as a test substance for measuring liver plasma flow in humans and can play an important role in pathology study and diagnosis of the diabetes induced by excessive cell apoptosis and the functional disease of the liver.[9,10]

Owing to the complexities arising from a direct thermodynamic study on proteins, it is needed to choose some small solutes that incorporate some of the structural features found in proteins.[11−13] The hydrogen bond link with amide is the most important secondary structure in proteins, so we choose amides as the studied objects.[14,15] As an extension to our previous study,[16,17] the present work is aimed at measuring the enthalpies of mixing of D-sorbitol with acetamide and *N*,*N*-dimethylformamide (DMF) in aqueous sodium chloride solutions. By analyzing the results, the heterotactic enthalpic interaction coefficients of D-sorbitol with acetamide and DMF in aqueous sodium chloride solutions with different molalities are obtained.

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Materials

D-Sorbitol and acetamide were both purchased from Aldrich, and the purity is better than 99 %. They were dried under reduced pressure at 323 K before being used. Analytical reagent grade DMF (purity > 99 %, purchased from the Shanghai Chem. Co.) was dried by storage over 0.4 nm molecular sieves for 2 days and then was distilled under reduced pressure. 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. The aqueous sodium chloride solutions, which were used as mixed solvents, the aqueous amide solutions (amide + sodium chloride + water) and the aqueous D-sorbitol solutions (D-sorbitol + sodium chloride + water) were all prepared by mass using a Mettler AG 135 balance whose precision is ± 0.00001 g. The molality range of aqueous sodium chloride solutions was (0 to 0.60) mol·kg^{-1}. The molality ranges of aqueous D-sorbitol, acetamide, and DMF 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 to avoid possible contamination.

Apparatus and Procedure

The enthalpies of dilution and mixing were determined with a 2277−204 Measuring Cylinder 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 details of this apparatus, associated equipment, and the experimental procedure have been reported elsewhere.[18−22] The variation of flow rates was less than 0.1 % both before and after a complete dilution or mixing experiment. The relative mean deviation in weighing was 0.01 %. The relative mean deviation

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

m(NaCl) / mol·kg^{-1}	$m_{x,i}$ / mol·kg^{-1}	$m_{y,i}$ / mol·kg^{-1}	m_x / mol·kg^{-1}	m_y / mol·kg^{-1}	$\Delta H_{dil(x)}$ / J·kg^{-1}	$\Delta H_{dil(y)}$ / J·kg^{-1}	ΔH_{mix} / J·kg^{-1}	ΔH^* / J·kg^{-1}
0.0000	0.1000	0.1000	0.0507	0.0497	−0.18	0.09	0.82	0.91
	0.1500	0.1500	0.0760	0.0746	−0.28	0.08	2.20	2.40
	0.1800	0.1800	0.0912	0.0895	−0.36	0.07	3.38	3.67
	0.2000	0.2000	0.1013	0.0994	−0.40	0.07	4.27	4.60
	0.2200	0.2200	0.1114	0.1090	−0.45	0.06	5.23	5.62
	0.2500	0.2500	0.1265	0.1236	−0.54	0.05	6.83	7.32
	0.2800	0.2800	0.1416	0.1384	−0.63	0.04	8.61	9.20
	0.3000	0.3000	0.1517	0.1478	−0.70	0.03	9.93	10.60
	0.3200	0.3200	0.1617	0.1576	−0.78	0.01	11.28	12.05
	0.3500	0.3500	0.1768	0.1721	−0.90	−0.01	13.49	14.40
	0.3800	0.3800	0.1919	0.1864	−1.02	−0.04	15.92	16.98
	0.4000	0.4000	0.2019	0.1966	−1.12	−0.07	17.51	18.70
0.1000	0.1000	0.1000	0.0505	0.0492	−0.32	0.05	0.71	0.98
	0.1500	0.1500	0.0756	0.0738	−0.45	0.02	2.15	2.58
	0.1800	0.1800	0.0907	0.0885	−0.52	−0.02	3.24	3.78
	0.2000	0.2000	0.1007	0.0983	−0.56	−0.05	4.17	4.78
	0.2200	0.2200	0.1107	0.1079	−0.61	−0.09	5.04	5.74
	0.2500	0.2500	0.1257	0.1222	−0.67	−0.16	6.70	7.53
	0.2800	0.2800	0.1407	0.1369	−0.74	−0.24	8.43	9.41
	0.3000	0.3000	0.1506	0.1462	−0.81	−0.31	9.69	10.81
	0.3200	0.3200	0.1606	0.1559	−0.88	−0.38	10.99	12.25
	0.3500	0.3500	0.1755	0.1702	−1.02	−0.49	13.14	14.65
	0.3800	0.3800	0.1906	0.1844	−1.20	−0.63	15.35	17.18
	0.4000	0.4000	0.2004	0.1944	−1.35	−0.73	16.70	18.78
0.2000	0.1000	0.1000	0.0506	0.0496	−0.45	−0.01	0.71	1.17
	0.1500	0.1500	0.0759	0.0743	−0.60	−0.10	2.08	2.78
	0.1800	0.1800	0.0910	0.0891	−0.66	−0.17	3.33	4.16
	0.2000	0.2000	0.1011	0.0990	−0.68	−0.23	4.23	5.14
	0.2200	0.2200	0.1111	0.1086	−0.70	−0.30	5.22	6.22
	0.2500	0.2500	0.1261	0.1229	−0.73	−0.42	6.85	8.00
	0.2800	0.2800	0.1412	0.1374	−0.74	−0.56	8.66	9.96
	0.3000	0.3000	0.1512	0.1473	−0.77	−0.66	9.91	11.34
	0.3200	0.3200	0.1611	0.1570	−0.83	−0.77	11.22	12.82
	0.3500	0.3500	0.1758	0.1717	−0.95	−0.96	13.13	15.04
	0.3800	0.3800	0.1908	0.1856	−1.14	−1.17	15.34	17.65
	0.4000	0.4000	0.2007	0.1955	−1.32	−1.31	16.69	19.32
0.3000	0.1000	0.1000	0.0520	0.0494	−0.38	−0.08	0.68	1.14
	0.1500	0.1500	0.0779	0.0740	−0.53	−0.22	2.05	2.80
	0.1800	0.1800	0.0934	0.0887	−0.60	−0.33	3.23	4.16
	0.2000	0.2000	0.1037	0.0986	−0.64	−0.42	4.06	5.12
	0.2200	0.2200	0.1140	0.1082	−0.67	−0.52	4.98	6.17
	0.2500	0.2500	0.1295	0.1226	−0.72	−0.69	6.47	7.88
	0.2800	0.2800	0.1449	0.1370	−0.77	−0.88	8.08	9.73
	0.3000	0.3000	0.1552	0.1465	−0.81	−1.02	9.23	11.06
	0.3200	0.3200	0.1654	0.1562	−0.88	−1.18	10.35	12.41
	0.3500	0.3500	0.1808	0.1706	−1.00	−1.43	12.10	14.53
	0.3800	0.3800	0.1961	0.1846	−1.19	−1.72	13.95	16.86
	0.4000	0.4000	0.2063	0.1947	−1.37	−1.91	14.95	18.23
0.4000	0.1000	0.1000	0.0518	0.0497	−0.36	−0.12	0.62	1.10
	0.1500	0.1500	0.0777	0.0745	−0.48	−0.30	1.93	2.71
	0.1800	0.1800	0.0932	0.0894	−0.54	−0.45	3.09	4.08
	0.2000	0.2000	0.1036	0.0995	−0.56	−0.56	3.96	5.08
	0.2200	0.2200	0.1140	0.1091	−0.59	−0.68	4.92	6.19
	0.2500	0.2500	0.1295	0.1236	−0.62	−0.90	6.47	7.99
	0.2800	0.2800	0.1450	0.1381	−0.68	−1.14	8.15	9.97
	0.3000	0.3000	0.1554	0.1476	−0.74	−1.32	9.36	11.42
	0.3200	0.3200	0.1658	0.1573	−0.83	−1.52	10.54	12.89
	0.3500	0.3500	0.1812	0.1717	−1.04	−1.83	12.33	15.20
	0.3800	0.3800	0.1967	0.1857	−1.35	−2.19	14.48	18.02
	0.4000	0.4000	0.2069	0.1955	−1.62	−2.43	15.44	19.49
0.5000	0.1000	0.1000	0.0517	0.0494	−0.22	−0.16	0.74	1.12
	0.1500	0.1500	0.0774	0.0740	−0.37	−0.39	2.31	3.07
	0.1800	0.1800	0.0928	0.0887	−0.47	−0.57	3.46	4.50
	0.2000	0.2000	0.1030	0.0986	−0.53	−0.71	4.31	5.55
	0.2200	0.2200	0.1133	0.1082	−0.60	−0.86	5.26	6.72
	0.2500	0.2500	0.1286	0.1227	−0.70	−1.12	6.77	8.59
	0.2800	0.2800	0.1439	0.1370	−0.81	−1.42	8.43	10.66
	0.3000	0.3000	0.1541	0.1464	−0.89	−1.64	9.64	12.17
	0.3200	0.3200	0.1643	0.1560	−0.98	−1.88	10.83	13.69
	0.3500	0.3500	0.1796	0.1706	−1.12	−2.25	12.61	15.98
	0.3800	0.3800	0.1948	0.1846	−1.27	−2.69	14.69	18.65
	0.4000	0.4000	0.2049	0.1946	−1.40	−2.97	15.78	20.15
0.6000	0.1000	0.1000	0.0519	0.0502	0.01	−0.34	0.78	1.11
	0.1500	0.1500	0.0778	0.0752	−0.06	−0.78	2.33	3.17
	0.1800	0.1800	0.0933	0.0901	−0.11	−1.12	3.41	4.64
	0.2000	0.2000	0.1037	0.1001	−0.15	−1.39	4.29	5.83
	0.2200	0.2200	0.1140	0.1099	−0.19	−1.68	5.19	7.06
	0.2500	0.2500	0.1295	0.1245	−0.25	−2.15	6.66	9.06
	0.2800	0.2800	0.1450	0.1390	−0.32	−2.66	8.27	11.25
	0.3000	0.3000	0.1553	0.1486	−0.36	−3.01	9.45	12.82
	0.3200	0.3200	0.1656	0.1584	−0.42	−3.36	10.64	14.42
	0.3500	0.3500	0.1810	0.1730	−0.49	−3.85	12.60	16.94
	0.3800	0.3800	0.1965	0.1870	−0.59	−4.33	14.84	19.76
	0.4000	0.4000	0.2068	0.1968	−0.66	−4.60	16.29	21.55

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

m(NaCl) / mol·kg^{-1}	$m_{x,i}$ / mol·kg^{-1}	$m_{y,i}$ / mol·kg^{-1}	m_x / mol·kg^{-1}	m_y / mol·kg^{-1}	$\Delta H_{dil(x)}$ / J·kg^{-1}	$\Delta H_{dil(y)}$ / J·kg^{-1}	ΔH_{mix} / J·kg^{-1}	ΔH^* / J·kg^{-1}
0.0000	0.1000	0.1000	0.0502	0.0497	−1.52	0.09	1.89	3.32
	0.1500	0.1500	0.0756	0.0746	−3.60	0.08	4.82	8.34
	0.1800	0.1800	0.0893	0.0895	−5.42	0.07	6.71	12.06
	0.2000	0.2000	0.0994	0.0994	−6.79	0.07	8.27	14.99
	0.2200	0.2200	0.1098	0.1090	−8.18	0.06	10.08	18.20
	0.2500	0.2500	0.1247	0.1236	−10.54	0.05	12.92	23.41
	0.2800	0.2800	0.1392	0.1384	−13.32	0.04	15.92	29.20
	0.3000	0.3000	0.1493	0.1478	−15.46	0.03	17.87	33.30
	0.3200	0.3200	0.1598	0.1576	−17.53	0.01	20.30	37.82
	0.3500	0.3500	0.1742	0.1721	−20.97	−0.01	23.77	44.75
	0.3800	0.3800	0.1888	0.1864	−24.96	−0.04	27.14	52.14
	0.4000	0.4000	0.1993	0.1966	−27.64	−0.07	29.57	57.28
0.1000	0.1000	0.1000	0.0494	0.0492	−1.92	0.05	1.76	3.63
	0.1500	0.1500	0.0748	0.0738	−4.14	0.02	4.10	8.22
	0.1800	0.1800	0.0895	0.0885	−5.93	−0.02	6.17	12.12
	0.2000	0.2000	0.0996	0.0983	−7.42	−0.05	8.01	15.48
	0.2200	0.2200	0.1085	0.1079	−9.08	−0.09	9.46	18.63
	0.2500	0.2500	0.1219	0.1222	−11.55	−0.16	12.17	23.88
	0.2800	0.2800	0.1390	0.1369	−14.38	−0.24	15.03	29.65
	0.3000	0.3000	0.1501	0.1462	−16.23	−0.31	16.87	33.41
	0.3200	0.3200	0.1578	0.1559	−18.71	−0.38	18.95	38.04
	0.3500	0.3500	0.1736	0.1702	−21.98	−0.49	22.22	44.69
	0.3800	0.3800	0.1879	0.1844	−24.82	−0.63	26.41	51.86
	0.4000	0.4000	0.1972	0.1944	−27.69	−0.73	28.83	57.25
0.2000	0.1000	0.1000	0.0498	0.0496	−1.33	−0.01	1.37	2.71
	0.1500	0.1500	0.0744	0.0743	−3.35	−0.10	3.39	6.84
	0.1800	0.1800	0.0894	0.0891	−4.99	−0.17	5.93	11.09
	0.2000	0.2000	0.0999	0.0990	−6.26	−0.23	7.34	13.83
	0.2200	0.2200	0.1096	0.1086	−7.68	−0.30	9.78	17.76
	0.2500	0.2500	0.1242	0.1229	−10.08	−0.42	12.41	22.91
	0.2800	0.2800	0.1391	0.1374	−12.81	−0.56	15.25	28.62
	0.3000	0.3000	0.1481	0.1473	−14.81	−0.66	17.26	32.73
	0.3200	0.3200	0.1579	0.1570	−16.95	−0.77	19.29	37.01
	0.3500	0.3500	0.1720	0.1717	−20.43	−0.96	22.47	43.86
	0.3800	0.3800	0.1877	0.1856	−24.23	−1.17	25.36	50.76
	0.4000	0.4000	0.1973	0.1955	−26.94	−1.31	27.03	55.28
0.3000	0.1000	0.1000	0.0497	0.0494	−1.45	−0.08	1.59	3.12
	0.1500	0.1500	0.0745	0.0740	−3.72	−0.22	4.02	7.96
	0.1800	0.1800	0.0892	0.0887	−5.28	−0.33	6.18	11.79
	0.2000	0.2000	0.0990	0.0986	−6.72	−0.42	8.38	15.52
	0.2200	0.2200	0.1089	0.1082	−8.35	−0.52	9.96	18.83
	0.2500	0.2500	0.1237	0.1226	−10.71	−0.69	12.65	24.05
	0.2800	0.2800	0.1386	0.1370	−13.55	−0.88	15.19	29.62
	0.3000	0.3000	0.1485	0.1465	−15.57	−1.02	17.27	33.86
	0.3200	0.3200	0.1581	0.1562	−17.69	−1.18	19.16	38.03
	0.3500	0.3500	0.1728	0.1706	−21.18	−1.43	21.52	44.13
	0.3800	0.3800	0.1871	0.1846	−24.96	−1.72	24.43	51.11
	0.4000	0.4000	0.1973	0.1947	−27.79	−1.91	26.41	56.11
0.4000	0.1000	0.1000	0.0495	0.0497	−1.66	−0.12	1.52	3.30
	0.1500	0.1500	0.0742	0.0745	−3.79	−0.30	4.91	9.00
	0.1800	0.1800	0.0889	0.0894	−5.47	−0.45	7.34	13.26
	0.2000	0.2000	0.0986	0.0995	−6.94	−0.56	8.95	16.45
	0.2200	0.2200	0.1085	0.1091	−8.55	−0.68	10.54	19.77
	0.2500	0.2500	0.1232	0.1236	−10.87	−0.90	13.37	25.14
	0.2800	0.2800	0.1381	0.1381	−13.97	−1.14	15.76	30.87
	0.3000	0.3000	0.1480	0.1476	−15.83	−1.32	17.63	34.78
	0.3200	0.3200	0.1576	0.1573	−18.23	−1.52	19.16	38.91
	0.3500	0.3500	0.1722	0.1717	−21.65	−1.83	21.75	45.23
	0.3800	0.3800	0.1864	0.1857	−25.35	−2.19	23.96	51.50
	0.4000	0.4000	0.1966	0.1955	−27.84	−2.43	25.76	56.03
0.5000	0.1000	0.1000	0.0501	0.0494	−1.56	−0.16	1.54	3.26
	0.1500	0.1500	0.0745	0.0740	−3.49	−0.39	4.19	8.07
	0.1800	0.1800	0.0896	0.0887	−5.24	−0.57	7.64	13.45
	0.2000	0.2000	0.0993	0.0986	−6.59	−0.71	9.34	16.64
	0.2200	0.2200	0.1092	0.1082	−8.08	−0.86	11.05	19.99
	0.2500	0.2500	0.1242	0.1227	−10.53	−1.12	13.73	25.38
	0.2800	0.2800	0.1390	0.1370	−13.26	−1.42	16.33	31.01
	0.3000	0.3000	0.1484	0.1464	−15.32	−1.64	17.86	34.82
	0.3200	0.3200	0.1590	0.1560	−17.52	−1.88	19.46	38.86
	0.3500	0.3500	0.1728	0.1706	−20.93	−2.25	21.76	44.94
	0.3800	0.3800	0.1876	0.1846	−24.79	−2.69	23.41	50.89
	0.4000	0.4000	0.1978	0.1946	−27.27	−2.97	25.70	55.94
0.6000	0.1000	0.1000	0.0496	0.0502	−1.49	−0.34	0.83	2.66
	0.1500	0.1500	0.0736	0.0752	−3.18	−0.78	4.18	8.14
	0.1800	0.1800	0.0886	0.0901	−4.93	−1.12	6.92	12.97
	0.2000	0.2000	0.0987	0.1001	−6.28	−1.39	8.87	16.54
	0.2200	0.2200	0.1084	0.1099	−7.77	−1.68	10.74	20.19
	0.2500	0.2500	0.1235	0.1245	−10.22	−2.15	13.71	26.08
	0.2800	0.2800	0.1379	0.1390	−12.95	−2.66	16.50	32.11
	0.3000	0.3000	0.1474	0.1486	−15.01	−3.01	18.18	36.20
	0.3200	0.3200	0.1572	0.1584	−17.21	−3.36	19.91	40.48
	0.3500	0.3500	0.1719	0.1730	−20.62	−3.85	22.38	46.85
	0.3800	0.3800	0.1865	0.1870	−24.47	−4.33	24.22	53.02
	0.4000	0.4000	0.1962	0.1968	−26.96	−4.60	25.64	57.20

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

m(NaCl)	h_{xy}	h_{xxy}	h_{xyy}	SD
mol·kg^{-1}	J·kg·mol^{-2}	J·kg^2·mol^{-3}	J·kg^3·mol^{-4}	J·kg^{-1}
0.0000	261.9 ± 2.3[a]	2146.5 ± 486.6[a]	−2277.0 ± 504.9[a]	0.02
0.1000	279.7 ± 4.3[a]	2674.9 ± 805.7[a]	−2871.6 ± 837.8[a]	0.04
0.2000	297.0 ± 2.4[a]	2828.2 ± 554.2[a]	−3064.4 ± 570.8[a]	0.03
0.3000	313.2 ± 1.9[a]	2943.4 ± 396.1[a]	−3397.7 ± 422.6[a]	0.02
0.4000	331.9 ± 11.6[a]	6422.9 ± 1446.9[a]	−7083.2 ± 1566.6[a]	0.05
0.5000	349.4 ± 1.4[a]	4388.0 ± 286.6[a]	−4930.5 ± 304.1[a]	0.01
0.6000	369.7 ± 4.8[a]	3584.9 ± 614.0[a]	−4093.23 ± 659.5[a]	0.02

[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 *N*,*N*-Dimethylformamide with D-Sorbitol in Water and Aqueous Sodium Chloride Solutions at 298.15 K

m(NaCl)	h_{xy}	h_{xxy}	h_{xyy}	SD
mol·kg^{-1}	J·kg·mol^{-2}	J·kg^2·mol^{-3}	J·kg^3·mol^{-4}	J·kg^{-1}
0.0000	864.1 ± 11.8	−1079.0 ± 184.4	689.1 ± 189.9	0.09
0.1000	904.9 ± 17.8	−5097.8 ± 1061.7	4673.9 ± 1080.0	0.18
0.2000	946.9 ± 39.3	−3079.6 ± 329.9	2442.5 ± 335.7	0.28
0.3000	1008.2 ± 32.4	−2377.8 ± 631.6	1536.9 ± 844.9	0.29
0.4000	1088.1 ± 3.8	−2212.1 ± 658.6	1070.4 ± 672.8	0.02
0.5000	1152.3 ± 36.5	−2301.3 ± 533.5	963.2 ± 460.5	0.36
0.6000	1241.2 ± 41.5	−3359.5 ± 664.5	1808.7 ± 673.7	0.24

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 dilution enthalpies $\Delta H_{dil(x)}$ of solution x were calculated from the equation

$$\Delta H_{dil(x)} = P_x/(f_x + f_s - m_{x,i}M_x f_x) \quad (1)$$

where P_x is the dilution thermal power of solute x, $m_{x,i}$ is the initial molality of the solution x before dilution, M_x is the molar mass of the solute x, and f_x and f_s are the flow rates of solution x and the solvent, respectively. The dilution enthalpies $\Delta H_{dil(y)}$ of solution y can be calculated from eq 1 as long as subscript x in eq 1 is replaced by y.

The final molality m_x was calculated from the equation

$$m_x = m_{x,i}f_x/[f_s(m_{x,i}M_x + 1) + f_x] \quad (2)$$

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

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

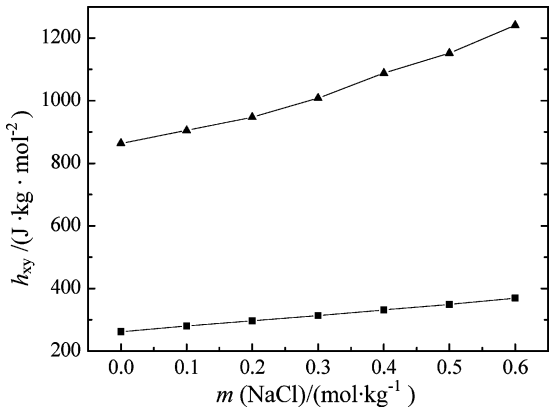

Figure 1. Enthalpic pairwise interaction coefficients (h_{xy}) of D-sorbitol with acetamide and *N*,*N*-dimethylformamide versus the molality m of sodium chloride in aqueous solutions at 298.15 K: ▲, *N*,*N*-dimethylformamide; ■, acetamide.

Results and Discussion

The results are analyzed in terms of the McMillan−Mayer theory.[23,24] The excess enthalpy $H^E(m_x, m_y)$ of a solution containing two solute species x and y can be obtained by

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

where w_1 is the mass of solvent, $H^E(m_x, m_y)/w_1$ 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 mol of x, and m_y mol of y. H^* is the standard enthalpy of 1 kg of pure solvent, and $H^\infty_{x,m}$ and $H^\infty_{y,m}$ 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. $\Delta H_{dil(x)}$, $\Delta H_{dil(y)}$, and ΔH_{mix} have been determined. To make the calculation easier, an auxiliary function ΔH^* was introduced

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

and combining eqs 4 and 5, it follows that

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

The experimental values of enthalpies of dilution and mixing of acetamide and DMF (x) with 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).

As there are some difficulties in the interpretation of the higher h coefficient, only the pairwise interactions are considered here. The enthalpic pairwise interaction coefficients are regarded as a measure of the heat effects (i.e., the enthalpy of interaction) when two solute species approach each other.[25] The physical meaning of the pair interaction coefficients is linked to the variation of the thermodynamic property when two hydrated molecules are brought from an infinite distance, where solute−solvent interactions prevail, to a finite distance where solute−solute, water-mediated interactions are operating.[26] Therefore, the enthalpic pairwise interaction coefficients h_{xy} are the results of solvation effects and direct solute−solute interaction effects.[27] Figure 1 shows the h_{xy} of D-sorbitol with acetamide and DMF versus the molality of sodium chloride in aqueous solutions.

From Figure 1, we can see that in water or in aqueous sodium chloride solutions the investigated values of h_{xy} for both sorbitol−acetamide and sorbitol−DMF systems are positive. These results indicate that energy is needed when the D-sorbitol molecule and acetamide or the DMF molecule approach each other. 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 (negative contribution to h_{xy}[28]), direct interaction between solute molecules and interaction of the solute molecules with the coexisting ions in the solvents, the latter including the electrostatic interaction of the carbonyl group or the amino group of acylamide molecules with the sodium or chloride ion, hydrogen bonding between these ions and the numerous hydroxyl groups of the polyol, etc. The value of h_{xy} for sorbitol−acetamide is less than that for the sorbitol−DMF system. This kind of difference is mainly ascribed to the different structure of the two acylamide molecules. When solvated molecules of acylamide and D-sorbitol approach each other, the degree of disruption of the hydration shells of DMF is higher than that of acetamide due to the presence of two methyl groups.

On the other hand, the values of h_{xy} for both the sorbitol−acetamide system and the sorbitol−DMF system increase positively with elevation of molality of sodium chloride solutions. This variation trend is the result of the influence of sodium chloride on the interaction of the formamide molecule and polyalcohol molecules. The larger molality of sodium chloride increases the difficulty of the departure of water molecules from the ion or solute molecule, which leads to a more positive enthalpy. Consequently, the value of h_{xy} of investigated systems becomes more positive with the elevated molality of sodium chloride.

Conclusion

In aqueous sodium chloride solutions, the calorimetric measurements of the enthalpies of mixing of two acylamides (acetamide and DMF) with D-sorbitol were carried out at 298.15 K. On the basis of the obtained results, the heterotactic enthalpic pairwise interaction coefficients h_{xy} between acylamide and D-sorbitol have been determined. The results show that the values of h_{xy} for both sorbitol−acetamide and sorbitol−DMF systems are positive. The value of h_{xy} for the sorbitol−DMF system is larger than that for the sorbitol−acetamide system at the same molality of sodium chloride. Furthermore, the values of h_{xy} increase with the elevated molality of sodium chloride.

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