Enthalpies of Dilution of (2*S*,3*R*,4*R*,5*R*)-Hexane-1,2,3,4,5,6-hexol in Water and Aqueous Sodium Halide Solutions at $T = (293.15 \text{ to } 318.15)$ K

Mingzhi Song,*,† Chuangang Fan,† Dezhi Sun,‡ and Zailong Zhang§

Department of Chemistry and Chemical Engineering, Binzhou College, Binzhou, Shandong, 256603, People's Republic of China, College of Chemistry and Chemical Engineering, Petroleum University of China, Qingdao, Shandong, 266555, People's Republic of China, and College of Chemistry, Liaocheng University, Liaocheng, Shandong, 252059, People's Republic of China

---

The enthalpies of dilution of (2*S*,3*R*,4*R*,5*R*)-hexane-1,2,3,4,5,6-hexol in water and aqueous sodium halide solutions have been determined by isothermal flow-mix microcalorimetry at $T = (293.15 \text{ to } 318.15)$ K. Experiential equations of apparent enthalpies of dilution varying with the concentration of the polylol have been obtained from the experimental data in terms of the improved McMillan−Mayer theory. Enthalpic interaction coefficients, h_2, h_3, and h_4, pairwise entropic interaction coefficient s_2, and Gibbs free energy pairwise coefficient g_2 have been calculated. The values of pairwise enthalpic interaction coefficient, h_2, have been discussed in the light of solute−solute and solute−solvent interactions. The results indicate that the values of h_2 show quite well that the straight-line dependence on temperature and pairwise entropic interaction coefficient, s_2, is a constant in the experimental range of temperature.

Introduction

(2*S*,3*R*,4*R*,5*R*)-Hexane-1,2,3,4,5,6-hexol, a polylol derived from glucose by the enzyme aldose reductase, is a common organic solute in many cells of human body.[1,2] It can be utilized as a test substance for the measurement of liver plasma flow in humans[3] and can be recommended as a cost-effective alternative to lactulose for the treatment of constipation in the elderly.[4] It plays a role in acute kidney injury.[5] As we all know, the main solvent in body fluid of human and animals is water in which various ions are coexistent. Interactions of polylol−polylol, polylol−water, and polylol−ions must be in existence and bound up with thermodynamic characters of the systems. So to study on the thermodynamic characters of the polylol in aqueous solutions is as important as to research those of such bioactive substances as amino acids with ions[6−8] in aqueous solutions. In the former work, the dilution enthalpies for (2*S*,3*R*,4*R*,5*R*)-hexane-1,2,3,4,5,6-hexol in pure water and aqueous sodium halide solutions at 313.15 K have already been studied.[9] To further investigate the temperature effect on the dilution enthalpy of this polylol, in the present work, we have measured the thermodynamic properties of (2*S*,3*R*,4*R*,5*R*)-hexane-1,2,3,4,5,6-hexol in pure water and four aqueous sodium halide solutions at (293.15, 298.15, 303.15, 308.15, and 318.15) K. The enthalpic interaction coefficients, h_2, h_3, and h_4 at each temperature, pairwise entropic interaction coefficient s_2, and Gibbs free energy pairwise coefficient g_2 have been obtained. The results are interpreted in terms of solute−solute and solute−solvent interactions according to the McMillan−Mayer theory.

Experimental Section

Reagents. (2*S*,3*R*,4*R*,5*R*)-Hexane-1,2,3,4,5,6-hexol was purchased from Aldrich, and the stated mass fraction purity was better than 0.99. They were dried under reduced pressure at 323 K before used. The purity was detected with an examination of optical rotation ($[\alpha]_D{}^{20}$). The experimental data determined in this laboratory for (2*S*,3*R*,4*R*,5*R*)-hexane-1,2,3,4,5,6-hexol were $[\alpha]_D{}^{20} = -1.99 \pm 0.02$ (−1.98 in the literature[10]). Sodium fluoride (NaF), sodium chloride (NaCl), sodium bromide (NaBr), and sodium iodide (NaI) (analytical reagents, mass fraction purity ≥ 0.997, Shanghai Chemical Reagent Company) were recrystallized from distilled water and dried under reduced pressure at 393 K. All of 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. Solutions were prepared by mass using a Mettler AE 200 balance precise to ± 0.0001 g. The molality of aqueous sodium halide is 0.500 $\text{mol}\cdot\text{kg}^{-1}$. The molality ranges of (2*S*,3*R*,4*R*,5*R*)-hxane-1,2,3,4,5,6-hexol are (0.10 to 0.50) $\text{mol}\cdot\text{kg}^{-1}$, with either pure water or 0.500 $\text{mol}\cdot\text{kg}^{-1}$ sodium halide aqueous solutions as solvent. All of the solutions were degassed with an ultrasonic wave and used within 12 h after preparation, and the uncertainty of the concentration was ± 0.0002 $\text{mol}\cdot\text{kg}^{-1}$.

Calorimetric Procedure. The enthalpies of dilution were measured with a 2277-204 measuring cylinder supported by a Thermometric 2277 thermal activity monitor[11] (Thermometric, Sweden) at $T = (293.15 \text{ to } 318.15)$ K. The performance of the apparatus was checked by measuring the relative apparent molar enthalpy of glycine in water, which is in good agreement with that reported in the literature,[11] and the accuracy of the calibration was better than 1 %. The solutions of (2*S*,3*R*,4*R*,5*R*)-hexane-1,2,3,4,5,6-hexol and their solvents were pumped through the mixing-flow vessel of the calorimeter using a LKB VS2-10R MIDI dual channel pumps. The variation in flow rates was less than 0.1 %. The flow rates were determined by the mass of the samples delivered in 8 min. The variation in rates was less

---

* Corresponding author. Department of Chemistry, Binzhou College, 5 Huanghe Road, Binzhou, Shandong 256603, People's Republic of China. Tel.: +86-543-3190097. E-mail: songmingzhi2010@163.com (Mingzhi Song).

† Binzhou College.

‡ Liaocheng University.

§ Petroleum University of China.

10.1021/je1007394

than 0.1 % both before and after a complete dilution experiment. Thermal effects of the dilute process have been obtained with the method described in the literature[12]

The enthalpies of dilution $\Delta_{\mathrm{dil}}H_{\mathrm{m}}$ were calculated from the equation[13]

$$\Delta_{\mathrm{dil}}H_{\mathrm{m}} = -P(1 + m_{\mathrm{i}}M)/m_{\mathrm{i}}f_2 \qquad (1)$$

where P is the dilution thermal power (μW), M is the molar mass of the polylol, and f_2 is the flow rate of (2*S*,3*R*,4*R*,5*R*)-hexane-1,2,3,4,5,6-hexol solutions, and m_{i} is the initial molality of the solution. The final molality m_{f} was calculated from the equation

$$m_{\mathrm{f}} = m_{\mathrm{i}}f_2/[f_1(1 + m_{\mathrm{i}}M) + f_2] \qquad (2)$$

where f_1 is the flow rate of diluents (water or aqueous sodium halide solutions). The uncertainty of $\Delta_{\mathrm{dil}}H_{\mathrm{m}}$ calculated according to eqs 1 and 2 was within ± 1 % based on the data of three iterations.

Results and Discussion

The molar excess enthalpy of a solution with molality m can be written as a power series of m with coefficients h_n by:[14,15]

$$H^{\mathrm{E}}_{\mathrm{m}} = H^{\mathrm{E}}/m = L_{2\varphi} = h_2m + h_3m^2 + h_4m^3 + ... \qquad (3)$$

where $L_{2\varphi}$ is the relative apparent molar enthalpy. The enthalpic interaction coefficients h_n which are related to the McMillan−Mayer coefficients measure the enthalpic interactions, mediated by the solvent, occurring between pairs, triplets, and higher-order multiplets of solute species. The molar enthalpy of dilution $\Delta_{\mathrm{dil}}H_m$ in terms of the excess enthalpy at initial molality m_{i} and final molality m_{f} is

$$\Delta_{\mathrm{dil}}H_{\mathrm{m}} = H^{\mathrm{exp}}m(m_{\mathrm{f}}) - H^{\mathrm{exp}}m(m_{\mathrm{i}}) = h_2(m_{\mathrm{f}} - m_{\mathrm{i}}) + h_3(m_{\mathrm{f}}^2 - m_{\mathrm{i}}^2) + h_4(m_{\mathrm{f}}^3 - m_{\mathrm{i}}^3) + ... \qquad (4)$$

where $H^{\mathrm{exp}}{}_{\mathrm{m}}(m_{\mathrm{f}})$ and $H^{\mathrm{exp}}{}_{\mathrm{m}}(m_{\mathrm{i}})$ are the molar excess (relative apparent molar) enthalpies of the solute in the solutions before and after dilution.

The pairwise h_2, triplet h_3, and higher terms are the enthalpic contributions to the corresponding virial coefficients of the excess Gibbs energy g_2, g_3, and so forth.[16] For the pairwise coefficient h_2:

$$h_2 = [\partial(g_2/T)/\partial(1/T)]_P \qquad (5)$$

and

$$h_2 = g_2 + Ts_2 \qquad (6)$$

where s_2, the entropic pairwise interaction coefficient, is in the series of virial coefficients of the excess entropy s_2, s_3, and so forth. Generally, h_2, g_2, and s_2 are all functions of temperature.

Table 1. Enthalpies of Dilution of (2*S*,3*R*,4*R*,5*R*)-Hexane-1,2,3,4,5,6-hexol in Pure Water and Sodium Halide Solutions at 293.15 K

m_{i} mol·kg^{-1}	m_{f} mol·kg^{-1}	$\Delta_{\mathrm{dil,exp.}}H_{\mathrm{m}}$ J·mol^{-1}	$\Delta_{\mathrm{dil,cal.}}H_{\mathrm{m}}$ J·mol^{-1}	m_{i} mol·kg^{-1}	m_{f} mol·kg^{-1}	$\Delta_{\mathrm{dil,exp.}}H_{\mathrm{m}}$ J·mol^{-1}	$\Delta_{\mathrm{dil,cal.}}H_{\mathrm{m}}$ J·mol^{-1}
Water							
0.1393	0.0676	4.20	4.76	0.3047	0.1487	6.41	6.45
0.1666	0.0813	5.07	5.07	0.3335	0.1638	6.65	6.66
0.1921	0.0937	5.35	5.36	0.3639	0.1791	6.88	6.87
0.2208	0.1074	6.15	6.02	0.3969	0.1948	7.10	7.10
0.2484	0.1208	6.21	6.20	0.4293	0.2108	7.28	7.27
0.2764	0.1348	6.46	6.51	0.4696	0.2302	7.59	7.46
NaF (0.5 mol·kg^{-1})							
0.1413	0.0686	−5.65	−5.56	0.3032	0.1483	−11.11	−11.12
0.1703	0.0826	−6.34	−6.45	0.3312	0.1617	−12.15	−12.18
0.1924	0.0937	−7.20	−7.16	0.3603	0.1760	−13.41	−13.29
0.2185	0.1067	−7.97	−8.03	0.3902	0.1906	−14.19	−14.30
0.2472	0.1208	−8.96	−9.04	0.4260	0.2074	−15.61	−15.66
0.2737	0.1335	−10.09	−10.01	0.4703	0.2286	−17.29	−17.20
NaCl (0.5 mol·kg^{-1})							
0.1459	0.0708	−3.30	−3.42	0.3094	0.1506	−8.14	−8.28
0.1695	0.0826	−4.23	−4.09	0.3376	0.1643	−9.17	−9.17
0.1943	0.0947	−4.80	−4.80	0.3674	0.1789	−10.21	−10.19
0.2229	0.1091	−5.75	−5.62	0.3979	0.1934	−11.11	−11.19
0.2510	0.1227	−6.40	−6.47	0.4354	0.2119	−12.35	−12.31
0.2817	0.1373	−7.39	−7.42	0.4778	0.2326	−13.79	−13.72
NaBr (0.5 mol·kg^{-1})							
0.1434	0.0686	−3.27	−3.25	0.3162	0.1539	−8.47	−8.46
0.1727	0.0831	−4.10	−4.13	0.3452	0.1685	−9.38	−9.33
0.2033	0.0981	−5.10	−5.05	0.3747	0.1826	−10.21	−10.25
0.2312	0.1122	−5.82	−5.87	0.4049	0.1972	−11.26	−11.29
0.2560	0.1245	−6.56	−6.61	0.4378	0.2137	−12.28	−12.32
0.2863	0.1395	−7.55	−7.53	0.4797	0.2338	−13.71	−13.66
NaI (0.5 mol·kg^{-1})							
0.1478	0.0718	−3.40	−3.47	0.3214	0.1562	−9.58	−9.49
0.1779	0.0862	−4.79	−4.55	0.3524	0.1712	−10.45	−10.51
0.2054	0.0996	−5.45	−5.52	0.3869	0.1879	−11.71	−11.67
0.2339	0.1134	−6.18	−6.52	0.4170	0.2031	−12.68	−12.62
0.2618	0.1267	−7.69	−7.50	0.4538	0.2216	−13.81	−13.70
0.2922	0.1423	−8.56	−8.48	0.4754	0.2324	−14.41	−14.41

In this work, pure water and the aqueous sodium halide solutions are regarded wholly as "solvents". Tables 1 to 5 give the experimental values of dilution enthalpies ($\Delta_{\mathrm{dil,exp.}}H_{\mathrm{m}}$) from (293.15 to 318.15) K, to which eq 4 was fitted with a least-squares procedure, together with the corresponding calculated values ($\Delta_{\mathrm{dil,cal.}}H_{\mathrm{m}}$) along with the initial and final molality (m_{i} and m_{f}) of (2*S*,3*R*,4*R*,5*R*)-hexane-1,2,3,4,5,6-hexol in different solvents. Table 6 lists the coefficients of eq 4 which were obtained from least-squares analysis of these results. Figure 1 shows the variations of h_2 coefficients for (2*S*,3*R*,4*R*,5*R*)-hexane-1,2,3,4,5,6-hexol within water and four aqueous sodium halide solutions from (293.15 to 318.15) K.

Since it is difficult to interpret the higher-order h coefficients, only the enthalpic pairwise coefficients h_2 are discussed here. The values of h_2 are the measurement of the interaction energy between a pair of solute molecules,[15] which may take place with coexistent electrolytes in aqueous solution. The interaction between two hydrated solute molecules is supposed to occur by the overlap of their hydration cospheres with the consequent release of water molecules from these cospheres to the bulk medium.[17] The overall effect thus reflects the following three superimposed processes:

1. Interaction between molecules of (2*S*,3*R*,4*R*,5*R*)-hexane-1,2,3,4,5,6-hexol, which is mainly a hydrogen bond between molecules. This makes a positive contribution to h_2.
2. Partial dehydration of the hydration shell of the polylol,[18,19] which makes another positive contribution to h_2.
3. Interaction between the polylol and the coexisting ions in the solvents.[20] This interaction weakens the above-mentioned two effects.

Isothermal Dilution Enthalpies and Enthalpic Pairwise Coefficients (h₂). From Table 6 we can see that whether in water or in aqueous sodium halide solutions, the values of

Table 2. Enthalpies of Dilution of (2*S*,3*R*,4*R*,5*R*)-Hexane-1,2,3,4,5,6-hexol in Pure Water and Sodium Halide Solutions at 298.15 K

m_i / mol·kg^{-1}	m_f / mol·kg^{-1}	$\Delta_{dil,exp.}H_m$ / J·mol^{-1}	$\Delta_{dil,cal.}H_m$ / J·mol^{-1}	m_i / mol·kg^{-1}	m_f / mol·kg^{-1}	$\Delta_{dil,exp.}H_m$ / J·mol^{-1}	$\Delta_{dil,cal.}H_m$ / J·mol^{-1}
Water							
0.1337	0.0651	1.19	1.15	0.2798	0.1369	0.26	0.23
0.1580	0.0773	0.93	0.97	0.3050	0.1492	0.13	0.11
0.1832	0.0894	0.75	0.79	0.3285	0.1611	0.03	0.02
0.2059	0.1007	0.61	0.64	0.3571	0.1751	−0.14	−0.08
0.2336	0.1143	0.49	0.47	0.3908	0.1914	−0.21	−0.20
0.2557	0.1249	0.37	0.35	0.4253	0.2084	−0.27	−0.29
NaF (0.5 mol·kg^{-1})							
0.1330	0.0657	−3.95	−4.03	0.2845	0.1377	−10.98	−11.51
0.1592	0.0783	−5.27	−5.21	0.3117	0.1497	−13.59	−12.96
0.1871	0.0917	−6.82	−6.54	0.3403	0.1624	−13.94	−14.45
0.2034	0.0998	−7.14	−7.32	0.3772	0.1794	−16.76	−16.22
0.2365	0.1144	−8.97	−9.08	0.4131	0.1959	−17.47	−17.82
0.2617	0.1268	−10.51	−10.35	0.4515	0.2126	−19.46	−19.39
NaCl (0.5 mol·kg^{-1})							
0.1381	0.0670	−3.53	−3.53	0.3019	0.1470	−10.20	−10.33
0.1659	0.0805	−4.70	−4.65	0.3329	0.1617	−11.63	−11.65
0.1920	0.0931	−5.59	−5.73	0.3628	0.1763	−12.81	−12.86
0.2193	0.1067	−6.84	−6.85	0.3938	0.1914	−14.21	−14.10
0.2455	0.1199	−8.07	−7.92	0.4249	0.2065	−15.24	−15.29
0.2743	0.1338	−9.23	−9.15	0.4614	0.2239	−16.67	−16.66
NaBr (0.5 mol·kg^{-1})							
0.1364	0.0664	−4.34	−4.39	0.3036	0.1481	−11.83	−12.07
0.1658	0.0809	−5.79	−5.73	0.3330	0.1626	−13.23	−13.36
0.1911	0.0932	−6.90	−6.90	0.3465	0.1692	−14.28	−13.93
0.2182	0.1063	−8.24	−8.17	0.3770	0.1838	−15.30	−15.24
0.2449	0.1192	−9.35	−9.41	0.4103	0.2006	−16.37	−16.52
0.2744	0.1338	−10.81	−10.75	0.4477	0.2190	−17.92	−17.89
NaI (0.5 mol·kg^{-1})							
0.1402	0.0684	−5.51	−5.46	0.2953	0.1438	−12.80	−12.73
0.1643	0.0803	−6.40	−6.55	0.3222	0.1577	−13.82	−13.93
0.1900	0.0928	−7.80	−7.75	0.3512	0.1723	−15.17	−15.27
0.2155	0.1051	−9.09	−8.96	0.3810	0.1865	−16.73	−16.69
0.2443	0.1194	−10.22	−10.28	0.4158	0.2030	−18.55	−18.37
0.2688	0.1312	−11.46	−11.46	0.4542	0.2221	−20.04	−20.13

Table 3. Enthalpies of Dilution of (2*S*,3*R*,4*R*,5*R*)-Hexane-1,2,3,4,5,6-hexol in Pure Water and Sodium Halide Solutions at 303.15 K

m_i / mol·kg^{-1}	m_f / mol·kg^{-1}	$\Delta_{dil,exp.}H_m$ / J·mol^{-1}	$\Delta_{dil,cal.}H_m$ / J·mol^{-1}	m_i / mol·kg^{-1}	m_f / mol·kg^{-1}	$\Delta_{dil,exp.}H_m$ / J·mol^{-1}	$\Delta_{dil,cal.}H_m$ / J·mol^{-1}
Water							
0.1148	0.0572	−0.56	−0.64	0.2969	0.1465	−4.24	−4.29
0.1448	0.0720	−1.35	−1.26	0.3317	0.1635	−5.01	−5.03
0.1748	0.0868	−1.90	−1.87	0.3656	0.179	−5.81	−5.82
0.2046	0.1011	−2.49	−2.47	0.3998	0.1963	−6.77	−6.68
0.2351	0.1162	−3.06	−3.05	0.4357	0.2131	−7.71	−7.70
0.2670	0.1318	−3.64	−3.68	0.4637	0.2269	−8.53	−8.54
NaF (0.5 mol·kg^{-1})							
0.1046	0.0521	−10.71	−10.60	0.2803	0.1387	−17.87	−18.29
0.1345	0.0670	−11.50	−11.73	0.3197	0.1577	−20.40	−20.33
0.1576	0.0785	−12.3	−12.66	0.3528	0.1741	−23.05	−22.07
0.1927	0.0957	−15.22	−14.16	0.3863	0.1895	−24.02	−23.98
0.2250	0.1118	−15.49	−15.61	0.4197	0.2062	−25.38	−25.83
0.2566	0.1271	−16.46	−16.25	0.4635	0.2269	−27.97	−28.40
NaCl (0.5 mol·kg^{-1})							
0.0987	0.0490	−4.98	−5.01	0.2843	0.1393	−14.02	−14.01
0.1276	0.0629	−6.27	−6.28	0.3184	0.1560	−15.78	−15.77
0.1550	0.076	−7.71	−7.60	0.3511	0.1711	−17.49	−17.55
0.1856	0.0913	−9.01	−9.07	0.3850	0.1880	−19.28	−19.33
0.2177	0.1070	−10.64	−10.64	0.4132	0.2010	−20.99	−20.90
0.2505	0.1229	−12.29	−12.28	0.4502	0.2186	−23.03	−22.93
NaBr (0.5 mol·kg^{-1})							
0.1079	0.0527	−4.92	−5.02	0.3087	0.1492	−15.67	−15.85
0.140	0.0687	−6.81	−6.67	0.3449	0.1660	−18.01	−17.92
0.1712	0.0834	−8.39	−8.30	0.3810	0.1835	−20.08	−19.92
0.2045	0.0994	−9.98	−10.08	0.4177	0.2001	−22.10	−22.05
0.2375	0.1151	−11.88	−11.89	0.4617	0.2212	−24.31	−24.47
0.2704	0.1307	−13.72	−13.73	0.4822	0.2302	−25.61	−25.67
NaI (0.5 mol·kg^{-1})							
0.1019	0.0494	−4.86	−4.89	0.2779	0.1334	−16.02	−15.98
0.1303	0.0630	−6.65	−6.61	0.3085	0.1475	−18.12	−18.02
0.1607	0.0775	−8.45	−8.49	0.3311	0.1584	−19.28	−19.48
0.1897	0.0915	−10.41	−10.30	0.3877	0.1847	−23.25	−23.19
0.2187	0.1053	−12.11	−12.15	0.4335	0.2058	−26.19	−26.169
0.2477	0.1190	−13.97	−14.03	0.4665	0.2207	−28.38	−28.30

pairwise enthalpic coefficients, h_2, for (2*S*,3*R*,4*R*,5*R*)-hexane-1,2,3,4,5,6-hexol are positive except for the value at 293.15 K. These results indicate that energy is needed to destroy the aqueous sheath of each polylol molecule when two molecules of polylol approach each other. The value of h_2 for (2*S*,3*R*,4*R*,5*R*)-hexane-1,2,3,4,5,6-hexol increases positively with the radius of the anion in aqueous sodium halide solutions at each temperature from (293.15 to 318.15) K. The reasons have already been explained earlier.[9]

Table 6 shows that the value of pairwise enthalpic coefficients, h_2, for (2*S*,3*R*,4*R*,5*R*)-hexane-1,2,3,4,5,6-hexol is negative at 293.15 K. This is because the hydration capacity of molecule is weaker at lower temperatures, so the energy emitted to form a hydrogen bond is higher than that absorbed to destroy the aqueous sheath of each polylol molecule. So, energy is given off when two polylol molecules approach each other at 293.15 K, and the value of h_2 is negative.

Table 6 also shows that, at (293.15 and 298.15) K, the values of h_2 for (2*S*,3*R*,4*R*,5*R*)-hexane-1,2,3,4,5,6-hexol in sodium fluoride solution are obviously higher than those in aqueous solution. The value of h_2 is mainly decided by the differentials of the energy emitted to form a hydrogen bond and the energy absorbed to destroy the aqueous sheath of each polylol molecule at the two temperatures. In the sodium halide solutions, because of the existence of the halide and sodium ions, when two polylol molecules approach each other, they not only need to overcome the bondage of water molecule of the aqueous sheath around themselves but also need to overcome their interactions with the ions, so the energy they absorbed during this process is far more than that emitted to form hydrogen bond. So, the values of h_2 for (2*S*,3*R*,4*R*,5*R*)-hexane-1,2,3,4,5,6-hexol in sodium fluoride solution are much higher than those in aqueous solution at the two temperatues.

Temperature Effect on Enthalpic Pairwise Coefficient, Entropic Pairwise Coefficients (s_2), and Gibbs Free Energy Pairwise Coefficient (g_2). Figure 1 shows that, in both pure water and aqueous sodium halide solutions, the value of pairwise enthalpic interaction coefficients h_2 of (2*S*,3*R*,4*R*,5*R*)-hexane-1,2,3,4,5,6-hexol increase with the temperature. According to the above-mentioned factors affecting h_2, the value of h_2 is mainly decided by the balance of the several factors. As is well-known, intermolecular interactions mainly consist of orientation force, dispersion force, induction force, and a hydrogen bond, and these interactions will decrease with the increase of temperature.

In the aqueous solutions of (2*S*,3*R*,4*R*,5*R*)-hexane-1,2,3,4,5,6-hexol, there are interactions between molecules of the polylol and water and the interactions between two polylols. When two polylol molecules approach each other, they not only should get rid of part water molecules of the hydration shell around themselves, which is an endothermic process, but also should overcome the interactions between polylol molecules, which is another endothermic process; on the other hand, hydrogen bonds between the molecules are produced when two polylol molecules approach each other, and this is an exothermic process. The contribution of the first two factors is more than the latter one, so the whole process is an endothermic process. As is well-known, the hydration ability of the molecule decreases with the

Table 4. Enthalpies of Dilution of (2*S*,3*R*,4*R*,5*R*)-Hexane-1,2,3,4,5,6-hexol in Pure Water and Sodium Halide Solutions at 308.15 K

m_i	m_f	$\Delta_{dil,exp.}H_m$	$\Delta_{dil,cal.}H_m$	m_i	m_f	$\Delta_{dil,exp.}H_m$	$\Delta_{dil,cal.}H_m$
$mol \cdot kg^{-1}$	$mol \cdot kg^{-1}$	$J \cdot mol^{-1}$	$J \cdot mol^{-1}$	$mol \cdot kg^{-1}$	$mol \cdot kg^{-1}$	$J \cdot mol^{-1}$	$J \cdot mol^{-1}$
Water							
0.1056	0.0560	−2.41	−2.42	0.3061	0.1619	−10.17	−10.10
0.1366	0.0730	−3.86	−3.67	0.3429	0.1809	−11.59	−11.53
0.1708	0.0909	−4.71	−4.98	0.3814	0.2008	−12.86	−13.09
0.2033	0.1082	−6.23	−6.23	0.4216	0.2217	−14.93	−14.82
0.2369	0.1258	−7.55	−7.48	0.4690	0.2459	−16.97	−16.96
0.2720	0.1441	−8.83	−8.80	0.4854	0.2541	−17.70	−17.74
NaF (0.5 $mol \cdot kg^{-1}$)							
0.1064	0.0588	−10.65	−10.71	0.2999	0.1651	−20.64	−20.61
0.1383	0.0765	−12.39	−12.11	0.3330	0.1829	−22.69	−22.45
0.1711	0.0946	−13.66	−13.67	0.3654	0.1999	−24.32	−24.43
0.2037	0.1127	−14.72	−15.01	0.3998	0.2189	−26.33	−26.49
0.2332	0.1283	−16.96	−16.94	0.4338	0.2369	−28.64	−28.615
0.2661	0.1466	−18.72	−18.61	0.4700	0.2563	−30.67	−30.86
NaCl (0.5 $mol \cdot kg^{-1}$)							
0.1412	0.0784	−9.63	−9.57	0.3458	0.1905	−19.67	−19.48
0.1740	0.0964	−10.86	−10.88	0.3761	0.2067	−21.31	−21.17
0.2063	0.1138	−12.44	−12.50	0.4095	0.2247	−23.04	−23.11
0.2406	0.1327	−14.15	−14.13	0.4439	0.2431	−25.08	−25.22
0.2780	0.1534	−15.95	−15.94	0.4744	0.2594	−26.99	−27.16
0.3135	0.1735	−18.39	−17.68	0.4984	0.2721	−28.95	−28.77
NaBr (0.5 $mol \cdot kg^{-1}$)							
0.1096	0.0597	−2.42	−2.44	0.2854	0.1538	−13.43	−13.46
0.1430	0.0777	−4.35	−4.43	0.3197	0.1723	−15.59	−15.74
0.1676	0.09114	−5.97	−5.94	0.3511	0.1887	−17.69	−17.77
0.1984	0.1077	−7.87	−7.83	0.3867	0.2071	−20.01	−20.15
0.2248	0.12178	−9.60	−9.56	0.4216	0.2263	−22.47	−22.48
0.2545	0.1375	−11.40	−11.43	0.4600	0.2460	−24.74	−24.81
NaI (0.5 $mol \cdot kg^{-1}$)							
0.1398	0.0724	−9.29	−9.35	0.3289	0.1690	−22.97	−23.08
0.1730	0.0895	−11.68	−11.738	0.3605	0.1847	−25.48	−25.53
0.2031	0.1049	−13.80	−13.85	0.3941	0.2015	−27.99	−28.07
0.2315	0.1192	−16.23	−16.18	0.4301	0.2191	−30.95	−30.87
0.2665	0.1368	−18.47	−18.53	0.4545	0.2313	−32.75	−32.69
0.2974	0.1528	−20.66	−20.73	0.4812	0.2305	−38.51	−38.52

Table 5. Enthalpies of Dilution of (2*S*,3*R*,4*R*,5*R*)-Hexane-1,2,3,4,5,6-hexol in Pure Water and Sodium Halide Solutions at 318.15 K

m_i	m_f	$\Delta_{dil,exp.}H_m$	$\Delta_{dil,cal.}H_m$	m_i	m_f	$\Delta_{dil,exp.}H_m$	$\Delta_{dilcal.}H_m$
$mol \cdot kg^{-1}$	$mol \cdot kg^{-1}$	$J \cdot mol^{-1}$	$J \cdot mol^{-1}$	$mol \cdot kg^{-1}$	$mol \cdot kg^{-1}$	$J \cdot mol^{-1}$	$J \cdot mol^{-1}$
Water							
0.1030	0.0523	−3.31	−3.27	0.2991	0.1506	−12.89	−12.84
0.1380	0.0699	−5.06	−5.13	0.3093	0.1557	−13.17	−13.31
0.1673	0.0848	−6.62	−6.59	0.3422	0.1715	−14.86	−14.92
0.1990	0.1003	−8.08	−8.18	0.3739	0.1876	−16.42	−16.39
0.2332	0.1177	−9.96	−9.77	0.4215	0.2110	−18.88	−18.79
0.2647	0.1334	−11.24	−11.25	0.4649	0.2322	−21.04	−21.12
NaF (0.5 $mol \cdot kg^{-1}$)							
0.1094	0.0574	−9.41	−9.57	0.2731	0.1428	−18.06	−18.66
0.1308	0.0686	−10.80	−10.65	0.3011	0.1575	−20.87	−20.43
0.1586	0.0833	−12.28	−12.09	0.3288	0.1710	−22.87	−22.37
0.1904	0.0998	−14.06	−13.81	0.3576	0.1862	−24.84	−24.37
0.2179	0.1143	−14.92	−15.33	0.3965	0.2060	−26.93	−27.34
0.2438	0.1278	−16.62	−16.84	0.4308	0.2239	−29.57	−30.09
NaCl (0.5 $mol \cdot kg^{-1}$)							
0.0965	0.0481	−6.59	−6.82	0.2720	0.1361	−17.18	−17.48
0.1237	0.0621	−8.59	−8.38	0.3004	0.1501	−19.49	−19.34
0.1540	0.0771	−10.50	−10.20	0.3342	0.1663	−21.83	−21.65
0.1831	0.0919	−11.94	−11.92	0.3719	0.1846	−24.45	−24.28
0.2123	0.1064	−13.42	−13.72	0.4186	0.2077	−27.49	−27.61
0.2412	0.1205	−15.53	−15.56	0.4543	0.2253	−30.05	−30.26
NaBr (0.5 $mol \cdot kg^{-1}$)							
0.1032	0.0526	−6.28	−6.28	0.2857	0.1449	−19.26	−19.29
0.1318	0.0677	−8.29	−8.24	0.3204	0.1625	−21.72	−21.76
0.1617	0.0828	−10.23	−10.35	0.3490	0.1769	−23.82	−23.82
0.1925	0.0984	−12.64	−12.55	0.3851	0.1946	−26.51	−26.48
0.2241	0.1143	−14.83	−14.82	0.4224	0.2134	−29.20	−29.17
0.2564	0.1303	−17.18	−17.16	0.4579	0.2308	−31.75	−31.79
NaI (0.5 $mol \cdot kg^{-1}$)							
0.0953	0.0486	−6.46	−6.58	0.2717	0.1370	−19.87	−19.89
0.1250	0.0637	−8.98	−8.84	0.3067	0.1546	−22.38	−22.46
0.1552	0.0790	−11.16	−11.12	0.3388	0.1704	−24.87	−24.88
0.1836	0.0933	−13.30	−13.24	0.3668	0.1844	−26.92	−26.94
0.2125	0.1078	−15.34	−15.41	0.4110	0.2055	−30.50	−30.36
0.2436	0.1231	−17.76	−17.77	0.4483	0.2240	−33.25	−33.15

increase of temperature, so when two polylol molecules approach each other, the energy absorbed to get rid of some water molecules of the hydration shell will decrease, and the energy absorbed to overcome the interaction between polylol molecules will decrease too. On the other hand, when hydrogen bonds produced, the liberated energy will decrease with the increase of temperature. So the value of h_2 is decided by the differentials of the energy changed above. In fact, the change of the latter factor is more than the first two ones, so the energy differentials will increase with the temperature. Thus, in aqueous (2*S*,3*R*,4*R*,5*R*)-hexane-1,2,3,4,5,6-hexol solution, the value of pairwise enthalpic interaction coefficients h_2 of (2*S*,3*R*,4*R*,5*R*)-hexane-1,2,3,4,5,6-hexol increased with the temperature.

In aqueous sodium halide solutions of (2*S*,3*R*,4*R*,5*R*)-hexane-1,2,3,4,5,6-hexol, the number of water molecules in the hydration shell around the polylol is relatively fewer because of the existence of halide and sodium ions. The hydration ability of ions will decrease with the increase of temperature, so more water molecules have the chance to go into the hydration shell around the polylol. But at the same time, the hydration ability of polylol and the interaction between polylols will decrease too. So, when two polylol molecules approach each other, along with the increase of temperature, the change of energy mainly depends on the competitive balance of the change of the above interactions. The experiment data show that, at the same sodium halide solution, the value of pairwise enthalpic interaction coefficients h_2 of (2*S*,3*R*,4*R*,5*R*)-hexane-1,2,3,4,5,6-hexol increases with the increase of temperature, which indicates that the endothermic effect plays a dominant role in the whole process.

In the experimental range of temperature, values of h_2 show a linear dependence on temperature, as in eq 6 (Figure 1). For each system:

$$h_2 = -1794.9(\pm 12.1) + 6.03(\pm 0.09)(T/\mathrm{K}) \qquad (\text{in } \mathrm{H_2O}) \quad (7)$$

$$h_2 = -791.7(\pm 9.8) + 2.7(\pm 0.06)(T/\mathrm{K}) \qquad (\text{in NaF}/0.5\ \mathrm{mol \cdot kg^{-1}}) \quad (8)$$

$$h_2 = -855.9(\pm 10.8) + 3.0(\pm 0.05)(T/\mathrm{K}) \qquad (\text{in NaCl}/0.5\ \mathrm{mol \cdot kg^{-1}}) \quad (9)$$

$$h_2 = -820.6(\pm 7.8) + 2.9(\pm 0.06)(T/\mathrm{K}) \qquad (\text{in NaBr}/0.5\ \mathrm{mol \cdot kg^{-1}}) \quad (10)$$

$$h_2 = -596.8(\pm 8.2) + 2.3(\pm 0.03)(T/\mathrm{K}) \qquad (\text{in NaI}/0.5\ \mathrm{mol \cdot kg^{-1}}) \quad (11)$$

The errors (in eqs 7 to 11) are estimated according to the calorimetric results of three iterations.

Table 6. Enthalpic Interaction Coefficients of (2*S*,3*R*,4*R*,5*R*)-Hexane-1,2,3,4,5,6-hexol in Water and Sodium Halide Solutions (0.5 mol·kg^{-1}) from (293.15 to 318.15) K

temperature K	h_2 J·kg·mol^{-2}	h_3 J·kg^2·mol^{-3}	h_4 J·kg^3·mol^{-4}	R^2	SD[a]
		H_2O			
293.15	−25.93 (± 0.91)	4.55 (± 0.19)	10.70 (± 0.51)	0.9989	0.12
298.15	22.80 (± 0.89)	−19.86 (± 1.7)	8.05 (± 2.5)	0.9948	0.03
303.15	57.50 (± 1.03)	−59.12 (± 1.10)	77.06 (± 1.31)	0.9997	0.05
308.15	81.24 (± 3.98)	−3.60 (± 3.11)	9.06 (± 2.71)	0.9991	0.18
313.15[b]	104.61 (± 2.35)	−68.39 (± 5.8)	76.75 (± 5.23)	0.9994	0.36
318.15	132.90 (± 2.13)	−93.76 (± 1.91)	93.27 (± 3.35)	0.9997	0.10
		NaF (0.5 mol·kg^{-1})			
293.15	23.69 (± 0.29)	100.98 (± 2.15)	−87.75 (± 1.35)	0.9989	0.14
298.15	38.45 (± 0.21)	157.24 (± 2.61)	−175.31 (± 1.31)	0.9946	0.43
303.15	44.67 (± 0.35)	87.66 (± 0.83)	−47.24 (± 0.97)	0.9930	0.31
308.15	55.81 (± 1.18)	167.58 (± 3.15)	−116.24 (± 2.35)	0.9987	0.38
313.15[b]	67.5 (± 3.2)	93.2 (± 6.6)	−55.9 (± 5.3)	0.9991	0.26
318.15	101.02 (± 2.69)	−0.25 (± 0.02)	72.33 (± 2.11)	0.9972	0.46
		NaCl (0.5 mol·kg^{-1})			
293.15	37.88 (± 0.33)	36.48 (± 1.13)	−20.81 (± 1.23)	0.9994	0.09
298.15	51.86 (± 0.76)	75.24 (± 1.43)	−79.34 (± 1.02)	0.9995	0.10
303.15	68.74 (± 0.51)	57.95 (± 0.56)	−40.43 (± 0.99)	0.9999	0.07
308.15	82.57 (± 1.01)	13.93 (± 0.35)	22.26 (± 0.33)	0.9994	0.24
313.15	93.97 (± 2.35)	1.65 (± 0.69)	35.81 (± 2.92)	0.9996	0.14
318.15[b]	116.48 (± 2.13)	−1.95 (± 0.16)	33.06 (± 0.53)	0.9993	0.24
		NaBr (0.5 mol·kg^{-1})			
293.15	48.34 (± 0.46)	18.47 (± 0.23)	−9.50 (± 0.32)	0.9997	0.05
298.15	68.33 (± 0.75)	66.31 (± 0.58)	−85.12 (± 0.99)	0.9988	0.17
303.15	86.88 (± 1.34)	41.39 (± 0.78)	−35.53 (± 0.91)	0.9997	0.13
308.15	96.89 (± 1.01)	36.96 (± 0.59)	−16.84 (± 0.53)	0.9999	0.11
313.15[b]	108.20 (± 4.64)	67.21 (± 3.56)	−60.59 (± 2.53)	0.9992	0.28
318.15	126.60 (± 1.52)	37.43 (± 0.43)	−31.17 (± 0.31)	0.9999	0.07
		NaI (0.5 mol·kg^{-1})			
293.15	72.60 (± 1.09)	−7.31 (± 0.88)	6.47 (± 0.79)	0.9981	0.17
298.15	84.52 (± 1.02)	16.75 (± 0.96)	−15.57 (± 0.36)	0.9995	0.12
303.15	94.77 (± 0.95)	66.78 (± 0.69)	−64.01 (± 0.87)	0.9998	0.09
308.15	105.29 (± 1.91)	37.49 (± 0.78)	−55.74 (± 0.93)	0.9902	0.15
313.15[b]	115.04 (± 5.33)	−290.85 (± 11.8)	292.37 (± 2.85)	0.9995	0.23
318.15	132.06 (± 1.03)	39.47 (± 0.59)	−37.45 (± 0.43)	0.9999	0.07

[a] SD is the standard deviation. [b] See ref 9.

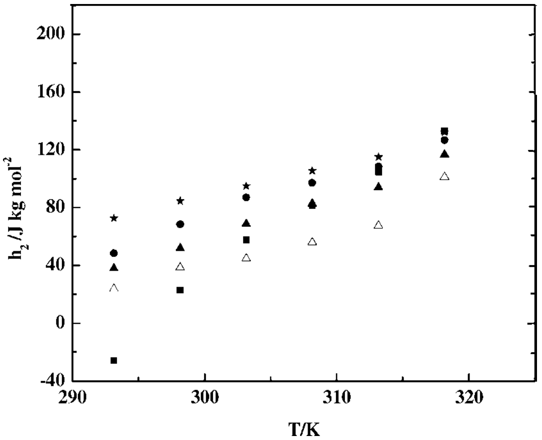

Figure 1. Pairwise enthalpic interaction coefficients of (2*S*,3*R*,4*R*,5*R*)-hexane-1,2,3,4,5,6-hexol in five different solvents from (293.15 to 318.15) K: ■, H_2O; △, NaF; ▲, NaCl; ●, NaBr; ★, NaI.

The intercept of each line denotes the pairwise Gibbs free energy interaction coefficient g_2, and the slope denotes the pairwise entropic interaction coefficient s_2 (Figure 1). From eq 7 to 11 we can see that whether in pure water or in aqueous sodium halide solutions the value of the pairwise entropic interaction coefficient s_2 is positive, which indicates that the entropy will increase when two polylol molecules approach each other in the range of experimental temperature. This is because during the process of two (2*S*,3*R*,4*R*,5*R*)-hexane-1,2,3,4,5,6-hexol molecules approaching each other, two factors influence the entropy changes: first, the structural reorganization of each component in the solution will increase the confusion degrees of the system, making a positive contribution to s_2; second, the reorganization of the hydrogen bond between two polylol molecules makes a negative contribution to s_2. The former will perform a dominant role in the whole interaction, so the value of s_2 is positive. From the above equations we can also see that the value of the Gibbs free energy pairwise coefficient g_2 is negative, which indicates that the Gibbs free energy decreases when two (2*S*,3*R*,4*R*,5*R*)-hexane-1,2,3,4,5,6-hexol molecules approach each other; that is, the process of two polylol molecules approaching each other is spontaneous during the experimental temperature range. However, there are many components in the solution, and the total free energy is also decided by third and more interaction coefficients g_3, g_4, and so forth, and other influence factors, so the Gibbs free energy pairwise coefficient g_2 cannot decide the spontaneity of the whole process.

The plots of h_2 versus T for the halides are essentially parallel (Figure 1), which means that the halogen ions affect the pairwise interacting entropy of the polyol, s_2, nearly in the same strength. However, the absolute value of pairwise interacting Gibbs free energy, g_2, diminishes with the elongation of radius of the halogen anion (except fluorine ion). This change in tendency might have something to do with dispersion force, since the larger the anion, the stronger the dispersion force between it with the polyol molecule and the weaker the spontaneity of the process in which a pair of the polyol molecules approach each other.

Conclusion

Enthalpies of dilution of (2*S*,3*R*,4*R*,5*R*)-hexane-1,2,3,4,5,6-hexol in water and aqueous sodium halide solutions were measured by isothermal flow-mixing microcalorimetry from (293.15 to 318.15) K. The values of pairwise enthalpic interaction coefficient, h_2, pairwise entropic interaction coefficient, s_2, and Gibbs free energy pairwise coefficient, g_2, have been discussed in the light of solute−solute and solute−solvent interactions, and the results are as follows:

1. At each experimental temperature except for 293.15 K, the value of the enthalpic pairwise coefficients h_2 of D-sorbitol is positive in water and sodium halide solutions.

2. The value of enthalpic pairwise coefficients h_2 of D-sorbitol increases with the increase of temperature in the same solvent. The value of entropic pairwise coefficient s_2 is positive, while the value of Gibbs free energy pairwise coefficient g_2 is negative. This is mainly decided by the partial dehydration of the hydration shell of the polylol and direct interaction between molecules of (2*S*,3*R*,4*R*,5*R*)-hexane-1,2,3,4,5,6-hexol.

Literature Cited

(1) Kracke, G. R.; Preston, G. G.; Stanley, T. H. Identification of a Sorbitol Permease in Human Erythrocytes. *Am. J. Physiol.* **1994**, *266*, 343–350.

(2) Grunewald, R. W.; Weber, I. I.; Kinne, R. K. Renal Inner Medullary Sorbitol Metabolism. *Am. J. Physiol.* **1995**, *269*, 696–701.

(3) Keiding, S.; Engsted, E.; Ott, P. Sorbitol as a Test Substance for Measurement of Liver Plasma Flow in Humans. *Hepatology* **1998**, *28*, 50–56.

(4) Lederle, F. A.; Busch, D. L.; Mattox, K. M.; West, M. J.; Aske, D. M. Cost-effective Treatment of Constipation in the Elderly: A Randomized Double-Blind Comparison of Sorbitol and Lactulose. *Am. J. Med.* **1990**, *89*, 597–601.

(5) Yagihashi, S.; Mizukami, H.; Ogasawara, S.; Yamagishi, S.; Nukada, H.; Kato, N.; Hibi, C.; Chung, S.; Chung, S. The role of the polyol pathway in acute kidney injury caused by hindlimb ischaemia in mice. *J. Pathol.* **2010**, *220*, 530–541.

(6) Liu, X. R.; He, S. Y.; Song, D. S.; Hu, R. Z. Thermochemical Properties of $Ln(Gly)_4Im(ClO_4)_3 \cdot nH_2O$ (Ln = Gd, Tb, Dy, Y). *Thermochim. Acta* **2002**, *390*, 55–59.

(7) Kocheergina, L. A.; Zelenin, O. Y. The Thermodynamic Characteristics of Complex Formation of Ni^{2+} Ions and DL-Leucine. *Russ. J. Phys. Chem.* **2001**, *75*, 705–710.

(8) Yu, L.; Hu, X.; Lin, R.; Zhang, H.; Xu, G. Enthalpies of Dilution and Enthalpies of Mixing of α-Amino Acids + Pyridine and α-Amino Acids + Methylpyridine in Aqueous Solutions at 298.15 K. *J. Chem. Eng. Data* **2003**, *48*, 990–994.

(9) Song, M.; Zhu, L.; We, X.; Wang, S.; Sun, D. Enthalpic Interaction of D-Sorbitol and D-Mannitol in Water and Aqueous Sodium Halide Solutions at 313.15 K. *J. Chem. Eng. Data* **2005**, *50*, 769–773.

(10) Weast, R. C.; Tuve, G. R. *CRC Handbook of Chemistry and Physics*, 55th ed.; The Chemical Rubber Co.: Boca Raton, FL, 1974−1975.

(11) Wadso, I. Trends in Isothermal Microcalorimetry. *Chem. Soc. Rev.* **1997**, *26*, 79–86.

(12) Ren, X.; Ni, Y.; Lin, R. Enthalpies of Dilution of Glycine, L-Serine and L-Valine in Mixtures of Water and *N*,*N*-dimethylformamide at 298.15 K. *Thermochim. Acta* **2000**, *348*, 19–24.

(13) Yu, L.; Lin, R.; Hu, X.; Xu, G. Enthalpies of Interaction of L-Valine and L-Threonine with Pyridine and Methylpyridine in Aqueous Solutions at 298.15 K. *J. Chem. Eng. Data* **2003**, *48*, 1591–1595.

(14) Franks, F.; Pedley, M.; Reid, D. S. Solute Interactions in Dilute Solutions (Part I). *J. Chem. Soc., Faraday Trans.* **1976**, *729*, 359–367.

(15) Sijpkes, A. H.; Staneke, P. O.; Somsen, G. Enthalpies of Interaction of Some *N*-Acetyl Amides of L-Serine, L-Threonine and L-Hydroxyprotine Dissolved in *N*,*N*-Dimethylformamide at 298.15 K. *Thermochim. Acta* **1990**, *167*, 65–72.

(16) Abbate, M.; Barone, G.; Borghesani, G.; Cirillo, G.; Giancola, C.; Remelli, M. Dilution enthalpies of alkanols in concentrated aqueous solutions of urea at 25 °C. *J. Solution Chem.* **1993**, *22*, 695–706.

(17) Sun, D.; Song, M.; Du, X.; Li, D. Enthalpies of dilution of L-cystine in aqueous solutions of sodium hydroxide, potassium hydroxide and hydrochloric acid. *Thermochim. Acta* **2005**, *429*, 81–86.

(18) Giorgio Soldi, L.; Marcus, Y.; Blandamer, M. J.; Cullis, P. M. Titration calorimetric determination of the pairwise interaction parameters of glycerol, D-threitol, mannitol, and D-glucitol in dilute aqueous solutions. *J. Solution Chem.* **1995**, *24*, 201–209.

(19) Amold, P.; Lilley, T. H. Aqueous solutions containing amino acids and peptides 14. The enthalpy of interaction of β-alanine and urea. *J. Chem. Thermodyn.* **1985**, *17*, 99–100.

(20) Davis, K. G.; Lilley, T. H. Aqueous Solutions Containing Amino Acids and Peptides. Part 25. The Enthalpy of Interaction at 298.15 K of Glycine with Potassium Halides. *Thermochim. Acta* **1986**, *107*, 267–276.

Received for review July 13, 2010. Accepted September 17, 2010. The fund project is Binzhou College "Young Innovation" Science Fund Project (BZXYQNLG2005013).

JE1007394