Enthalpies of Dilution of Acetamide and *N*,*N*-Dimethylformamide in Aqueous Sodium Chloride Solutions at 298.15 K

Min Liu,*[,†] Lanying Zhu,[‡] Bin Li,[†] Qiang Zhao,[†] and Dezhi Sun[†]

College of Chemistry and Chemical Engineering, Liaocheng University, Liaocheng 252059, People's Republic of China, and College of Life Science and Bioengineering, Liaocheng University, Liaocheng 252059, People's Republic of China

The enthalpies of dilution of acetamide and *N*,*N*-dimethylformamide (DMF) in pure water and aqueous sodium chloride solutions have been determined using flow microcalorimetry at 298.15 K. The homogeneous enthalpic interaction coefficients (h_2, h_3, h_4) in the range of sodium chloride molality, (0 to 0.6) $\text{mol}\cdot\text{kg}^{-1}$, have been calculated according to the McMillan−Mayer theory. It is found that the enthalpic pairwise interaction coefficients h_2 of acetamide and DMF are all positive in aqueous sodium chloride solution and become more positive with an increase in the molality of sodium chloride. The value of h_2 of acetamide is less than that of DMF in pure water and an aqueous solution of the same sodium chloride molality. The results are discussed in terms of the solute−solute and solute−solvent interactions.

Introduction

The study of the thermodynamic stability of the native structure of proteins has proved quite challenging and still remains a subject of extensive investigation. However, it is quite difficult to study the interactions between proteins directly because the structures of proteins in different solvents are very complicated. Therefore, one useful approach is to study their model compounds[1–4] (amino acids, small peptides, and their derivatives) and their additivity schemes, which may be possible to estimate thermodynamics properties of the completely unfolded polypeptide chain of the proteins. As model compounds of polypeptides,[5–7] the hydrogen bond link with amide is the most important secondary structure in proteins, so we choose amides as the studied objects.

Lilley et al. reported the enthalpic interaction coefficients of some acylamides including acetamide and DMF in pure water.[8] However, biological fluids of living organisms contain a specified quantity of ions, especially sodium, potassium, and chloride ions, which are indispensable for the metabolic processes of a living organism to proceed.[9] Therefore, studies on the interactions between acylamides in aqueous sodium chloride solutions would be helpful to understand the stabilizing mechanism of proteins in the biological systems. However, recent research has focused on the dissolution or mixing enthalpies between various acylamides and electrolytes.[10,11] A survey of the literature indicates a lack of experimental data of the enthalpies of the dilution of acylamides in aqueous electrolyte solutions.

Isothermal microcalorimetry has become a very effective technique that can measure weak interaction of biochemical species in solution.[12–15] Thus, the present work reports measurements of the enthalpies of dilution of acetamide and DMF in aqueous sodium chloride solutions using flow microcalorimetry. The results are interpreted in terms of solute−solute interactions and solvent effects.

Experimental Section

Reagents. Acetamide was purchased from Aldrich, and the purity is better than 99 %. It was 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 molecular sieves of 0.4 nm 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. 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) $\text{mol}\cdot\text{kg}^{-1}$. The molality ranges of aqueous acetamide and DMF were all (0.10 to 0.40) $\text{mol}\cdot\text{kg}^{-1}$. All the solutions were degassed with ultrasonic waves and used within 12 h of preparation.

Calorimetric Procedure. The enthalpies of dilution were determined with a 2277-204 Measuring Cylinder and a Thermometric 2277 Thermal Activity Monitor (Thermometric, Sweden) at 298.15 K. Details of this apparatus, associated equipment, and the experimental procedure have been reported elsewhere.[16–19] The solutions of acylamides and their solvents 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 details of the thermodynamic procedures have been described elsewhere.[20,21]

The enthalpies of dilution $\Delta_{\text{dil}}H_{\text{m}}$ were calculated from the equation[22]

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

in which P is the dilution thermal power; m_{i} and M are the initial molality and the molar mass of one of the acylamides, respectively;

---

* Corresponding author. E-mail: liumin_panpan@163.com. Fax: +86-635-8239121.
[†] College of Chemistry and Chemical Engineering.
[‡] College of Life Science and Bioengineering.

10.1021/je8000393 CCC: $40.75

Table 1. Molar Enthalpies of Dilution $\Delta_{dil}H_m$ of Acetamide in Water and Aqueous Sodium Chloride Solutions at 298.15 K[a]

$\frac{m_i}{mol\cdot kg^{-1}}$	$\frac{m_f}{mol\cdot kg^{-1}}$	$\frac{\Delta_{dil}H_m}{J\cdot mol^{-1}}$	$\frac{\delta^*}{J\cdot mol^{-1}}$	$\frac{m_i}{mol\cdot kg^{-1}}$	$\frac{m_f}{mol\cdot kg^{-1}}$	$\frac{\Delta_{dil,exp}H_m}{J\cdot mol^{-1}}$	$\frac{\delta^*}{J\cdot mol^{-1}}$
			$m(NaCl) = 0.0000$ mol·kg^{-1}				
0.1000	0.0507	−3.52	0.01	0.2800	0.1416	−4.47	0.02
0.1500	0.0760	−3.71	0.01	0.3000	0.1517	−4.63	0.01
0.1800	0.0912	−3.90	−0.04	0.3200	0.1617	−4.83	−0.03
0.2000	0.1013	−3.95	0.02	0.3500	0.1768	−5.07	−0.01
0.2200	0.1114	−4.07	0.01	0.3800	0.1919	−5.33	0.01
0.2500	0.1265	−4.26	0.02	0.4000	0.2019	−5.53	0.01
			$m(NaCl) = 0.1000$ mol·kg^{-1}				
0.1000	0.0505	−6.28	−0.01	0.2800	0.1407	−5.28	0.02
0.1500	0.0756	−5.92	0.02	0.3000	0.1506	−5.35	0.00
0.1800	0.0907	−5.70	0.01	0.3200	0.1606	−5.45	0.01
0.2000	0.1007	−5.58	−0.01	0.3500	0.1755	−5.80	−0.02
0.2200	0.1107	−5.48	−0.03	0.3800	0.1906	−6.28	0.01
0.2500	0.1257	−5.32	0.01	0.4000	0.2004	−6.75	0.02
			$m(NaCl) = 0.2000$ mol·kg^{-1}				
0.1000	0.0506	−8.90	−0.02	0.2800	0.1412	−5.24	0.07
0.1500	0.0759	−7.90	−0.02	0.3000	0.1512	−5.10	0.06
0.1800	0.0910	−7.20	−0.02	0.3200	0.1611	−5.15	−0.02
0.2000	0.1011	−6.73	−0.01	0.3500	0.1758	−5.40	−0.05
0.2200	0.1111	−6.28	0.01	0.3800	0.1908	−5.95	0.01
0.2500	0.1261	−5.75	−0.03	0.4000	0.2007	−6.58	0.02
			$m(NaCl) = 0.3000$ mol·kg^{-1}				
0.1000	0.0520	−7.38	−0.01	0.2800	0.1449	−5.33	−0.01
0.1500	0.0779	−6.85	0.00	0.3000	0.1552	−5.25	0.00
0.1800	0.0934	−6.45	−0.01	0.3200	0.1654	−5.30	−0.02
0.2000	0.1037	−6.18	−0.02	0.3500	0.1808	−5.52	0.01
0.2200	0.1140	−5.88	0.01	0.3800	0.1961	−6.08	−0.01
0.2500	0.1295	−5.58	−0.03	0.4000	0.2063	−6.62	0.00
			$m(NaCl) = 0.4000$ mol·kg^{-1}				
0.1000	0.0518	−6.92	−0.02	0.2800	0.1450	−4.72	0.00
0.1500	0.0777	−6.23	0.01	0.3000	0.1554	−4.75	0.05
0.1800	0.0932	−5.75	0.00	0.3200	0.1658	−5.02	0.01
0.2000	0.1036	−5.45	−0.02	0.3500	0.1812	−5.72	−0.02
0.2200	0.1140	−5.17	−0.02	0.3800	0.1967	−6.85	−0.02
0.2500	0.1295	−4.82	0.01	0.4000	0.2069	−7.84	0.04
			$m(NaCl) = 0.5000$ mol·kg^{-1}				
0.1000	0.0517	−4.18	0.00	0.2800	0.1439	−5.65	0.00
0.1500	0.0774	−4.78	0.00	0.3000	0.1541	−5.75	0.03
0.1800	0.0928	−5.07	−0.03	0.3200	0.1643	−5.95	−0.02
0.2000	0.1030	−5.18	0.00	0.3500	0.1796	−6.23	−0.03
0.2200	0.1133	−5.30	0.00	0.3800	0.1948	−6.54	0.01
0.2500	0.1286	−5.48	0.00	0.4000	0.2049	−6.83	0.00
			$m(NaCl) = 0.6000$ mol·kg^{-1}				
0.1000	0.0519	0.15	0	0.2800	0.1450	−2.18	0.02
0.1500	0.0778	−0.77	0	0.3000	0.1553	−2.35	0.01
0.1800	0.0933	−1.22	−0.02	0.3200	0.1656	−2.55	−0.04
0.2000	0.1037	−1.44	0.01	0.3500	0.1810	−2.72	0.02
0.2200	0.1140	−1.68	−0.01	0.3800	0.1965	−2.98	0.01
0.2500	0.1295	−1.92	0.03	0.4000	0.2068	−3.18	−0.01

[a] $\delta = \Delta_{dil}H_m - \Delta_{dil}H_m(calcd)$, where $\Delta_{dil}H_m(calcd)$ was calculated from eq 4 with coefficients for this equation.

and f_2 is the flow rate of acetamide or DMF solutions. The uncertainty of $\Delta_{dil}H_m$ calculated according to eq 1 was estimated to be within ± 0.01 J·mol^{-1} based on the uncertainties of the measured variables (uncertainties of P, m_i, and f_2 are ± 0.2 μW, ± 0.0001 mol·kg^{-1}, and ± 0.002 mg·s^{-1}, respectively).

The final molality m_f, which is a necessary parameter in data processing, can be calculated from the equation

$$m_f = m_i f_2 / [f_1(1 + m_i M) + f_2] \qquad (2)$$

where f_1 is the flow rate of diluents (water or aqueous sodium chloride solutions).

Results and Discussion

Information about the interaction mechanism can be inferred from the pairwise interaction coefficients of the virial expansion of an excess thermodynamic property. According to the McMillan−Mayer theory,[23–25] thermodynamic properties of multicomponent solutions can be expressed using a viral expansion in molality that relates the nonideal contributions of any total thermodynamic function to a series of interaction parameters. If aqueous sodium chloride solution is regarded as the "solvent", the excess enthalpy per kilogram of solvent (H^E) of a solution containing either acetamide or DMF at molality m is given by

$$H^E = h_2 m^2 + h_3 m^3 + h_4 m^4 + ... \qquad (3)$$

where h_2, h_3, h_4, etc. are the enthalpic coefficients representing pairwise, triplet, quart, etc., higher-order interactions between solvated solute species. The molar enthalpy change ($\Delta_{dil}H_m$)

Table 2. Molar Enthalpies of Dilution $\Delta_{dil}H_m$ of *N,N*-Dimethylformamide in Water and Aqueous Sodium Chloride Solutions at 298.15 K

m_i / mol·kg^{-1}	m_f / mol·kg^{-1}	$\Delta_{dil}H_m$ / J·mol^{-1}	δ / J·mol^{-1}	m_i / mol·kg^{-1}	m_f / mol·kg^{-1}	$\Delta_{dil,exp}H_m$ / J·mol^{-1}	$\Delta_{dil,exp}H_m$ / J·mol^{-1}
m(NaCl) = 0.0000 mol·kg^{-1}							
0.1000	0.0502	−30.38	0.03	0.2800	0.1392	−96.14	0.04
0.1500	0.0756	−48.35	−0.02	0.3000	0.1493	−103.25	0.03
0.1800	0.0893	−60.15	−0.03	0.3200	0.1598	−110.04	0.01
0.2000	0.0994	−67.33	−0.01	0.3500	0.1742	−121.18	−0.04
0.2200	0.1098	−74.20	0.01	0.3800	0.1888	−132.10	−0.12
0.2500	0.1247	−85.03	0.04	0.4000	0.1993	−138.59	0.11
m(NaCl) = 0.1000 mol·kg^{-1}							
0.1000	0.0494	−39.07	0.04	0.2800	0.1390	−101.48	0.00
0.1500	0.0748	−56.97	−0.07	0.3000	0.1501	−107.10	−0.03
0.1800	0.0895	−67.68	0.00	0.3200	0.1578	−115.13	−0.01
0.2000	0.0996	−74.41	0.01	0.3500	0.1736	−123.96	−0.01
0.2200	0.1085	−82.03	0.03	0.3800	0.1879	−133.75	0.04
0.2500	0.1219	−93.23	0.04	0.4000	0.1972	−140.37	−0.01
m(NaCl) = 0.2000 mol·kg^{-1}							
0.1000	0.0498	−26.70	0.00	0.2800	0.1391	−92.52	−0.02
0.1500	0.0744	−45.80	−0.03	0.3000	0.1481	−100.33	−0.02
0.1800	0.0894	−56.73	0.01	0.3200	0.1579	−107.48	−0.02
0.2000	0.0999	−63.50	0.01	0.3500	0.1720	−118.73	0.00
0.2200	0.1096	−70.91	0.01	0.3800	0.1877	−128.88	0.05
0.2500	0.1242	−81.85	0.00	0.4000	0.1973	−136.48	−0.04
m(NaCl) = 0.3000 mol·kg^{-1}							
0.1000	0.0497	−29.20	0.08	0.2800	0.1386	−96.38	−0.01
0.1500	0.0745	−48.91	−0.07	0.3000	0.1485	−103.56	−0.03
0.1800	0.0892	−59.87	0.09	0.3200	0.1581	−110.97	−0.03
0.2000	0.0990	−67.36	0.08	0.3500	0.1728	−122.02	−0.03
0.2200	0.1089	−74.64	0.06	0.3800	0.1871	−133.57	−0.01
0.2500	0.1237	−85.61	0.02	0.4000	0.1973	−140.78	0.03
m(NaCl) = 0.4000 mol·kg^{-1}							
0.1000	0.0495	−33.54	−0.01	0.2800	0.1381	−99.86	0.01
0.1500	0.0742	−53.08	0.02	0.3000	0.1480	−106.68	0.01
0.1800	0.0889	−64.41	−0.01	0.3200	0.1576	−113.70	0.01
0.2000	0.0986	−71.81	−0.02	0.3500	0.1722	−124.09	−0.01
0.2200	0.1085	−78.93	−0.02	0.3800	0.1864	−134.91	−0.04
0.2500	0.1232	−89.55	−0.01	0.4000	0.1966	−141.51	0.02
m(NaCl) = 0.5000 mol·kg^{-1}							
0.1000	0.0501	−31.08	−0.01	0.2800	0.1390	−97.83	−97.82
0.1500	0.0745	−51.46	0.04	0.3000	0.1484	−104.91	0.00
0.1800	0.0896	−62.64	0.01	0.3200	0.1590	−110.90	0.00
0.2000	0.0993	−70.15	0.00	0.3500	0.1728	−121.62	0.03
0.2200	0.1092	−77.30	0.00	0.3800	0.1876	−131.49	0.06
0.2500	0.1242	−87.63	−0.02	0.4000	0.1978	−137.90	−0.05
m(NaCl) = 0.6000 mol·kg^{-1}							
0.1000	0.0496	−29.96	−0.06	0.2800	0.1379	−97.76	−0.02
0.1500	0.0736	−50.92	0.02	0.3000	0.1474	−104.69	0.00
0.1800	0.0886	−62.53	−0.03	0.3200	0.1572	−111.20	0.02
0.2000	0.0987	−69.76	−0.05	0.3500	0.1719	−120.95	0.06
0.2200	0.1084	−77.10	−0.05	0.3800	0.1865	−130.61	0.10
0.2500	0.1235	−87.30	−0.04	0.4000	0.1962	−137.29	−0.10

on diluting a solution of nonelectrolytic solute from an initial molality m_i to a final molality m_f can be written as

$$\Delta_{dil}H_m = H_m^E(m_f) - H_m^E(m_i) = h_2(m_f - m_i) + h_3(m_f^2 - m_i^2) + h_4(m_f^3 - m_i^3) + ... \quad (4)$$

in which $H_m^E(m_i)$ and $H_m^E(m_f)$ are the molar excess enthalpies of the solute in the solutions before and after dilution.

Tables 1 and 2 give the experimental values of dilution enthalpies ($\Delta_{dil}H_m$), which were fitted to eq 4 by a least-squares procedure with an intercept of 0, together with the corresponding calculated values ($\Delta_{dil}H_{m,calcd}$) along with the initial and final molalities (m_i and m_f) of the acylamides in various aqueous sodium chloride solutions.

Tables 3 and 4 list the coefficients of eq 4 that were obtained from least-squares analysis of the above results. Since it is difficult to interpret the higher order h_n coefficients,[26–28] only the enthalpic pairwise coefficients h_2 are discussed here. The h_2 values of acetamide and DMF in pure water are (1.24 and 740.20) J·kg·mol^{-2}, respectively, which are in good agreement with those obtained by Lilley et al. (acetamide: 1.1 J·kg·mol^{-2};

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

m(NaCl) / mol·kg^{-1}	h_2 / J·kg·mol^{-2}	h_3 / J·kg^2·mol^{-3}	h_4 / J·kg^3·mol^{-4}	SD / J·mol^{-1}
0.0000	1.2 ± 3.4[a]	17.7 ± 9.6[a]	−2.7 ± 10.8[a]	0.02
0.1000	15.4 ± 2.4[a]	−126.6 ± 6.7[a]	225.4 ± 7.6[a]	0.01
0.2000	27.3 ± 5.8[a]	−282.9 ± 16.4[a]	461.5 ± 18.4[a]	0.04
0.3000	40.8 ± 3.4[a]	−249.9 ± 9.4[a]	383.1 ± 10.5[a]	0.02
0.4000	52.2 ± 4.3[a]	−334.0 ± 12.1[a]	554.6 ± 13.5[a]	0.03
0.5000	64.9 ± 3.4[a]	−142.5 ± 9.5[a]	163.3 ± 10.7[a]	0.02
0.6000	77.5 ± 4.1[a]	−129.4 ± 11.6[a]	116.1 ± 12.9[a]	0.03

[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 in Water and Aqueous Sodium Chloride Solutions at 298.15 K

m(NaCl) mol·kg^{-1}	h_2 J·kg·mol^{-2}	h_3 J·kg^2·mol^{-3}	h_4 J·kg^3·mol^{-4}	SD J·mol^{-1}
0.0000	740.2 ± 9.7	−31.4 ± 27.7	2.7 ± 31.5	0.06
0.1000	811.2 ± 5.70	−259.3 ± 16.2	131.3 ± 18.5	0.04
0.2000	848.2 ± 4. 8	−336.4 ± 13.6	334.6 ± 15.4	0.03
0.3000	901.9 ± 17.4	−464.5 ± 49.6	484.5 ± 56.3	0.11
0.4000	942.0 ± 3.2	−558.8 ± 9.2	496.9 ± 10.4	0.02
0.5000	997.6 ± 5.0	−655.5 ± 14.2	527.9 ± 16.1	0.03
0.6000	1034.4 ± 14.8	−710.7 ± 42.2	532.4 ± 48.0	0.10

DMF: 737.3 J·kg·mol^{-2}).[8] Figure 1 shows the variations of h_2 coefficients for both acetamide and DMF with increasing molalities of aqueous sodium chloride solutions. There is an approximate linear relation between the pairwise coefficients h_2 and the molality of sodium chloride aqueous solution in which acetamide or DMF is diluted. The relations were obtained with the method of least-squares as follows

$$h_2/\mathrm{J\cdot kg\cdot mol^{-2}} = (2.1 \pm 0.5^*) + (125.9 \pm 1.3^*)m(\mathrm{NaCl}) \qquad (\text{acetamide} + \mathrm{NaCl} + \mathrm{H_2O} \quad \mathrm{SD}^{**} = 0.7\ \mathrm{J\cdot kg\cdot mol^{-2}}) \quad (5)$$

$$h_2/\mathrm{J\cdot kg\cdot mol^{-2}} = (751.9 \pm 5.8^*) + (481.\ 9 \pm 16.1^*)m(\mathrm{NaCl}) \qquad (\mathrm{DMF} + \mathrm{NaCl} + \mathrm{H_2O} \quad \mathrm{SD}^{**} = 8.5\ \mathrm{J\cdot kg\cdot mol^{-2}}) \quad (6)$$

(*The values are the standard errors given by the computer during the fit linear analysis; ** standard derivation.)

From Figure 1, it can be seen that the values of pairwise enthalpic coefficients h_2 for the two acylamides are positive for all of the aqueous salt solutions investigated, and the value of h_2 for acetamide is less than that for DMF in aqueous solutions. This could be attributed to the cooperative effects of partial dehydration of the hydration shell (positive contribution to h_2), solvent reorganization in the neighborhood of the hydrophobic groups (negative contribution to h_2[29]), and direct interaction between the acylamide molecules.

On the other hand, the values of h_2 for both acetamide and DMF increase positively with elevation of molality of sodium chloride solutions, which are the result of the influence of salt on the interaction of acylamide molecules. The direct interaction between two solute molecules provokes partial dehydration of dissolved molecules or ions of the electrolyte near them, which is an endothermic process.

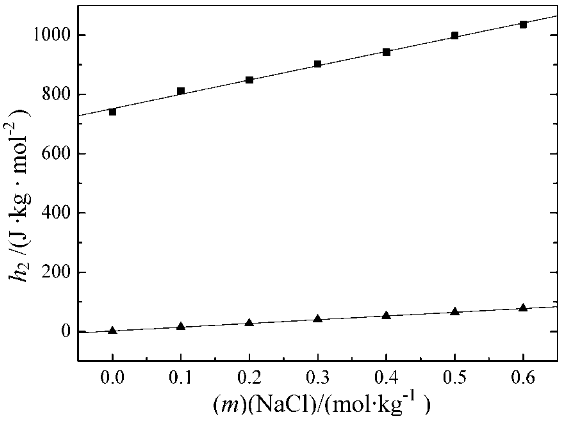

Figure 1. Enthalpic pairwise interaction coefficients h_2 of acetamide and *N,N*-dimethylformamide versus the molality m of sodium chloride in aqueous solutions at 298.15 K: ■, *N,N*-dimethylformamide; ▲, acetamide.

Another endothermic effect resulted from the removal of a number of water molecules from the acetamide or DMF hydration shells. Therefore, the partial dehydration of solutes gives positive contribution to h_2. The larger the molality of sodium chloride is, the more difficult it is for the water molecules to depart from the solute ion or acylamide molecule and the more positive the contribution from desolvation to h_2 will be. Consequently, pairwise enthalpic interaction coefficients h_2 of acetamide and DMF become more positive with the elevated molality of sodium chloride.

Additionally, it can be seen from eq 5 and eq 6 that the increasing rate of the h_2 coefficient (dh_2/dm(NaCl)) for DMF (481.9 J·kg^2·mol^{-3}) is larger than that for acetamide (125.9 J·kg^2·mol^{-3}). This is mainly ascribed to the difference in the structure of the two acylamide molecules. When two molecules of DMF approach each other, the degree of disruption of the hydration shells is higher than that of acetamide due to the presence of two methyl groups. A larger value of dh_2/dm(NaCl) for DMF means that it is more difficult to destroy its hydration shells in higher molality of the salt than that in lower molality of the salt.

Conclusion

Enthalpies of dilution of acetamide and DMF in pure water and aqueous sodium chloride solutions at different salt molalities were measured by isothermal flow-mixing microcalorimetry at 298.15 K. Experimental enthalpies of dilution were correlated with a virial expansion equation, to give the enthalpic interaction coefficients, h_2, h_3, and h_4. The different structure of acylamide and the salt molality make a contribution to the different values of h_2.

Literature Cited

(1) Hackel, M.; Hinz, H. J.; Hedwig, G. R. The partial molar volumes of some tetra- and entapeptides in aqueous solution: a test of amino acid side-chain group additivity for unfolded proteins. *Phys. Chem. Chem. Phys.* **2000**, *2*, 4843–4849.

(2) Liu, M.; Sun, D. Z.; Lin, R. S.; Qu, X. K.; Wang, X. Studies on the enthalpic interactions of formamide and N,N-dimethylformamide with myo-inositol in aqueous sodium chloride solutions at 298.15 K. *J. Chem. Eng. Data* **2007**, *52*, 783–788.

(3) Palecz, B. Enthalpic Pair interaction coefficient between zwitterions of L-α-amino acids and urea molecule as a hydrophobicity parameter of amino acid side chains. *J. Am. Chem. Soc.* **2005**, *127*, 17768–17771.

(4) Soto, A.; Arce, A.; Khoshkbarchi, M. K. Effect of cation and anion of an electrolyte on apparent molar volume, isentropic compressibility and refractive index of glycine in aqueous solutions. *Biophys. Chem.* **1999**, *76*, 73–82.

(5) Lilley, T. H. The interplay between solute solvation and solute-solute interactions in solutions containing amino acids, peptides and related species. *Pure Appl. Chem.* **1993**, *65*, 2551–2560.

(6) Lilley, T. H. Interactions in solution: The interplay between solute solvation and solute-solute interactions. *Pure Appl. Chem.* **1994**, *66*, 429–434.

(7) Klotz, I. M.; Russo, S. F.; Hanlon, S.; Stake, M. A. Protonation of amides in a helix-breaking solvent. *J. Am. Chem. Soc.* **1964**, *86*, 4774–4778.

(8) Cheek, P. J.; Lilley, T. H. The enthalpies of interaction of some amides with urea in water at 25 °C. *J. Chem. Soc., Faraday Trans. I* **1988**, *84*, 1927–1940.

(9) Von Hippel, P. H.; Schleich, T. Ion effects on the solution structure of biological macromolecules. *Acc. Chem. Res.* **1969**, *2*, 257–265.

(10) Lu, Y.; Chen, Y. B.; Bai, T. C.; Lu, J. S. The enthalpic interaction parameters of acetamide with sodium halides in water at 198.15 K. *Thermochim. Acta* **1995**, *253*, 85–91.

(11) Lu, Y.; Cheng, Q. T.; Chen, Y. B.; Bai, T. C.; Lu, J. S. The enthalpic interaction parameters of acetamide with some alkali-metal chlorides in water at 198.15 K. *Thermochim. Acta* **1999**, *334*, 29–32.

(12) Castronuovo, G.; Elia, V.; Niccoli, M.; Velleca, F. Calorimetric studies of hydrophobic interactions of alkanols in concentrated aqueous solutions of glucose: Implications for the mechanism of protein stabilization by sugars. *Thermochim. Acta* **2002**, *389*, 1–9.

(13) Iloukhani, H.; Parsa, J. B.; Saboury, A. A. Excess molar enthalpies of binary containing *N, N*-dimethylformamide + six 2-alkonols (C_3-C_8) at 300.15 K. *J. Chem. Eng. Data* **2000**, *45*, 1016–1018.

(14) Muμnoz, E.; Yanes, C.; Maestre, A. Mixing enthalpies of alkylureas with electrolytes in water at 298.15 K. *J. Chem. Eng. Data* **2001**, *46*, 423–427.

(15) Wei, X. M.; Hu, X. G.; Shao, S.; Lin, R. S.; Li, S. Q. Enthalpic interactions of amino acids in aqueous glucose solutions at 298.15 K. *Thermochim. Acta* **2000**, *362*, 1–6.

(16) Liu, M.; Lin, R. S.; Sun, D. Z. Enthalpies of dilution of D-p-hydroxyphenylglycine in buffer solutions at different pH. *J. Solution Chem.* **2006**, *35*, 1007–1015.

(17) Yu, L.; Zhu, Y.; Hu, X. G.; Pang, X. H. Enthalpies of dilution of N, N-dimethylformamide with polyalcohols in aqueous solutions at 298.15 K. *J. Chem. Eng. Data* **2006**, *51*, 1110–1114.

(18) Shao, S.; Hu, X. G.; Lin, R. S. Enthalpic interactions of L-alanine and L-serine in aqueous urea solutions. *Thermochim. Acta* **2000**, *360*, 93–100.

(19) Yu, L.; Lin, R. S.; Hu, X. G.; Xu, G. Y. Enthalpic interaction of amino acids with ethanol in aqueous solutions at 25. *J. Solution Chem.* **2003**, *32*, 273–281.

(20) Sun, D. Z.; Zheng, W. Q.; Qu, X. K.; Li, L. Enthalpies of dilution for myo-inosotol in aqueous alkali salt and alkaline earth metal salt solutions. *J. Chem. Eng. Data* **2007**, *52*, 898–901.

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

(22) Li, L.; Zhu, L. Y.; Qiu, X. M.; Sun, D. Z.; Di, Y. Y. Concentration effect of sodium chloride on enthalpic interaction coefficients of D-mannitol and D-sorbitol in aqueous solution. *J. Therm. Anal. Calorim.* **2007**, *89*, 295–301.

(23) McMillan, W. G.; Mayer, J. E. The statistical thermodynamics of multicomponent systems. *J. Chem. Phys.* **1945**, *13*, 276–305.

(24) Lilley, T. H. Thermodynamic relationships of 1:1 electrolytes. *Faraday Soc.* **1968**, *64*, 2947–2950.

(25) Franks, F.; Pedley, M.; Reid, D. S. Solute interactions in dilute aqueous solutions. Part 1.—Microcalorimetric study of the hydrophobic interaction. *J. Chem. Soc., Faraday Trans.I* **1976**, *72*, 359–367.

(26) Wang, X.; Zhang, R.; Xu, L.; Lin, R. S. The dilution enthalpies of formamide in mixtures of water and propanol at 298.15 K. *J. Mol. Liq.* **2007**, *133*, 111–115.

(27) Yu, L.; Hu, X. G.; Lin, R. S.; Zhang, H. L.; Xu, G. Y. 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.

(28) Song, M. Z.; Zhu, L. Y.; Wei, X. L.; Wang, S. B.; Sun, D. Z. Enthalpic interaction of D-sorbitol and D-Mannitol in water and aqueous sodium halide solutions at 313.15K. *J. Chem. Eng. Data* **2005**, *50*, 769–773.

(29) Wang, X.; Xu, L.; Lin, R. S.; Sun, D. Z. Enthalpies of dilution of glycine, L-alanine and L-serine in aqueous potassium chloride solutions. *Thermochim. Acta* **2005**, *425*, 31–37.

Received for review January 14, 2008. Accepted April 30, 2008. The authors are grateful to the Natural Science Foundation of Shandong Province of China (No. 2004zx15) for support.

JE8000393