J. Chem. Eng. Data 1993, 38, 83-87

Thermodynamics of Aqueous Guanidinium Hydrochloride Solutions in the Temperature Range from 283.15 to 313.15 K

George I. Makhatadze,*,† Javier Fernandez,‡ Ernesto Freire,† Terence H. Lilley,‡ and Peter L. Privalov†

Department of Biology and Biocalorimetric Center, The Johns Hopkins University, Baltimore, Maryland 21218, and Biothermodynamics Laboratory, Department of Chemistry, The University, Sheffield S3 7HF, U.K.

The densities, apparent molar volumes, apparent molar heat capacities, enthalpies of dilution, and activity coefficients of aqueous guanidinium hydrochloride solutions over a wide molality range and over the temperature range 298.15–313.15 K are reported.

Introduction

Although aqueous solutions of the electrolyte guanidinium hydrochloride (GdmCl) are widely used in protein structure stability studies, there are few data for these solutions. Some information on osmotic and activity coefficients (*1–3*) and densities (*4, 5*) is available on solutions at 298.15 K. These are insufficient for the quantitative evaluation of thermodynamic information on the denaturing action of GdmCl at different temperatures on native protein structures (*6*).

In order to determine the temperature dependence of the apparent molar volume and of the activity coefficients of GdmCl in aqueous solution, we have measured the densities of aqueous GdmCl solutions at 283.15, 290.15, 298.15, 306.15, and 313.15 K, the enthalpies of dilution at 298.15 K, and the apparent molar heat capacities in the temperature range 283.15–313.15 K.

Experimental Section

The commercial product of GdmCl (Aldrich, catalog no. 17,725-3) was recrystallized from water and dried for several days over P_2O_5. Its purity was checked according to the procedures described by Nozaki (*7*). Aqueous solutions of GdmCl were prepared by mass using degassed MONO-Q water.

Density measurements were performed using a capillary vibrational densimeter DMA-60/602 (Anton Paar, Austria). The densitometric cell was thermostated by a refrigerated bath equipped with a digital controller (RTE-210, NESLAB Instruments) which provides a temperature stability of ±0.01 °C. The accuracy of the density measurements was 3×10^{-6} g·cm^{-3}. Densities were measured at five different temperatures: 283.15, 290.15, 298.15, 306.15, and 313.15 K. The procedures used for the density measurements and the calculation of the apparent molar volumes were the same as those described previously (*8, 9*).

The apparent molar heat capacity, $\Phi C_{p,2}(T)$, of the solute at temperature T was determined by measuring the heat capacity difference between the solution and solvent by a precise scanning microcalorimeter DASM-4M (NPO "Biopribor", Russia) with a fixed operational volume of calorimetric cells, according to the equation

$$\Phi C_{p,2}(T) = C_{p,1}{*}(T)\frac{\Phi V_2(T)}{V_1{*}(T)} - \Delta C_p(T)\frac{M_2}{m_f(T)} \qquad (1)$$

In this, $m_f(T)$ is the mass of the solute in the calorimetric cell at a given temperature, and all other symbols are defined in the Glossary. The molar heat capacity and the molar volume of the solvent were taken from ref 10. The precision of the measurements of the heat capacity difference is 1.2×10^{-4} J·K^{-1}. More details about the procedure used for the heat capacity measurements with this calorimeter, and its application to the solution chemistry of low molecular weight compounds, can be found elsewhere (*8, 11*).

Table I. Densities, ρ, of Aqueous Solutions of GdmCl at Different Molalities, m

m/ (mol·kg^{-1})	ρ/(g·cm^{-3}) 283.15 K	290.15 K	298.15 K	306.15 K	313.15 K
0.1895		1.003 748	1.001 890	0.999 490	
0.5039		1.011 671	1.009 554	1.006 961	
0.7894		1.018 413	1.016 184	1.013 483	
0.9875	1.024 576		1.020 606		1.015 119
1.2461		1.028 628	1.026 191	1.023 319	
2.3104	1.052 088		1.046 992		1.040 917
2.6833		1.056 540	1.053 577	1.050 336	
3.8984	1.078 806		1.072 802		1.066 194
4.1487		1.079 441	1.076 420	1.073 009	
5.6736	1.102 794		1.096 095		1.088 938
6.4396		1.108 605	1.104 763	1.101 076	
7.7557	1.125 334		1.118 008		1.110 783
8.5600		1.129 295	1.125 291	1.121 194	
10.6897	1.149 823		1.141 970		1.134 383
11.1511		1.149 510	1.145 202	1.141 211	
14.1282	1.171 403		1.163 117		1.155 247
15.0559		1.172 357	1.167 913	1.163 656	

Table II. Coefficients of Equation 2 at Different Temperatures

T/K	A_ρ	B_ρ
283.15	0.0207 ± 0.0006	0.2866 ± 0.0003
290.15	0.0301 ± 0.0009	0.2769 ± 0.0005
298.15	0.0330 ± 0.0001	0.2710 ± 0.0003
306.15	0.0358 ± 0.0007	0.2668 ± 0.0003
313.15	0.0378 ± 0.0007	0.2644 ± 0.0004

Calorimetric measurements on the enthalpies of dilution of GdmCl were performed using two types of microcalorimeters: (a) A Microcal Omega isothermal titration microcalorimeter. The principles of operation of this calorimeter have been described elsewhere (*12*). (b) A modified LKB microcalorimeter, experimental procedures for which have been described previously (*13*). In view of the high viscosity of the more concentrated solutions used, checks on the efficiency of mixing were made by varying the flow rates.

Data Treatment and Results

(a) *Density and Apparent Molar Volume.* The densities of aqueous solutions of GdmCl at different molalities and

---

† The Johns Hopkins University.
‡ The University.

0021-9568/93/1738-0083$04.00/0 © 1993 American Chemical Society

Table III. Apparent Molar Volumes, ΦV_2, of GdmCl at Different Molalities, *m*, and Mass Fractions, *w*

		$\Phi V_2/(\mathrm{cm^3 \cdot mol^{-1}})$						
$m/(\mathrm{mol \cdot kg^{-1}})$	w	283.15 K	288.15 K	293.15 K	298.15 K	303.15 K	308.15 K	313.15 K
1	0.0872	68.81	69.31	69.76	70.16	70.50	70.79	71.01
2	0.1604	69.19	69.65	70.07	70.44	70.75	71.02	71.24
3	0.2228	69.51	69.93	70.32	70.67	70.97	71.23	71.44
4	0.2765	69.77	70.17	70.54	70.86	71.15	71.40	71.60
5	0.3232	70.00	70.38	70.72	71.04	71.31	71.55	71.75
6	0.3643	70.20	70.56	70.89	71.19	71.45	71.68	71.88
7	0.4007	70.37	70.71	71.03	71.32	71.58	71.80	71.99
8	0.4332	70.52	70.85	71.16	71.44	71.69	71.91	72.09
9	0.4623	70.66	70.98	71.27	71.54	71.78	72.00	72.19
10	0.4886	70.78	71.09	71.37	71.64	71.87	72.08	72.27
11	0.5124	70.89	71.19	71.46	71.72	71.95	72.16	72.34
12	0.5341	70.99	71.28	71.55	71.80	72.03	72.23	72.41
13	0.5539	71.08	71.36	71.62	71.87	72.09	72.30	72.47
14	0.5722	71.16	71.44	71.69	71.93	72.15	72.35	72.53
15	0.5890	71.24	71.50	71.76	71.99	72.21	72.41	72.58

Table IV. Apparent Molar Heat Capacities, $\Phi C_{p,2}$, of GdmCl in Aqueous Solution

	$\Phi C_{p,2}/(\mathrm{J \cdot K^{-1} \cdot mol^{-1}})$						
$m/(\mathrm{mol \cdot kg^{-1}})$	283.15 K	288.15 K	293.15 K	298.15 K	303.15 K	308.15 K	313.15 K
0.1762	23	38	50	58	66	70	73
0.4775	35	47	56	65	69	74	76
0.7495	51	61	69	76	80	84	87
1.1891	60	69	76	81	86	89	91
2.6120	80	86	91	95	98	101	103
4.0729	92	97	101	105	107	109	112
6.3889	107	110	113	116	118	120	121
8.4901	113	116	118	120	122	124	126
11.0847	121	123	126	127	129	131	132
14.9903	131	133	135	136	138	139	140

Table V. Temperature Dependencies of the Relative Apparent Molar Heat Capacities, Φ_J, of GdmCl at Different Rounded Molalities, *m*[a]

	$\Phi_J/(\mathrm{J \cdot K^{-1} \cdot mol^{-1}})$						
$m/(\mathrm{mol \cdot kg^{-1}})$	283.15 K	288.15 K	293.15 K	298.15 K	303.15 K	308.15 K	313.15 K
1.0	47	41	36	32	30	29	30
2.0	67	57	50	45	41	40	40
3.0	79	68	60	53	49	47	48
4.0	88	76	66	59	55	53	53
5.0	94	82	72	64	60	57	58
6.0	100	86	76	68	63	61	62
7.0	104	91	80	72	67	65	66
8.0	109	94	83	75	70	68	69
9.0	113	98	86	78	73	71	72
10.0	116	101	90	81	76	74	75
11.0	120	105	93	84	79	77	78
12.0	123	108	96	87	82	79	81
13.0	126	111	99	90	85	82	83
14.0	129	114	102	93	88	85	86

[a] $\sigma = 0.7$.

temperatures are presented in Table I. The values obtained for the densities of GdmCl aqueous solution, at 298.15 K, are in excellent agreement with those reported earlier (*4, 5*).

The dependence of the densities of the aqueous solution of GdmCl on the mass fraction of GdmCl can be described by the equation

$$\rho(T) = \rho^*(T)(1 + B_\rho(T)w + A_\rho(T)w^2) \qquad (2)$$

The values obtained for $A_\rho(T)$ and $B_\rho(T)$ at the temperatures studied are listed in Table II.

The density data allow the calculation of the apparent molar volume of GdmCl in aqueous solution using

$$\Phi V_2 = \frac{M_2}{\rho} - \frac{(\rho - \rho^*)}{m\rho\rho^*} \qquad (3)$$

The calculated values for the apparent molar volumes of GdmCl in aqueous solutions at selected temperatures and at different molalities are presented in Table III. These apparent molar volumes were used in the calculation of the apparent molar heat capacities of GdmCl [see eq 1].

(*b*) ***Apparent Molar Heat Capacity and Relative Apparent Molar Heat Capacity.*** The apparent molar heat capacities determined from the scanning calorimetric experiments are presented in Table IV. These experimental data were fitted to obtain the relative apparent molar heat capacity (*14, 15*):

$$\Phi_J = \Phi C_{p,2} - \Phi C_{p,2}^{\infty} \qquad (4)$$

It was found that the relative apparent molar heat capacity can be represented by the equation

$$\Phi_J^{\mathrm{calcd}}(T)/(\mathrm{J \cdot K^{-1} \cdot mol^{-1}}) = A_J(\rho_0 m)^{1/2} + B_J m + C_J m^{3/2} + D_J m^2 + E_J m^{5/2} \qquad (5)$$

Table VI. Enthalpies of Dilution of GdmCl Solutions at 298.15 K[a]

m_i/(mol·kg^{-1})	m_f/(mol·kg^{-1})	$\Delta_{dil}H_m$/(J·mol^{-1})	m_i/(mol·kg^{-1})	m_f/(mol·kg^{-1})	$\Delta_{dil}H_m$/(J·mol^{-1})
		Short-Chord Dilutions			
1.1722	1.1675	5.99	8.3940	8.3450	14.81
2.5759	2.5648	8.36	10.8789	10.8084	16.87
4.0163	3.9975	10.74	14.8499	14.7381	18.30
6.3048	6.2715	13.34			
		Long-Chord Dilutions			
0.5001	0.3303	185.5	7.8056	1.3803	3289.0
0.5001	0.2466	252.2	9.1270	5.8932	1059.8
0.5001	0.1636	329.6	9.1270	5.0063	1454.8
0.9994	0.6526	384.7	9.1270	3.1192	2258.3
0.9994	0.4845	568.2	9.1270	2.1264	3122.9
0.9994	0.3198	735.2	9.1270	1.5369	3649.8
0.9995	0.6526	381.0	10.5810	6.6810	1126.9
0.9995	0.4844	568.9	10.5810	5.6413	1538.7
0.9995	0.3197	749.7	10.5810	3.8459	2418.3
0.9995	0.6502	366.4	10.5810	2.3501	3328.4
0.9995	0.4818	551.9	10.5810	1.6919	3847.0
0.9995	0.3174	718.1	12.2574	7.5466	1189.6
1.4997	0.9687	502.5	12.2574	6.3302	1588.1
1.4997	0.7154	760.3	12.2574	4.2669	2529.3
1.4997	0.4697	1007.1	12.2574	2.5831	3562.0
1.9998	1.2770	634.7	12.2574	1.8521	4065.6
1.9998	0.9380	955.0	14.1890	8.4919	1255.7
1.9998	0.6127	1276.0	14.1890	7.0721	1712.2
2.4994	1.5781	740.6	14.1890	4.7099	2664.1
2.4994	1.1531	1128.1	14.1890	2.8236	3742.7
2.4994	0.7494	1539.5	14.1890	2.0160	4323.9
3.8267	2.6879	704.3	16.3043	9.4670	1275.0
3.8267	2.3397	956.1	16.3043	7.8260	1783.2
3.8267	1.6850	1486.4	16.3043	5.1488	2807.4
3.8267	0.7951	2297.5	16.3043	3.0571	3838.3
5.6200	3.8375	852.1	16.3043	2.1738	4475.1
5.6200	3.3122	1168.9	19.2042	10.7146	1344.6
5.6200	2.3481	1820.6	19.2042	8.7749	1863.4
5.6200	1.4841	2508.9	19.2042	5.6868	2897.1
5.6200	1.0848	2884.0	19.2042	3.3376	4094.2
7.8056	5.1447	1003.2	19.2042	2.3617	4738.8

[a] More significant figures are being held than the experimental precision warrants, but they were retained to minimize the rounding error in the data fitting routine.

where A_J is the Debye–Hückel limiting law parameter (*16*) and the other parameters are obtained from the fitting routine. Their temperature dependencies were found to be of the forms

$$A_J/(\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-3/2}{\cdot}dm^{3/2}}) = -67.52 + 0.324(T/\mathrm{K}) \quad (6)$$

$$\mathrm{B_J}/(\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-2}{\cdot}kg}) = 5545.15 - 35.426(T/\mathrm{K}) + 0.0565378(T/\mathrm{K})^2 \quad (7)$$

$$C_J/(\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-5/2}{\cdot}kg^{3/2}}) = -3947.9 + 25.3564(T/\mathrm{K}) - 0.040709(T/\mathrm{K})^2 \quad (8)$$

$$D_J/(\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-3}{\cdot}kg^2}) = 1123.73 - 7.2551(T/\mathrm{K}) + 0.0117079(T/\mathrm{K})^2 \quad (9)$$

$$E_J/(\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-7/2}{\cdot}kg^{5/2}}) = -115.39 + 0.748494(T/\mathrm{K}) - 0.0012133(T/\mathrm{K})^2 \quad (10)$$

Values of the relative apparent molar heat capacities of GdmCl in aqueous solution at different temperatures calculated at round molalities are listed in Table V together with the standard deviation σ defined as

$$\sigma^2 = \sum[\Phi_J^{\mathrm{calcd}} - \Phi_J^{\mathrm{exptl}}]^2/(N - n) \quad (11)$$

where N is the number of data points and n is the number of coefficients of fitting.

(c) Enthalpies of Dilution of Aqueous Solution of GdmCl at 298.15 K. The experimental enthalpies of dilution of solutions of GdmCl at different molalities at 298.15 K are presented in Table VI. The results of the "short-chord" dilution experiments performed using the Microcal Omega titration calorimeter are in good agreement with the results of the "long-chord" dilution experiments on the modified LKB microcalorimeter.

These results were analyzed using methods given in refs 14 and 15. The enthalpy of dilution is related to the relative apparent molar enthalpies of the initial and the final solutions by

$$\Delta_{\mathrm{dil}}H_{\mathrm{m}} = \Phi_{\mathrm{L}}(m_f) - \Phi_{\mathrm{L}}(\mathrm{m_i}) \quad (12)$$

The relative apparent molar enthalpies can be expressed as a half-integral power series of molality:

$$\Phi_{\mathrm{L}}(\mathrm{J{\cdot}mol^{-1}}) = A_{\mathrm{L}}(T_0)(\rho^* m)^{1/2} + B_{\mathrm{L}}(T_0)m + C_{\mathrm{L}}(T_0)m^{3/2} + D_{\mathrm{L}}(T_0)m^2 + E_{\mathrm{L}}(T_0)m^{5/2} \quad (13)$$

In this $A_L(T_0)$ is the Debye–Hückel limiting law constant and can be taken, according to refs 17 and 18, as 1945 J·mol^{-1} at T_0 = 298.15 K, and $B_L(T_0)$, $C_L(T_0)$, $D_L(T_0)$, $E_L(T_0)$ are the fitting parameters to the experimental results. The values obtained for these parameters at 298.15 K are $B_L(T_0)$ = −3386.95 J·kg·mol^{-2}, $C_L(T_0)$ = 1252.93 J·kg$^{-3/2}$·mol$^{-5/2}$, $D_L(T_0)$ = −209.260 J·kg^{-2}·mol^{-3}, and $E_L(T_0)$ = 13.611 J·kg$^{-5/2}$·mol$^{-7/2}$. The standard deviation of the fit defined according to eq 11 is 44 J·mol^{-1}.

To obtain the temperature dependence of the Φ_L values, it is necessary to use (*16*)

$$\Phi_{\mathrm{J}} = (\partial\Phi_{\mathrm{L}}/\partial \mathrm{T})_{P,m} \quad (14)$$

This expression was integrated to give $\Phi_L(T)$ as a power series

Table VII. Temperature Dependencies of the Relative Partial Molar Enthalpies, $\Delta H_{m,2}$, of GdmCl at Different Rounded Molalities, *m*

	$\Delta H_{m,2}$/(J·mol^{-1})						
m/(mol·kg^{-1})	283.15 K	288.15 K	293.15 K	298.15 K	303.15 K	308.15 K	313.15 K
1.0	−2201	−1866	−1577	−1322	−1092	−875	−661
2.0	−4003	−3556	−3169	−2829	−2522	−2233	−1949
3.0	−5268	−4762	−4321	−3931	−3575	−3240	−2910
4.0	−6204	−5659	−5183	−4758	−4369	−4000	−3634
5.0	−6927	−6353	−5848	−5397	−4981	−4585	−4191
6.0	−7511	−6909	−6379	−5905	−5466	−5047	−4627
7.0	−8001	−7371	−6817	−6320	−5860	−5418	−4975
8.0	−8427	−7768	−7189	−6668	−6186	−5723	−5257
9.0	−8808	−8120	−7514	−6968	−6462	−5975	−5487
10.0	−9155	−8439	−7804	−7231	−6698	−6186	−5674
11.0	−9473	−8731	−8067	−7464	−6902	−6361	−5823
12.0	−9764	−8999	−8307	−7672	−7076	−6503	−5937
13.0	−10024	−9245	−8526	−7855	−7221	−6612	−6015
14.0	−10250	−9465	−8721	−8014	−7337	−6686	−6055

Table VIII. Molal Activity Coefficients, $\gamma_{\pm,m}$, of GdmCl in Aqueous Solutions at Different Temperatures and Rounded Molalities, *m*

	$\gamma_{\pm,m}$						
$m/(\text{mol·kg}^{-1})$	283.15 K	288.15 K	293.15 K	298.15 K	303.15 K	308.15 K	313.15 K
1.0	0.512	0.516	0.519	0.522	0.524	0.525	0.527
2.0	0.411	0.417	0.422	0.427	0.430	0.434	0.437
3.0	0.349	0.355	0.361	0.366	0.371	0.375	0.378
4.0	0.307	0.314	0.320	0.326	0.331	0.335	0.339
5.0	0.279	0.286	0.293	0.298	0.304	0.308	0.313
6.0	0.259	0.266	0.273	0.279	0.284	0.289	0.293
7.0	0.244	0.251	0.258	0.263	0.269	0.274	0.278
8.0	0.232	0.239	0.246	0.251	0.257	0.262	0.266
9.0	0.222	0.229	0.235	0.241	0.247	0.252	0.256
10.0	0.213	0.220	0.227	0.232	0.238	0.243	0.247
11.0	0.205	0.212	0.218	0.224	0.230	0.235	0.239
12.0	0.198	0.205	0.211	0.217	0.222	0.227	0.232
13.0	0.191	0.198	0.204	0.210	0.215	0.220	0.224
14.0	0.184	0.191	0.197	0.203	0.208	0.213	0.217

Table IX. Molar Activity Coefficients, $\gamma_{\pm,c}$, of GdmCl in Aqueous Solutions at Different Temperatures and Rounded Molarities, *c*[a]

	$\gamma_{\pm,c}$						
$c/(\text{mol·dm}^{-3})$	283.15 K	288.15 K	293.15 K	298.15 K	303.15 K	308.15 K	313.15 K
1.0	0.541	0.546	0.550	0.552	0.556	0.558	0.559
2.0	0.452	0.459	0.466	0.471	0.475	0.480	0.483
3.0	0.400	0.408	0.415	0.423	0.429	0.434	0.439
4.0	0.373	0.383	0.393	0.401	0.408	0.415	0.421
5.0	0.365	0.376	0.387	0.396	0.404	0.412	0.420
6.0	0.366	0.379	0.391	0.401	0.410	0.419	0.428
7.0	0.370	0.384	0.396	0.408	0.419	0.429	0.437

[a] Molar activity coefficients listed refer to the molarity of solutions measured at 298.15 K.

of temperature (*19*):

$$\Phi_L(T)/(\text{J·mol}^{-1}) = f + gT + hT^2 + kT^3 \qquad (15)$$

The relative partial molar enthalpy of the solute can be obtained from the relative apparent molar enthalpy:

$$\Delta H_{m,2}/(\text{J·mol}^{-1}) = \Phi_L + \frac{m^{1/2}}{2}\frac{\partial \Phi_L}{\partial m^{1/2}} = f_L + g_L T + h_L T^2 + k_L T^3 \qquad (16)$$

where f_L is evaluated from the value of Φ_L at a given temperature (298.15 K in the present instance), and g_L, h_L, and k_L are related to the temperature dependencies of the coefficients A_J, B_J, C_J, D_J, and E_J (see eqs 6–10).

Values of the relative partial molar enthalpies of GdmCl in aqueous solution at different temperatures calculated at round molalities are listed in Table VII.

The relative partial molar enthalpy of the solute is related to changes in the mean molal activity coefficient, $\gamma_{\pm,m}$, by

$$\int \mathrm{d} \ln \gamma_{\pm,m} = -\int (\Delta H_{m,2}/\nu R T^2)\, \mathrm{d}T \qquad (17)$$

Substitution of eq 16 into eq 17 gives

$$\ln\left(\frac{\gamma_{\pm,m}(T)}{\gamma_{\pm,m}(T_0)}\right) = \frac{f_L}{\nu R}\left(\frac{1}{T} - \frac{1}{T_0}\right) - \left(\frac{g_L}{\nu R}\right)\ln\frac{T}{T_0} - \frac{h_L}{\nu R}(T - T_0) - \frac{k_L}{2\nu R}(T^2 - T_0^{\,2}) \qquad (18)$$

where $\gamma_{\pm,m}(T)$ and $\gamma_{\pm,m}(T_0)$ are the molal activity coefficients at any given temperature T and at the reference temperature T_0, respectively. The values of $\gamma_{\pm,m}(T_0)$ at $T_0 = 298.15$ K were taken from ref 20.

The values for the molal activity coefficients calculated by eq 18 at different temperatures and round molalities are presented in Table VIII. Molar activity coefficients were calculated from the molal activity coefficients, and the densities are listed in Table IX at different temperatures and round molarities.

Acknowledgment

We thank P. J. Cheek for experimental assistance with some of the measurements (Sheffield).

Glossary

A_ρ, B_ρ	coefficients in eq 2
A_J, B_J, C_J, D_J, E_J	coefficients in eq 5
A_L, B_L, C_L, D_L, E_L	coefficients in eq 13
$C_{p,1}{}^*$	molar heat capacity of water, $\text{J·K}^{-1}\text{·mol}^{-1}$
$\Phi C_{p,2}$	apparent molar heat capacity of the solute, $\text{J·K}^{-1}\text{·mol}^{-1}$
$\Phi C_{p,2}{}^\infty$	apparent molar heat capacity of the solute at infinite dilution, $\text{J·K}^{-1}\text{·mol}^{-1}$
c	molarity of the solution, mol·dm^{-3}
f, g, h, k	coefficients in eqs 15 and 16
$\Delta_{\text{dil}} H_m$	molar enthalpy of dilution, J·mol^{-1}
$\Delta H_{m,2}$	$= H_{m,2} - H_{m,2}{}^\infty$, relative partial molar enthalpy of the solute, J·mol^{-1}
m	molality of the solution, mol·kg^{-1}
M_2	molar mass of the solute
R	gas constant, $\text{J·K}^{-1}\text{·mol}^{-1}$
T	temperature, K
$V_1{}^*$	molar volume of water, $\text{cm}^3\text{·mol}^{-1}$
ΦV_2	apparent molar volume of the solute, $\text{cm}^3\text{·mol}^{-1}$
w	mass fraction of the solute in solution
$\gamma_{\pm,m}$	molality-based activity coefficient
$\gamma_{\pm,c}$	molarity-based activity coefficient
ν	number of ions formed by one molecule of electrolyte
ρ	density of the solution, g·cm^{-3}
ρ^*	density of the solvent, g·cm^{-3}
σ	standard deviation in units of fitted data, eq 11

Φ_J	relative apparent molar heat capacity, $J{\cdot}K^{-1}{\cdot}mol^{-1}$
Φ_L	relative apparent molar enthalpy, $J{\cdot}mol^{-1}$

Subscripts

i	initial value
f	final value

Superscripts

calcd	calculated value
exptl	experimental value

Literature Cited

(1) Bonner, O. D. *J. Chem. Thermodyn.* **1976**, *8*, 1167.
(2) Schrier, M. Y.; Schrier, E. E. *J. Chem. Eng. Data* **1977**, *22*, 73.
(3) Macaskill, J. B.; Robinson, R. A.; Bates, R. G. *J. Chem. Eng. Data* **1977**, *22*, 411.
(4) Kawahara, K.; Tanford, C. *J. Biol. Chem.* **1966**, *241*, 3228.
(5) Hedwig, G. R.; Lilley, T. H.; Linsdell, H. *J. Chem. Soc., Faraday Trans.* **1991**, *87*, 2975.
(6) Makhatadze, G. I.; Privalov, P. L. *J. Mol. Biol.* **1992**, *226*, 491.
(7) Nozaki, Y. *Methods Enzymol.* **1986**, *26*, 43.
(8) Makhatadze, G. I.; Privalov, P. L. *J. Solution Chem.* **1989**, *18*, 927.
(9) Makhatadze, G. I.; Medvedkin, V. N.; Privalov, P. L. *Biopolymers* **1990**, *30*, 1001.
(10) Weast, R. W. *Handbook of Chemistry and Physics*; Chemical Rubber Co.: Cleveland, OH, 1970.
(11) Pirvalov, P. L.; Potekhin, S. A. *Methods Enzymol.* **1986**, *131*, 4.
(12) Wiseman, T.; Williston, S.; Brandts, J. F.; Lin, L.-N. *Anal. Biochem.* **1989**, *179*, 131.
(13) Cheek, P. J.; Lilley, T. H. *J. Chem. Soc., Faraday Trans.* **1988**, *84*, 1927.
(14) Fortier, J.-L.; Leduc, P.-A.; Desnoyers, J. E. *J. Solution Chem.* **1974**, *3*, 323.
(15) Fortier, J.-L.; Desnoyers, J. E. *J. Solution Chem.* **1976**, *5*, 297.
(16) Millero, F. J. In *Activity Coefficients in Electrolyte Solutions*; Pitkowicz, R. M., Ed.; CRC Press: Boca Raton, FL, 1979; Vol. 2, Chapter 2, p 63.
(17) Pitzer, K. S.; Simonson, J. M. *J. Phys. Chem.* **1986**, *90*, 3005.
(18) Phutela, R. C.; Pitzer, K. S. *J. Phys. Chem.* **1986**, *90*, 895.
(19) Snipes, H. P.; Manly, C.; Ensor, D. D. *J. Chem. Eng. Data* **1975**, *20*, 287.
(20) Pace, C. N. *Methods Enzymol.* **1986**, *131*, 266.

Received for review April 13, 1992. Revised September 4, 1992. Accepted September 19, 1992. This study was supported by the NSF Biological Research Centers Award (DIR-8721059) to G.I.M. and P.L.P., NIH Grant RR 04328 to E.F., and the Ministerio de Educacion y Ciencia, Spain, with an FPU grant (EX91 16532774).