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Partial Molar Volumes and Isentropic Compressibilities of Amino Acids in Dilute Aqueous Solutions

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The densities and speeds of sound in dilute aqueous solutions of the amino acids, L-asparagine, L-glutamine, L-histidine, L-aspartic acid monosodium salt, L-glutamic acid monosodium salt, L-lysine monohydrochloride, L-arginine monohydrochloride, and L-histidine monohydrochloride, were measured at (5, 15, 25, 35, and 45) °C. Partial molar volumes and partial molar isentropic compressibilities of these amino acids at infinite dilution were evaluated and discussed in connection with the electrostatic interactions between the charged groups of amino acid side chains and solvent water.

Introduction

It is well-known that the stabilization of native conformations of biopolymers is caused by the various noncovalent interactions such as hydrogen bonding, electrostatic, and hydrophobic interactions. In aqueous protein solutions, the amino acid residues of a polypeptide chain interact with each other and with the surrounding water by these noncovalent forces. Therefore, the characterization of the thermodynamic properties of hydration can assist in the understanding of the conformational stability and the functional properties of proteins in solution. However, since proteins are particularly complex macromolecules, it is difficult to resolve the various interactions that participate in protein hydration. One of the useful approaches for interpreting the thermodynamic properties of protein solutions is the comparative study of various low-molecular-weight model compounds. Amino acids have been often used as the most convenient substances to estimate the individual contribution of monomeric units in proteins.

Volumetric properties of solution are believed to be sensitive to the nature of hydration. A number of experimental data of the partial molar volumes of amino acids have been reported (Hakin et al., 1995; Høiland, 1986). It is, however, recognized that amino acids in aqueous solution have oppositely charged carboxyl and amino groups that may influence the hydration of the adjacent amino acid side chains. For this reason the use of the other model compounds such as *N*-acetyl amino acid amides (Hedwig et al., 1991; Mishra and Ahluwalia, 1984) or oligopeptides (Hedwig, 1988) has been recommended. Kikuchi et al. (1995, 1996) have shown that the partial molar volumes, $V_2°(\mathrm{Ra})$, or isentropic compressibilities, $K_2°(\mathrm{Ra})$, of nonpolar side chains evaluated from amino acid series are, in most cases, smaller than the values of $V_2°(\mathrm{Rn})$ or $K_2°(\mathrm{Rn})$ calculated from the data for acetyl amino acid amide series. For valine or leucine, for example, the $V_2°(\mathrm{Ra})$ value is smaller by about 0.5 $\mathrm{cm^3{\cdot}mol^{-1}}$ than that for $V_2°(\mathrm{Rn})$ and the $K_2°(\mathrm{Ra})$ value is smaller by about 2 $\mathrm{cm^3{\cdot}mol^{-1}{\cdot}GPa^{-1}}$ than that for $K_2°(\mathrm{Rn})$.

On the other hand, it may be expected that such a charge effect is less significant in the case of amino acids with a polar side chain. In a recent communication from this laboratory, it was shown that the partial molar volumes or compressibilities of seryl or threonyl groups are almost the same when calculated from the data of the two series, amino acids and acetyl amino acid amides (Mizuguchi et al. 1997). In the present work, we have studied other hydrophilic amino acids having a polar or an ionic side chain.

Experimental Section

The amino acids used in this study, L-asparagine (Asn), L-glutamine (Gln), L-histidine (His), L-aspartic acid monosodium salt (AspNa), L-glutamic acid monosodium salt (GluNa), L-lysine monohydrochloride (LysHCl), L-arginine monohydrochloride (ArgHCl), and L-histidine monohydrochloride (HisHCl), were guaranteed reagents obtained from several suppliers: Asn (>99%) and Gln (>98%) were obtained from Nacalai Tesque, Inc., Kyoto; AspNa (>98%) and GluNa (>99%) were obtained from Junsei Chemical Co., Ltd., Tokyo; the other amino acids (>99%) were obtained from Wako Pure Chemical Industries, Ltd., Osaka. These samples were used without further purification. All solutions were made by mass with deionized and distilled water.

The solution densities were measured by an oscillating-tube densimeter (DMA 60/601, Anton Paar, Austria) with an accuracy of $\pm 2 \times 10^{-6}$ $\mathrm{g{\cdot}cm^{-3}}$. The speeds of sound in the solutions were measured at a frequency of about 5 MHz using a sing-around velocimeter constructed in our laboratory. The accuracy of the measurements of the speed of sound was estimated to be better than 1 $\mathrm{cm{\cdot}s^{-1}}$ for the dilute solution range studied. The temperature of the fluid surrounding the measuring cell of the densimeter or velocimeter was maintained within ±0.002 °C by using a quartz temperature controller. Details of the apparatus, calibrations, and experimental procedures have been described previously (Sakurai et al., 1994).

Results and Discussion

The apparent molar volumes, V_ϕ, of the solutes were calculated by using the following equation

$$V_\phi = M_2/\rho - (\rho - \rho_1)/m\rho\rho_1 \qquad (1)$$

where M_2 is the solute molar mass, m is molality, and ρ_1 and ρ are the densities of water and the solution, respec-

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Table 1. Density Differences and Apparent Molar Volumes for Aqueous Solutions of Amino Acids at 5, 15, 25, 35, and 45 °C

m/ mol·kg^{-1}	$10^3(\rho - \rho_1)$/ g·cm^{-3}	V_ϕ/ cm^3·mol^{-1}	m/ mol·kg^{-1}	$10^3(\rho - \rho_1)$/ g·cm^{-3}	V_ϕ/ cm^3·mol^{-1}	m/ mol·kg^{-1}	$10^3(\rho - \rho_1)$/ g·cm^{-3}	V_ϕ/ cm^3·mol^{-1}
				L-Asparagine				
				$t = 5$ °C				
0.010 33	0.599	74.10	0.049 60	2.864	74.17	0.079 97	4.600	74.25
0.021 78	1.261	74.13	0.059 97	3.457	74.21	0.088 10	5.061	74.29
0.032 36	1.872	74.11	0.070 34	4.051	74.23	0.096 22	5.522	74.32
0.040 92	2.364	74.16						
				$t = 15$ °C				
0.011 14	0.625	76.00	0.049 43	2.765	75.99	0.079 34	4.418	76.11
0.021 49	1.205	75.98	0.058 75	3.280	76.05	0.088 43	4.920	76.13
0.031 40	1.760	75.96	0.068 71	3.832	76.07	0.096 45	5.359	76.16
0.041 04	2.298	75.98						
				$t = 25$ °C				
0.011 69	0.640	77.42	0.051 32	2.799	77.43	0.077 47	4.213	77.47
0.022 15	1.212	77.39	0.060 30	3.286	77.43	0.085 59	4.649	77.50
0.031 11	1.702	77.36	0.068 84	3.748	77.45	0.094 96	5.152	77.52
0.041 63	2.274	77.38						
				$t = 35$ °C				
0.008 83	0.476	78.29	0.050 78	2.719	78.50	0.074 49	3.978	78.56
0.019 45	1.046	78.41	0.058 79	3.145	78.53	0.082 33	4.393	78.55
0.032 12	1.724	78.44	0.066 68	3.563	78.55	0.091 28	4.865	78.58
0.042 15	2.257	78.53						
				$t = 45$ °C				
0.005 14	0.271	79.62	0.038 96	2.060	79.34	0.066 73	3.519	79.35
0.010 98	0.582	79.34	0.049 39	2.610	79.33	0.073 72	3.886	79.36
0.020 04	1.061	79.36	0.058 86	3.106	79.35	0.079 69	4.197	79.36
0.028 63	1.516	79.31						
				L-Glutamine				
				$t = 5$ °C				
0.008 62	0.483	90.02	0.046 66	2.597	90.26	0.076 21	4.221	90.37
0.017 39	0.973	90.12	0.056 82	3.156	90.32	0.086 91	4.806	90.41
0.028 28	1.578	90.20	0.066 75	3.703	90.34	0.097 85	5.404	90.43
0.035 92	2.001	90.26						
				$t = 15$ °C				
0.009 23	0.500	91.98	0.051 82	2.785	92.18	0.078 30	4.194	92.23
0.020 19	1.090	92.08	0.059 85	3.212	92.21	0.088 66	4.741	92.27
0.031 10	1.676	92.13	0.068 27	3.660	92.22	0.099 64	5.319	92.30
0.041 93	2.256	92.16						
				$t = 25$ °C				
0.006 81	0.358	93.70	0.038 88	2.038	93.64	0.066 75	3.490	93.65
0.014 10	0.742	93.58	0.047 49	2.488	93.64	0.077 81	4.063	93.66
0.022 86	1.203	93.52	0.057 28	3.000	93.61	0.088 45	4.613	93.68
0.030 40	1.596	93.61						
				$t = 35$ °C				
0.006 81	0.351	94.76	0.042 64	2.197	94.67	0.074 03	3.812	94.54
0.013 04	0.673	94.71	0.052 00	2.677	94.67	0.082 80	4.257	94.58
0.021 86	1.128	94.69	0.063 92	3.288	94.64	0.092 44	4.744	94.63
0.031 78	1.637	94.73						
				$t = 45$ °C				
0.008 13	0.416	95.35	0.044 01	2.240	95.46	0.073 34	3.721	95.49
0.018 06	0.920	95.57	0.052 97	2.690	95.53	0.082 66	4.192	95.46
0.026 65	1.357	95.52	0.062 80	3.188	95.50	0.091 71	4.645	95.49
0.035 91	1.826	95.55						
				L-Histidine				
				$t = 5$ °C				
0.018 02	1.073	95.50	0.056 68	3.358	95.58	0.083 16	4.911	95.63
0.030 80	1.832	95.51	0.064 16	3.796	95.63	0.092 06	5.429	95.66
0.043 52	2.582	95.57	0.075 30	4.451	95.62			
				$t = 15$ °C				
0.022 97	1.332	97.07	0.067 69	3.902	97.17	0.089 57	5.152	97.17
0.040 32	2.338	96.97	0.076 95	4.431	97.17	0.095 51	5.487	97.21
0.056 19	3.246	97.11	0.085 11	4.897	97.18			
				$t = 25$ °C				
0.022 79	1.281	98.97	0.071 41	3.998	98.90	0.096 72	5.399	98.93
0.039 10	2.195	98.92	0.081 09	4.531	98.96	0.103 31	5.762	98.94
0.058 79	3.296	98.90	0.088 92	4.966	98.95			

Table 1 (Continued)

m/ mol·kg^{-1}	$10^3(\rho - \rho_1)$/ g·cm^{-3}	V_ϕ/ cm^3·mol^{-1}	m/ mol·kg^{-1}	$10^3(\rho - \rho_1)$/ g·cm^{-3}	V_ϕ/ cm^3·mol^{-1}	m/ mol·kg^{-1}	$10^3(\rho - \rho_1)$/ g·cm^{-3}	V_ϕ/ cm^3·mol^{-1}
L-Histidine								
t = 35 °C								
0.031 68	1.748	100.08	0.077 97	4.293	99.94	0.102 10	5.612	99.89
0.050 88	2.809	99.94	0.087 37	4.807	99.92	0.107 18	5.890	99.88
0.064 63	3.562	99.96	0.095 71	5.264	99.90			
t = 45 °C								
0.023 72	1.292	101.02	0.062 21	3.382	100.91	0.089 18	4.841	100.84
0.038 51	2.097	100.96	0.074 21	4.032	100.87	0.095 96	5.207	100.82
0.051 28	2.790	100.92	0.081 01	4.399	100.85			
L-Aspartic Acid Monosodium								
t = 5 °C								
0.011 62	1.110	59.52	0.038 12	3.626	59.74	0.092 91	8.765	60.20
0.016 23	1.550	59.50	0.050 36	4.782	59.85	0.113 29	10.657	60.37
0.022 43	2.140	59.53	0.061 61	5.842	59.92	0.135 04	12.653	60.61
0.028 77	2.742	59.61	0.072 06	6.822	60.00			
t = 15 °C								
0.007 43	0.687	62.51	0.041 63	3.831	62.79	0.104 41	9.535	63.13
0.011 63	1.075	62.60	0.054 33	4.995	62.81	0.124 72	11.358	63.26
0.020 67	1.908	62.61	0.068 83	6.314	62.91	0.145 18	13.189	63.38
0.028 46	2.621	62.82	0.086 51	7.919	63.02			
t = 25 °C								
0.005 71	0.523	63.34	0.037 70	3.407	64.43	0.092 42	8.280	64.88
0.010 60	0.964	63.93	0.049 28	4.444	64.53	0.111 31	9.947	65.00
0.018 36	1.666	64.13	0.061 90	5.569	64.67	0.130 75	11.656	65.10
0.026 63	2.411	64.31	0.075 90	6.816	64.76	0.142 48	12.677	65.21
t = 35 °C								
0.017 48	1.559	65.63	0.064 40	5.697	66.09	0.086 00	7.594	66.14
0.034 39	3.058	65.81	0.072 31	6.394	66.10	0.094 42	8.326	66.20
0.046 27	4.107	65.92	0.077 12	6.816	66.11	0.110 29	9.712	66.24
0.057 66	5.107	66.05	0.080 45	7.110	66.10			
t = 45 °C								
0.008 76	0.773	66.57	0.049 06	4.314	66.65	0.103 61	9.043	66.99
0.017 34	1.531	66.46	0.069 87	6.124	66.81	0.019 07	10.372	67.07
0.024 97	2.201	66.56	0.085 48	7.477	66.89	0.139 01	12.082	67.15
0.036 07	3.177	66.57						
L-Glutamic Acid Monosodium								
t = 5 °C								
0.019 46	1.829	74.94	0.100 13	9.308	75.44	0.158 99	14.648	75.86
0.040 59	3.807	75.02	0.119 75	11.099	75.58	0.180 39	16.571	75.99
0.061 37	5.740	75.15	0.140 25	12.961	75.72	0.205 94	18.845	76.16
0.080 17	7.477	75.29						
t = 15 °C								
0.025 53	2.331	77.60	0.086 50	7.825	78.02	0.141 81	12.723	78.38
0.041 58	3.787	77.73	0.103 12	9.305	78.14	0.158 74	14.208	78.48
0.055 92	5.082	77.82	0.118 67	10.683	78.24	0.175 85	15.700	78.58
0.070 83	6.420	77.96						
t = 25 °C								
0.023 93	2.132	79.80	0.100 89	8.905	80.10	0.156 21	13.687	80.36
0.038 91	3.464	79.80	0.124 22	10.926	80.24	0.174 29	15.235	80.45
0.057 57	5.111	79.89	0.142 40	12.517	80.18	0.187 41	16.354	80.51
0.080 17	7.096	80.00						
t = 35 °C								
0.015 65	1.375	81.12	0.077 42	6.746	81.39	0.121 59	10.535	81.58
0.026 73	2.340	81.31	0.091 35	7.946	81.45	0.136 60	11.811	81.65
0.046 02	4.025	81.27	0.104 96	9.113	81.51	0.149 84	12.934	81.71
0.059 46	5.192	81.33						
t = 45 °C								
0.024 17	2.102	81.88	0.073 37	6.344	82.07	0.170 13	14.535	82.44
0.041 59	3.610	81.95	0.097 96	8.442	82.18	0.219 80	18.665	82.62
0.058 74	5.087	82.03	0.118 21	10.165	82.24			
L-Lysine Monohydrochloride								
t = 5 °C								
0.011 66	0.717	121.06	0.094 54	5.636	122.34	0.156 89	9.227	122.70
0.027 64	1.679	121.69	0.105 84	6.294	122.41	0.170 15	9.979	122.77
0.062 91	3.780	122.10	0.123 62	7.324	122.50	0.195 38	11.404	122.88
0.078 41	4.692	122.23	0.139 41	8.230	122.61	0.207 64	12.088	122.95

Table 1 (Continued)

m/mol·kg^{-1}	$10^3(\rho - \rho_1)$/g·cm^{-3}	V_ϕ/cm^3·mol^{-1}	m/mol·kg^{-1}	$10^3(\rho - \rho_1)$/g·cm^{-3}	V_ϕ/cm^3·mol^{-1}	m/mol·kg^{-1}	$10^3(\rho - \rho_1)$/g·cm^{-3}	V_ϕ/cm^3·mol^{-1}
L-Lysine Monohydrochloride								
$t = 15$ °C								
0.010 58	0.627	123.32	0.063 33	3.697	123.86	0.140 31	8.054	124.30
0.020 37	1.202	123.52	0.075 64	4.404	123.94	0.159 92	9.144	124.39
0.030 48	1.795	123.59	0.091 88	5.328	124.05	0.177 54	10.115	124.47
0.040 15	2.358	123.67	0.107 25	6.200	124.13	0.197 94	11.231	124.57
0.051 29	3.003	123.79	0.124 52	7.171	124.22			
$t = 25$ °C								
0.014 32	0.828	124.94	0.049 14	2.809	125.33	0.139 53	7.830	125.75
0.023 58	1.364	124.82	0.069 84	3.973	125.46	0.163 80	9.147	125.86
0.035 41	2.038	125.02	0.088 89	5.039	125.52	0.190 03	10.557	125.97
0.040 38	2.313	125.28	0.113 33	6.392	125.64	0.205 48	11.383	126.02
$t = 35$ °C								
0.007 51	0.426	126.28	0.063 91	3.596	126.33	0.132 04	7.335	126.59
0.012 99	0.738	126.12	0.078 90	4.427	126.40	0.154 91	8.564	126.70
0.023 20	1.317	126.13	0.095 85	5.359	126.48	0.177 64	9.779	126.78
0.033 08	1.874	126.18	0.112 41	6.266	126.53	0.201 13	11.023	126.87
0.048 07	2.713	126.27						
$t = 45$ °C								
0.009 82	0.558	126.44	0.055 81	3.127	126.91	0.125 01	6.922	127.09
0.023 75	1.341	126.68	0.064 12	3.588	126.93	0.144 74	7.984	127.17
0.031 56	1.779	126.75	0.080 25	4.470	127.06	0.157 52	8.668	127.22
0.041 31	2.323	126.81	0.091 82	5.112	127.02	0.180 46	9.891	127.28
0.047 46	2.667	126.81	0.109 94	6.102	127.07	0.201 82	11.021	127.34
L-Arginine Monohydrochloride								
$t = 5$ °C								
0.015 05	1.122	135.96	0.073 23	5.379	136.47	0.150 60	10.867	137.01
0.026 56	1.975	136.03	0.088 71	6.493	136.59	0.185 17	13.261	137.23
0.042 93	3.176	136.25	0.105 42	7.687	136.69	0.200 54	14.313	137.32
0.058 79	4.333	136.37	0.129 45	9.384	136.89			
$t = 15$ °C								
0.011 77	0.850	138.39	0.069 78	4.973	138.76	0.165 22	11.528	139.34
0.023 47	1.693	138.36	0.090 16	6.394	138.91	0.196 79	13.641	139.50
0.032 40	2.333	138.36	0.115 67	8.157	139.06	0.205 37	14.212	139.54
0.049 48	3.544	138.62	0.141 07	9.893	139.22			
$t = 25$ °C								
0.011 62	0.824	139.84	0.068 95	4.807	140.47	0.152 70	10.459	140.90
0.022 86	1.611	140.15	0.097 51	6.758	140.62	0.181 63	12.366	141.05
0.032 17	2.263	140.20	0.123 56	8.513	140.77	0.203 15	13.771	141.15
0.048 86	3.422	140.35						
$t = 35$ °C								
0.009 07	0.640	140.43	0.063 19	4.358	141.51	0.148 86	10.071	142.02
0.014 74	1.035	140.69	0.080 24	5.511	141.63	0.177 83	11.962	142.13
0.029 97	2.087	141.14	0.113 66	7.749	141.83	0.202 73	13.567	142.25
0.045 23	3.134	141.35						
$t = 45$ °C								
0.006 37	0.440	142.32	0.038 36	2.632	142.38	0.112 16	7.573	142.79
0.013 45	0.927	142.35	0.049 07	3.357	142.50	0.134 27	9.025	142.88
0.020 00	1.377	142.34	0.068 90	4.693	142.60	0.170 84	11.403	143.02
0.027 63	1.899	142.38	0.091 16	6.182	142.68	0.208 00	13.784	143.16
L-Histidine Monohydrochloride								
$t = 5$ °C								
0.016 70	1.360	110.04	0.046 12	3.731	110.30	0.067 96	5.474	110.46
0.029 22	2.375	110.08	0.054 08	4.373	110.28	0.079 05	6.358	110.48
0.038 37	3.112	110.19	0.061 83	4.984	110.45	0.090 66	7.274	110.58
$t = 15$ °C								
0.012 91	1.021	112.39	0.047 22	3.709	112.68	0.071 14	5.562	112.84
0.024 99	1.973	112.47	0.056 19	4.405	112.75	0.077 39	6.043	112.88
0.036 76	2.893	112.62	0.063 45	4.967	112.79			
$t = 25$ °C								
0.023 32	1.805	114.10	0.067 56	5.117	114.51	0.090 20	6.885	114.60
0.038 89	3.000	114.24	0.075 45	5.773	114.55	0.099 15	7.556	114.66
0.053 27	4.097	114.35	0.083 27	6.364	114.58			
$t = 35$ °C								
0.032 09	2.446	115.32	0.080 60	6.085	115.65	0.097 73	7.357	115.72
0.054 90	4.164	115.52	0.090 00	6.785	115.68	0.105 18	7.909	115.74
0.067 58	5.115	115.57						
$t = 45$ °C								
0.016 04	1.213	116.22	0.047 58	3.580	116.36	0.068 08	5.098	116.54
0.028 26	2.134	116.22	0.055 46	4.164	116.44	0.074 49	5.570	116.59
0.038 58	2.909	116.29	0.062 27	4.669	116.50	0.078 56	5.870	116.61

Table 2. Speed of Sound Differences and Apparent Molar Isentropic Compressibilities for Aqueous Solutions of Amino Acids at 5, 15, 25, 35, and 45 °C

m/ mol·kg^{-1}	$(u - u_1)$/ m·s^{-1}	K_ϕ/ cm^3·mol^{-1}·GPa^{-1}	m/ mol·kg^{-1}	$(u - u_1)$/ m·s^{-1}	K_ϕ/ cm^3·mol^{-1}·GPa^{-1}	m/ mol·kg^{-1}	$(u - u_1)$/ m·s^{-1}	K_ϕ/ cm^3·mol^{-1}·GPa^{-1}
L-Asparagine								
$t = 5$ °C								
0.008 49	0.733	−51.62	0.052 85	4.504	−50.45	0.077 83	6.638	−50.29
0.022 34	1.891	−50.31	0.059 85	5.107	−50.47	0.086 42	7.366	−50.17
0.035 39	3.023	−50.74	0.068 13	5.816	−50.42	0.095 15	8.110	−50.09
0.044 98	3.836	−50.56						
$t = 15$ °C								
0.012 11	0.960	−41.25	0.056 18	4.384	−40.14	0.076 26	5.946	−39.95
0.026 88	2.094	−40.27	0.062 91	4.908	−40.08	0.085 01	6.624	−39.86
0.038 21	2.992	−40.44	0.069 38	5.415	−40.06	0.094 67	7.349	−39.61
0.047 22	3.677	−40.10						
$t = 25$ °C								
0.012 89	0.943	−33.92	0.053 37	3.835	−32.92	0.075 59	5.428	−32.78
0.026 11	1.883	−33.23	0.061 28	4.396	−32.81	0.083 52	6.013	−32.84
0.037 17	2.691	−33.33	0.068 24	4.901	−32.82	0.092 92	6.658	−32.59
0.044 76	3.218	−32.99						
$t = 35$ °C								
0.016 57	1.148	−29.42	0.052 99	3.568	−28.16	0.077 47	5.178	−27.77
0.026 54	1.792	−28.38	0.060 54	4.062	−27.99	0.085 74	5.741	−27.81
0.035 27	2.355	−27.91	0.069 31	4.663	−28.06	0.095 49	6.408	−27.84
0.044 37	2.996	−28.31						
$t = 45$ °C								
0.010 15	0.662	−25.83	0.049 93	3.201	−25.11	0.078 88	5.019	−24.76
0.019 81	1.283	−25.56	0.061 02	3.892	−24.89	0.086 83	5.519	−24.69
0.029 72	1.923	−25.50	0.070 37	4.493	−24.90	0.094 11	5.981	−24.66
0.039 52	2.545	−25.31						
L−Glutamine								
$t = 5$ °C								
0.010 99	1.035	−48.06	0.051 93	4.908	−47.93	0.078 44	7.382	−47.43
0.022 89	2.160	−48.07	0.061 14	5.779	−47.86	0.088 19	8.300	−47.35
0.032 29	3.067	−48.43	0.069 08	6.521	−47.71	0.098 41	9.246	−47.15
0.042 46	4.026	−48.22						
$t = 15$ °C								
0.014 02	1.225	−37.87	0.052 36	4.504	−36.75	0.078 30	6.728	−36.53
0.024 56	2.115	−36.98	0.060 32	5.195	−36.77	0.089 53	7.684	−36.40
0.035 29	3.038	−36.90	0.068 44	5.895	−36.73	0.100 26	8.598	−36.29
0.043 93	3.785	−36.90						
$t = 25$ °C								
0.011 66	0.937	−30.01	0.063 30	5.010	−29.07	0.084 63	6.685	−28.89
0.026 90	2.144	−29.55	0.071 28	5.632	−28.95	0.090 49	7.137	−28.79
0.042 13	3.348	−29.34	0.077 57	6.138	−29.00	0.099 56	7.835	−28.65
0.053 45	4.256	−29.39						
$t = 35$ °C								
0.013 41	0.996	−24.33	0.043 48	3.220	−24.17	0.066 82	4.939	−24.06
0.025 63	1.896	−24.13	0.052 14	3.856	−24.09	0.074 81	5.495	−23.78
0.034 29	2.533	−24.06	0.060 39	4.493	−24.34	0.082 79	6.093	−23.85
$t = 45$ °C								
0.010 45	0.714	−19.83	0.049 76	3.452	−20.33	0.075 99	5.237	−20.03
0.022 93	1.595	−20.46	0.057 99	4.002	−20.12	0.084 88	5.855	−20.06
0.031 22	2.168	−20.40	0.066 30	4.577	−20.12	0.093 74	6.483	−20.14
0.040 54	2.801	−20.18						
L−Histidine								
$t = 5$ °C								
0.019 97	2.135	−55.94	0.063 36	6.738	−55.14	0.089 09	9.419	−54.49
0.038 34	4.085	−55.51	0.072 13	7.709	−55.42	0.094 96	10.002	−54.16
0.052 22	5.545	−55.14	0.081 09	8.671	−55.38			
$t = 15$ °C								
0.021 19	1.926	−39.66	0.063 47	5.717	−38.85	0.090 09	8.057	−38.27
0.039 52	3.564	−39.10	0.072 00	6.478	−38.73	0.098 04	8.783	−38.31
0.050 37	4.541	−38.98	0.081 31	7.288	−38.45			
$t = 25$ °C								
0.017 04	1.369	−29.28	0.048 24	3.955	−30.13	0.073 96	6.029	−29.75
0.029 03	2.358	−29.74	0.057 06	4.701	−30.33	0.082 29	6.800	−30.38
0.040 55	3.296	−29.72	0.066 58	5.483	−30.28			
$t = 35$ °C								
0.015 86	1.264	−26.73	0.052 00	4.099	−26.19	0.077 25	6.054	−25.90
0.029 09	2.310	−26.56	0.062 33	4.925	−26.29	0.084 26	6.621	−26.01
0.041 52	3.287	−26.39	0.071 08	5.607	−26.19			

Table 2 (Continued)

m/ mol·kg^{-1}	$(u - u_1)$/ m·s^{-1}	K_ϕ/ cm^3·mol^{-1}·GPa^{-1}	m/ mol·kg^{-1}	$(u - u_1)$/ m·s^{-1}	K_ϕ/ cm^3·mol^{-1}·GPa^{-1}	m/ mol·kg^{-1}	$(u - u_1)$/ m·s^{-1}	K_ϕ/ cm^3·mol^{-1}·GPa^{-1}
L-Histidine								
$t = 45$ °C								
0.023 44	1.638	−19.87	0.060 64	4.220	−19.69	0.085 43	5.903	−19.42
0.039 06	2.723	−19.77	0.069 92	4.848	−19.55	0.092 19	6.424	−19.74
0.050 63	3.520	−19.66	0.076 70	5.282	−19.29			
L−Aspartic Acid Monosodium								
$t = 5$ °C								
0.019 84	2.810	−114.99	0.076 92	10.597	−110.53	0.111 32	15.282	−109.21
0.035 55	4.973	−113.27	0.091 13	12.558	−110.15	0.120 28	16.474	−108.74
0.046 03	6.415	−112.57	0.104 15	14.304	−109.46	0.136 61	18.648	−107.98
0.056 35	7.835	−112.03						
$t = 15$ °C								
0.006 18	0.743	−90.54	0.067 25	8.508	−93.03	0.121 20	15.321	−91.81
0.014 41	1.842	−95.10	0.089 45	11.377	−92.96	0.130 54	16.502	−91.62
0.033 74	4.287	−94.16	0.105 93	13.430	−92.36	0.139 48	17.620	−91.38
0.044 98	5.764	−94.56						
$t = 25$ °C								
0.009 28	1.113	−84.00	0.046 14	5.502	−82.76	0.097 75	11.565	−81.19
0.015 98	1.902	−83.33	0.060 09	7.139	−82.23	0.119 65	14.118	−80.58
0.020 91	2.470	−82.67	0.079 13	9.402	−81.84	0.142 84	16.811	−79.96
0.032 87	3.893	−82.59						
$t = 35$ °C								
0.006 44	0.727	−75.73	0.052 33	5.830	−74.07	0.119 37	13.171	−72.44
0.013 04	1.457	−74.97	0.071 73	7.969	−73.59	0.133 45	14.680	−72.05
0.023 10	2.579	−74.72	0.093 38	10.355	−73.13	0.141 66	15.612	−72.04
0.034 28	3.806	−74.17						
$t = 45$ °C								
0.015 48	1.680	−71.03	0.054 36	5.812	−69.46	0.093 71	9.901	−68.14
0.028 32	3.058	−70.49	0.069 42	7.351	−68.65	0.111 91	11.766	−67.60
0.035 69	3.839	−70.12	0.084 44	8.894	−68.11	0.142 28	14.921	−67.03
0.042 59	4.553	−69.63						
L−Glutamic Acid Monosodium								
$t = 5$ °C								
0.022 78	3.515	−115.43	0.111 80	17.036	−111.42	0.163 86	24.835	−109.43
0.049 71	7.639	−114.13	0.127 33	19.365	−110.79	0.177 71	26.890	−108.89
0.072 25	11.042	−112.88	0.143 50	21.804	−110.24	0.197 70	29.872	−108.21
0.093 98	14.332	−112.02						
$t = 15$ °C								
0.020 56	2.908	−96.21	0.098 78	13.804	−93.22	0.154 62	21.479	−91.48
0.042 16	5.947	−95.39	0.118 70	16.549	−92.58	0.177 06	24.552	−90.85
0.065 28	9.132	−94.10	0.140 90	19.605	−91.92	0.202 05	27.968	−90.18
0.079 90	11.187	−93.83						
$t = 25$ °C								
0.023 74	3.154	−83.99	0.094 56	12.399	−81.56	0.161 00	20.871	−79.52
0.039 20	5.196	−83.49	0.111 94	14.658	−81.14	0.184 67	23.902	−79.00
0.060 61	7.999	−82.72	0.132 17	17.289	−80.70	0.202 83	26.211	−78.58
0.076 62	10.078	−82.15						
$t = 35$ °C								
0.015 01	1.936	−77.64	0.076 05	9.431	−73.74	0.141 85	17.353	−71.79
0.028 45	3.590	−75.81	0.110 11	13.568	−72.76	0.161 65	19.730	−71.34
0.042 57	5.326	−74.94	0.122 68	15.053	−72.28	0.194 14	23.613	−70.65
0.055 15	6.872	−74.41						
$t = 45$ °C								
0.007 14	0.857	−70.63	0.086 17	10.053	−67.45	0.134 26	15.510	−66.16
0.017 18	2.045	−69.89	0.102 00	11.867	−67.05	0.152 32	17.585	−65.87
0.036 51	4.307	−68.94	0.119 08	13.812	−66.62	0.168 23	19.408	−65.62
0.058 53	6.859	−68.15						
L−Lysine Monohydrochloride								
$t = 5$ °C								
0.020 72	3.265	−78.38	0.078 77	12.237	−75.74	0.147 04	22.626	−73.56
0.038 20	5.987	−77.45	0.097 03	15.059	−75.30	0.160 35	24.628	−73.15
0.052 40	8.185	−76.81	0.111 46	17.239	−74.69	0.181 29	27.750	−72.46
0.065 12	10.152	−76.37	0.128 44	19.806	−74.09	0.208 99	31.835	−71.53
$t = 15$ °C								
0.018 57	2.765	−64.57	0.113 65	16.424	−60.39	0.175 78	25.136	−58.64
0.035 82	5.371	−64.94	0.133 67	19.261	−59.86	0.196 57	27.964	−57.93
0.061 03	8.975	−62.72	0.152 83	21.945	−59.29	0.211 60	30.033	−57.55
0.084 87	12.339	−61.33						

Table 2 (Continued)

m/ mol·kg^{-1}	$(u - u_1)$/ m·s^{-1}	K_ϕ/ cm^3·mol^{-1}·GPa^{-1}	*m*/ mol·kg^{-1}	$(u - u_1)$/ m·s^{-1}	K_ϕ/ cm^3·mol^{-1}·GPa^{-1}	*m*/ mol·kg^{-1}	$(u - u_1)$/ m·s^{-1}	K_ϕ/ cm^3·mol^{-1}·GPa^{-1}
L-Lysine Monohydrochloride								
$t = 25$ °C								
0.010 17	1.376	−51.25	0.063 59	8.632	−50.76	0.124 49	16.696	−49.13
0.025 28	3.460	−51.93	0.074 12	10.043	−50.50	0.148 14	19.782	−48.54
0.035 42	4.837	−51.60	0.086 25	11.632	−49.98	0.176 46	23.460	−47.92
0.044 83	6.109	−51.30	0.101 23	13.615	−49.60	0.203 09	26.891	−47.35
0.055 50	7.560	−51.14						
$t = 35$ °C								
0.006 67	0.845	−43.29	0.066 64	8.648	−44.41	0.144 73	18.509	−42.64
0.014 29	1.826	−43.87	0.080 07	10.345	−43.96	0.163 75	20.883	−42.28
0.027 62	3.544	−44.00	0.096 66	12.455	−43.60	0.183 31	23.299	−41.89
0.041 39	5.394	−45.01	0.110 75	14.282	−43.54	0.195 14	24.749	−41.64
0.052 92	6.886	−44.75	0.129 12	16.555	−42.96	0.202 83	25.720	−41.57
$t = 45$ °C								
0.007 54	0.961	−42.27	0.055 06	6.861	−40.33	0.139 43	17.046	−38.65
0.015 42	1.927	−40.80	0.075 50	9.359	−39.88	0.159 79	19.464	−38.34
0.023 63	2.980	−41.39	0.088 90	10.981	−39.57	0.179 86	21.815	−37.98
0.036 42	4.569	−40.92	0.113 73	13.984	−39.14	0.203 79	24.612	−37.62
L−Arginine Monohydrochloride								
$t = 5$ °C								
0.013 24	2.059	−76.95	0.077 86	11.925	−73.94	0.164 38	24.654	−70.22
0.026 47	4.105	−76.33	0.099 72	15.188	−72.95	0.190 48	28.410	−69.22
0.043 94	6.776	−75.35	0.127 48	19.271	−71.67	0.209 09	31.059	−68.51
0.061 68	9.494	−74.79						
$t = 15$ °C								
0.017 10	2.460	−60.66	0.083 20	11.729	−57.75	0.151 23	20.841	−54.85
0.036 76	5.248	−59.61	0.105 04	14.688	−56.72	0.154 81	21.386	−55.01
0.053 74	7.632	−58.86	0.129 95	18.034	−55.73	0.160 28	22.046	−54.57
0.067 51	9.534	−58.15						
$t = 25$ °C								
0.013 35	1.788	−49.48	0.075 99	10.010	−47.30	0.149 81	19.330	−44.89
0.029 99	3.988	−48.64	0.097 73	12.776	−46.45	0.175 70	22.508	−44.08
0.046 64	6.190	−48.26	0.125 10	16.244	−45.63	0.206 84	26.297	−43.22
$t = 35$ °C								
0.012 43	1.495	−38.66	0.086 07	10.444	−38.42	0.169 72	20.240	−36.44
0.023 79	2.920	−39.93	0.113 41	13.686	−37.76	0.190 42	22.609	−35.96
0.044 82	5.495	−39.59	0.150 51	18.007	−36.83	0.206 17	24.387	−35.58
0.061 26	7.503	−39.33						
$t = 45$ °C								
0.011 16	1.320	−35.78	0.071 74	8.357	−34.17	0.128 17	14.655	−32.52
0.021 22	2.547	−36.69	0.087 54	10.156	−33.77	0.158 47	18.012	−31.92
0.040 06	4.712	−35.12	0.104 41	12.047	−33.28	0.202 45	22.793	−31.03
0.051 81	6.077	−34.81						
L−Histidine Monohydrochloride								
$t = 5$ °C								
0.029 09	3.812	−75.90	0.080 38	10.424	−73.94	0.099 35	12.806	−73.07
0.053 23	6.955	−75.12	0.087 10	11.264	−73.58	0.105 04	13.532	−72.92
0.070 29	9.121	−74.19	0.093 43	12.074	−73.40			
$t = 15$ °C								
0.033 62	3.901	−57.94	0.094 71	11.056	−57.46	0.122 00	14.212	−56.93
0.058 88	6.864	−57.90	0.105 60	12.334	−57.35	0.129 08	15.058	−56.94
0.079 12	9.238	−57.71	0.114 36	13.334	−57.10			
$t = 25$ °C								
0.021 90	2.440	−50.54	0.066 65	7.351	−49.23	0.094 16	10.322	−48.49
0.041 21	4.585	−50.15	0.076 25	8.396	−49.00	0.100 79	11.017	−48.22
0.055 99	6.197	−49.60	0.086 02	9.425	−48.56			
$t = 35$ °C								
0.023 47	2.419	−42.79	0.068 88	7.120	−42.45	0.097 87	10.005	−41.51
0.041 04	4.248	−42.83	0.080 35	8.278	−42.13	0.105 45	10.782	−41.44
0.057 04	5.884	−42.45	0.089 07	9.134	−41.77			
$t = 45$ °C								
0.017 76	1.760	−39.08	0.064 65	6.352	−37.99	0.086 08	8.436	−37.61
0.038 94	3.832	−38.39	0.073 25	7.169	−37.68	0.091 47	8.949	−37.46
0.053 42	5.258	−38.22	0.080 11	7.839	−37.60			

tively. The ρ_1 values were taken from the table given by Kell (1975): (0.999 964, 0.999 100, 0.997 045, 0.994 032, and 0.990 213) g·cm^{-3} at (5, 15, 25, 35, and 45) °C, respectively. The density differences, $\rho - \rho_1$, between solutions and pure water and the calculated V_ϕ values are summarized in Table 1.

The apparent molar isentropic compressibilities, K_ϕ, of the solutes were calculated using the equation

$$K_\phi = M_2\kappa/\rho - (\kappa_1\rho - \kappa\rho_1)/m\rho\rho_1 \qquad (2)$$

where κ and κ_1 are the isentropic compressibilities of the solution and water, respectively, and the other symbols are as defined for eq 1. The isentropic compressibility was determined from the speed of sound and density using the relation

$$\kappa = 1/u^2\rho \qquad (3)$$

The speed of sound differences, $u - u_1$, between solution and water and the K_ϕ values are given in Table 2. The u_1 values were taken from the table reported by Del Grosso and Mader (1972): (1426.162, 1465.931, 1496.687, 1519.808, and 1536.409) $\mathrm{m\cdot s^{-1}}$ at (5, 15, 25, 35, and 45) °C, respectively. The density values of the solutions used for the speed of sound measurements were calculated from eqs 4 or 5 for the apparent molar volume, described below.

For sufficiently dilute nonelectrolyte solutions, the variation of the apparent molar quantities, X_ϕ (X refers to V or K in the present study), with molality can be represented by the linear relation

$$X_\phi = X_2° + B_x m \qquad (4)$$

where $X_2°$ is infinite dilution value, which is equal to the partial molar quantity at infinite dilution, and B_x is the experimental slope.

In the case of dilute electrolyte solutions, the apparent molar quantities of electrolytes are usually fitted to a Redlich-type equation in terms of molarity, c

$$X_\phi = X_2° + S_x c^{1/2} + B_x c \qquad (5)$$

where S_x is a theoretical slope given by the Debye−Hückel limiting law and B_x is an empirical constant. The S_v values for the apparent molar volume of 1:1 electrolyte in water are (1.528, 1.696, 1.868, 2.046, and 2.233) $\mathrm{cm^3\cdot mol^{-3/2}\cdot L^{1/2}}$ at (5, 15, 25, 35, and 45) °C, respectively (Millero, 1979). For isentropic compressibility, unfortunately, the theoretical limiting slope S_k is not known, so we substituted isothermal S_k for isentropic S_k value, that is, (0.776, 1.744, 2.55, 3.26, and 3.913) $\mathrm{cm^3\cdot mol^{-3/2}\cdot L^{1/2}\cdot GPa^{-1}}$ for 1:1 electrolyte in water at (5, 15, 25, 35, and 45) °C, respectively (Millero, 1979). By using these theoretical limiting slopes one can adequately determine the limiting partial molar quantity, $X_2°$, from a linear plot of $(X_\phi - S_x c^{1/2})$ against c.

Equation 4 was fitted to our V_ϕ and K_ϕ data for the hydrophilic amino acids (Asn, Gln, and His) and eq 5 for the ionic amino acids (AspNa, GluNa, LysHCl, ArgHCl, and HisHCl). The parameters of eqs 4 or 5 were determined by using the method of weighted least squares taking into consideration the density precision of 2 ppm and speed of sound precision of 7 ppm and are summarized in Tables 3 and 4. The $V_2°$ and $K_2°$ values available in the literature are also included in these tables. The comparison shows that, in most cases, there is a reasonable agreement between our values and those from literature within experimental uncertainties.

The partial molar volumes of all the amino acids studied increase with increasing temperature, and furthermore their curves obtained are always concave downward. This feature is typical of aqueous electrolyte or hydrophilic nonelectrolyte solutions (Hepler, 1969). It is well-known that ionic groups of solute attract strongly surrounding water molecules, so-called electrostriction, which causes a large decrease both in volume and in compressibility of the solution. Since the partial molar compressibility is a more sensitive measure of solute−solvent interactions than is the partial molar volume (Høiland, 1986), the effect of electrostriction is more obvious for the former thermodynamic property. Thus, as can be seen from Table 4, the partial molar compressibilities of the amino acids are large negative at all temperatures studied.

Table 3. Limiting Partial Molar Volumes of Amino Acids in Water at 5, 15, 25, 35, and 45 °C

t/ °C	$V_2°$/ $\mathrm{cm^3\cdot mol^{-1}}$	B_v/ $\mathrm{cm^3\cdot kg\cdot mol^{-2}}$ [a]	$V_2°$(lit.)/ $\mathrm{cm^3\cdot mol^{-1}}$
		L-Asparagine	
5	74.03(0.01)[b]	2.9(0.2)	
15	75.87(0.01)	2.9(0.2)	76.0,[c] 76.28[d]
25	77.29(0.01)	2.3(0.2)	77.2,[c] 77.63,[d] 77.18,[e] 77.52,[f]
35	78.42(0.02)	1.7(0.3)	
40			78.8,[c] 79.07[d]
45	79.32(0.02)	0.5(0.3)	
55			79.5,[c] 80.48[d]
		L-Glutamine	
5	90.13(0.01)	3.1(0.2)	
15	92.05(0.01)	2.5(0.1)	92.3,[c] 92.29[d]
25	93.56(0.02)	1.2(0.3)	93.8,[c] 93.90,[d] 94.36,[e] 93.61,[g]
35	94.72(0.06)	−1.4(0.8)	
40			94.9,[c] 95.14,[d]
45	95.54(0.03)	−0.7(0.4)	
55			96.3,[c] 96.25,[d]
		L-Histidine	
5	95.48(0.02)	1.9(0.3)	
15	96.95(0.05)	2.6(0.7)	97.3[c]
25	98.89(0.03)	0.4(0.4)	98.8,[c] 99.14,[d] 98.3,[g] 98.79[h]
40			100.4[c]
35	100.07(0.03)	−1.7(0.3)	99.9[c]
45	101.05(0.01)	−2.4(0.1)	
55			101.6[c]
		L-Aspartic Acid Monosodium	
5	59.13(0.02)	6.6(0.2)	
15	62.27(0.02)	3.1(0.2)	
25	63.93(0.02)	4.0(0.2)	
35	65.47(0.03)	1.0(0.4)	
45	66.11(0.03)	1.6(0.2)	
		L-Glutaminic Acid Monosdium	
5	74.48(0.01)	4.8(0.1)	
15	77.21(0.02)	3.8(0.1)	
25	79.29(0.02)	2.1(0.1)	
35	80.76(0.02)	0.9(0.2)	
45	81.41(0.01)	0.7(0.1)	
		L-Lysine Monohydrochloride	
5	121.52(0.01)	3.6(0.1)	
15	123.26(0.01)	2.9(0.1)	124.5[c]
25	124.77(0.02)	2.1(0.1)	125.9,[c] 124.76[g]
35	125.74(0.01)	1.1(0.1)	
45	126.35(0.01)	0.0(0.1)	
		L-Arginine Monohydrochloride	
5	135.72(0.01)	4.7(0.1)	
15	138.08(0.02)	3.5(0.1)	
25	139.79(0.02)	2.6(0.1)	140.06[g]
35	140.82(0.02)	2.7(0.1)	
45	141.93(0.01)	1.1(0.1)	
		L-Histidine Monohydrochloride	
5	109.76(0.04)	4.0(0.6)	
15	112.15(0.06)	3.3(0.9)	
25	113.79(0.04)	2.9(0.6)	
35	114.96(0.05)	1.3(0.5)	
45	115.75(0.05)	3.0(0.8)	

[a] Unit for B_v in eq 5 for electrolyte solutions is $\mathrm{cm^3\cdot L\cdot mol^{-2}}$. [b] Standard deviations are in parentheses. [c] Kharakoz (1989). [d] Hakin et al. (1995). [e] Jolicoeur et al. (1986). [f] Hedwig (1991). [g] Mishra et al. (1984). [h] Millero et al. (1978).

Table 4. Limiting Partial Molar Isentropic Compressibilities of Amino Acids in Water at 5, 15, 25, 35, and 45 °C

t/ °C	$K_2°$/ $cm^3 \cdot mol^{-1} \cdot GPa^{-1}$	B_k/ $cm^3 \cdot kg \cdot mol^{-2} \cdot GPa^{-1}$ [a]	$K_2°$(lit.)/ $cm^3 \cdot mol^{-1} \cdot GPa^{-1}$
		L-Asparagine	
5	−50.9(0.1)[b]	9.1(1.4)	
15	−40.8(0.1)	12.2(1.7)	−40.4[c]
25	−33.4(0.1)	9.0(1.9)	−33.5,[c] −32.97,[d]
35	−28.5(0.2)	8.2(2.7)	
40			−26.5[c]
45	−25.7(0.1)	11.5(1.1)	
55			−22.5[c]
		L-Glutamine	
5	−48.8(0.1)	17.3(1.4)	
15	−37.4(0.1)	11.0(1.1)	−36.7[c]
25	−29.9(0.1)	12.8(1.1)	−28.9
35	−24.5(0.2)	8.0(3.6)	
40			−21.9[c]
45	−20.3(0.1)	2.9(1.6)	
55			−16.6[c]
		L-Histidine	
5	−56.7(0.7)	24.1(9.4)	
15	−39.8(0.1)	16.2(1.9)	−41.3[c]
25	−29.6(0.5)	−7.8(7.4)	−32.5,[c] −31.84[e]
35	−26.8(0.1)	10.2(2.7)	−25.9[c]
45	−19.7(0.3)	2.1(4.7)	
55			−18.0[c]
		L-Aspartic Acid Monosodium	
5	−114.8(0.1)	49.0(1.2)	
15	−95.5(0.1)	25.7(1.1)	
25	−84.2(0.1)	23.3(0.9)	
35	−75.6(0.1)	17.9(0.9)	
45	−71.1(0.1)	19.8(0.9)	
		L-Glutaminic Acid Monosdium	
5	−115.8(0.1)	37.6(0.5)	
15	−96.5(0.1)	28.7(0.5)	
25	−84.8(0.1)	26.2(0.4)	
35	−76.3(0.1)	22.8(0.5)	
45	−70.0(0.1)	18.0(0.7)	
		L-Lysine Monohydrochloride	
5	−78.6(0.1)	33.2(0.4)	
15	−64.6(0.1)	30.9(0.4)	−61.6[c]
25	−53.6(0.1)	21.2(0.4)	−51.8[c]
35	−46.2(0.1)	16.3(0.3)	
45	−41.9(0.1)	13.0(0.4)	
		L-Arginine Monohydrochloride	
5	−77.3(0.1)	41.7(0.5)	
15	−61.2(0.1)	38.0(0.7)	
25	−50.0(0.1)	28.3(0.5)	
35	−41.1(0.1)	20.5(0.4)	
45	−36.5(0.1)	19.5(0.4)	
		L-Histidine Monohydrochloride	
5	−77.2(0.2)	39.9(2.4)	
15	−59.0(0.1)	11.8(1.4)	
25	−51.6(0.1)	26.3(2.1)	
35	−44.2(0.1)	17.0(1.9)	
45	−39.6(0.2)	11.5(2.6)	

[a] Unit for B_k in eq 5 for electrolyte solutions is $cm^3 \cdot L \cdot mol^{-2} \cdot GPa^{-1}$. [b] Standard deviations are in parentheses. [c] Kharakoz (1991). [d] Hedwig (1991). [e] Millero et al. (1978).

In Figure 1 are shown the temperature dependences of the limiting partial molar isentropic compressibilities of the amino acids studied. The compressibility decreases steeply with decrease of temperature; that is characteristic for dilute aqueous mixtures, regardless of whether they are hydrophilic or hydrophobic solutes (Kikuchi et al., 1995; Sakurai et al., 1995). A particularly intriguing feature is that the negative partial molar isentropic compressibilities of two sodium salts (AspNa and GluNa) are significant in magnitude compared with the hydrochloride salts (LysHCl, ArgHCl, or HisHCl): the difference between the two salt series is more than 30 $cm^3 \cdot mol^{-1} \cdot GPa^{-1}$. This may be consistent with the difference between the partial molar isentropic compressibilities of sodium alkanecarboxylates and alkylammonium chlorides having the same alkyl groups: 40−50 $cm^3 \cdot mol^{-1} \cdot GPa^{-1}$ (Høiland, 1986). Therefore, if we assume the ionic partial molar compressibilities of Na^+ and Cl^- ions to be −33.5 and −17.0 $cm^3 \cdot mol^{-1} \cdot GPa^{-1}$, respectively (Conway, 1978), partial molar compressibility for the COO^- ion is more negative than that for the NH_3^+ ion by 23−33 $cm^3 \cdot mol^{-1} \cdot GPa^{-1}$. Since the contribution of a methylene group to the partial compressibility is negative at ambient temperature (Sakurai, 1995), the ions having larger hydrophobic groups may be expected to have more negative values of the partial molar compressibility. Therefore, taking into account that the alkyl chain in AspNa or GluNa is shorter than that in the hydrochloride salts, such a large difference suggests a stronger electrostriction effect by COO^- rather than by $NH3^+$ ion.

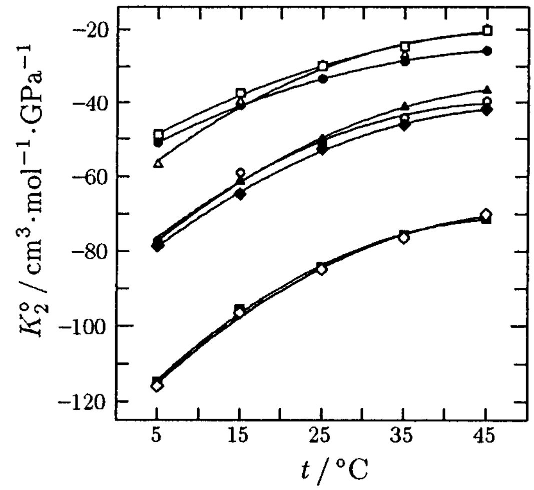

Figure 1. Temperature dependence of the limiting partial molar isentropic compressibilities of hydrophilic amino acids in dilute aqueous solutions: (□) L-glutamine; (●) L-asparagine; (△) L-histidine; (▲) L-arginine monohydrochloride; (◆) L-lysine monohydrochloride; (○) L-histidine monohydrochloride; (◇) L-glutamic acid monosodium; (■) L-aspartic acid monosodium.

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