Partial Molar Volumes and Adiabatic Compressibilities of Amino Acids in Dilute Aqueous Solutions at 5, 15, 25, 35, and 45 °C

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The densities and sound velocities in dilute aqueous solutions of 10 amino acids were measured at 5, 15, 25, 35, and 45 °C. The amino acids used were glycine, L-alanine, L-valine, L-leucine, L-isoleucine, DL-methionine, L-proline, L-phenylalanine, L-tryptophan, and L-tyrosine. Partial molar volumes and partial molar adiabatic compressibilities of these amino acids at infinite dilution were evaluated. The results were compared with those reported in the literature. The features of temperature dependence of the partial molar quantities were described.

Introduction

The interaction of protein with water in aqueous solution is an important factor for maintaining the native conformation of proteins. Consequently, the characterization of thermodynamic properties of protein hydration can assist in understanding the conformational stability and the unfolding behavior of globular proteins. Since proteins are particularly complex molecules, it is difficult to separate the various interactions which participate in protein hydration.

For a better understanding of the hydration behavior of proteins, one useful approach is to investigate the low molecular weight model compounds that contain atomic groups such as amino acid side chains and the peptide group of proteins. In fact, many studies on the thermodynamic properties of the model compounds in aqueous solution have been reported in the past.

Amino acids have been used widely as a model compound because they represent the fundamental substances for building proteins (Duke et al., 1994; Hakin et al., 1994; Jolicoeur and Boileau, 1978; Jolicoeur et al., 1986; Kharakoz, 1989, 1991; Millero et al., 1978; Ogawa et al., 1984). However, it is recognized that amino acids in aqueous solution have two oppositely charged carboxyl and amino groups that may interfere with the hydration of the adjacent amino acid side chains. Thus, the amino acids are necessarily the suitable model compounds for understanding the group contributions to the thermodynamic properties of protein hydration.

In order to overcome the influence of the charged end groups, several approaches have been attempted. One is to use amino acid derivatives without ionic groups as model compounds, e.g., *N*-acetyl amino acid amides (Hedwig et al., 1991; Leslie and Lilley, 1985) or cyclic dipeptides (Murphy and Gill, 1989). Another one is to use oligopeptides in which the charged end groups are far removed from side chains of interest and each other (Hedwig, 1988, 1993; Hedwig and Hoiland, 1993, 1994; Makhatadze et al., 1990).

Volumetric properties of solute, such as the partial molar volume and compressibility, are known to be sensitive to the nature of hydration. Further, the hydration effects are known to be very sensitive to temperature. However, it seems that at the present time there are not enough experimental data available concerning the temperature dependence of the volumetric properties of these model compounds.

In a following paper, we will report the partial molar volumes and adiabatic compressibilities of some *N*-acetyl amino acid amides in aqueous solution at various temperatures. It is interesting to compare the volumetric characteristics of these amino acid derivatives with those of the parent amino acids. Unfortunately, the majority of previous volumetric investigations of amino acids in aqueous solution has been confined at 25 °C, and few reliable results are available over the same experimental temperature range as that selected in our investigation.

To obtain the volumetric data for amino acids that can be compared with those of *N*-acetyl amino acid amides, we report here the partial molar volumes and adiabatic compressibilities of some hydrophobic amino acids in dilute aqueous solution at 5–45 °C.

Experimental Section

The amino acids used in this study, glycine (Gly), L-alanine (Ala), L-valine (Val), L-leucine (Leu), L-isoleucine (Ile), DL-methionine (Met), L-proline (Pro), L-phenylalanine (Phe), L-tryptophan (Trp), and L-tyrosine (Tyr), were guaranteed reagents obtained from several suppliers: Gly was obtained from Wako Pure Chemical Industries, Ltd.: Ala and Met were obtained from Takara Kohsan Co. Ltd.; the other amino acids were obtained from Nacalai Tesque, Inc. These samples were used without further purification. All solutions were made by mass with deionized and distilled water. The solution densities were measured by a vibrating tube densimeter (DMA 60/601, Anton Paar) with a precision of $\pm(2 \times 10^{-6})$ g·cm^{-3}. The sound velocities in the solutions were measured at a frequency of about 5 MHz with a precision of ±1 cm·s^{-1} using a sing-around velocimeter constructed in our laboratory. The temperature of the fluid surrounding the measuring cell of the densimeter and velocimeter was maintained within ±0.002 °C by using a quartz temperature controller. Details of the apparatus, their calibrations, and experimental procedures used have been described previously (Sakurai and Nakagawa, 1982; Sakurai et al., 1994, 1995).

With the exception of Trp and Tyr, the measurements of the densities and sound velocities of all amino acid solutions were carried out over the concentration range ca. 0.01–0.1 mol·kg^{-1}. Because of the low solubilities of Trp and Tyr in water, the maximum concentrations of these solutions were about 0.05 and 0.002 mol·kg^{-1}, respectively.

Results and Discussion

The density differences between solution and pure water ($\varrho - \varrho_1$) at 5, 15, 25, 35, and 45 °C are summarized in Table

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

t/°C	m/(mol·kg^{-1})	$10^3(\varrho-\varrho_1)$/(g·cm^{-3})	ϕ_v/(cm^3·mol^{-1})	m/(mol·kg^{-1})	$10^3(\varrho-\varrho_1)$/(g·cm^{-3})	ϕ_v/(cm^3·mol^{-1})	t/°C	m/(mol·kg^{-1})	$10^3(\varrho-\varrho_1)$/(g·cm^{-3})	ϕ_v/(cm^3·mol^{-1})	m/(mol·kg^{-1})	$10^3(\varrho-\varrho_1)$/(g·cm^{-3})	ϕ_v/(cm^3·mol^{-1})
						Glycine (75.07)[a]							
5	0.00812	0.275	41.186	0.05079	1.720	41.140	35	0.00996	0.311	43.898	0.06359	1.990	43.762
	0.01632	0.554	41.106	0.06066	2.053	41.136		0.02108	0.659	43.850	0.07325	2.292	43.756
	0.02498	0.848	41.090	0.07386	2.497	41.163		0.03101	0.970	43.822	0.08427	2.635	43.758
	0.03290	1.116	41.103	0.08799	2.971	41.185		0.03906	1.223	43.780	0.09822	3.071	43.742
	0.04169	1.413	41.129	0.10601	3.575	41.197		0.04746	1.487	43.754	0.11061	3.457	43.737
15	0.01038	0.340	42.261	0.05558	1.815	42.337		0.05562	1.742	43.751			
	0.02013	0.661	42.234	0.06409	2.092	42.353	45	0.01146	0.357	44.062	0.06171	1.914	44.092
	0.02875	0.942	42.284	0.07617	2.485	42.351		0.02016	0.628	44.010	0.07102	2.201	44.110
	0.03651	1.194	42.328	0.09153	2.984	42.354		0.02890	0.901	43.985	0.08263	2.557	44.144
	0.04520	1.479	42.306	0.10747	3.500	42.367		0.03945	1.228	44.018	0.09411	2.910	44.149
25	0.00888	0.284	43.083	0.05579	1.775	43.204		0.05048	1.567	44.090	0.10648	3.292	44.137
	0.01838	0.586	43.181	0.06518	2.074	43.194							
	0.02751	0.876	43.211	0.07594	2.414	43.205							
	0.03755	1.196	43.191	0.08790	2.794	43.199							
	0.04678	1.490	43.187	0.10219	3.246	43.199							
						L-Alanine (89.09)							
5	0.00951	0.291	58.508	0.05503	1.664	58.756	35	0.00835	0.236	60.975	0.05447	1.540	60.918
	0.01817	0.553	58.643	0.06513	1.968	58.763		0.01862	0.525	61.075	0.06449	1.824	60.889
	0.02707	0.822	58.682	0.07605	2.294	58.789		0.02965	0.839	60.918	0.07395	2.089	60.910
	0.03610	1.096	58.672	0.08850	2.666	58.811		0.03804	1.077	60.910	0.08635	2.439	60.887
	0.04517	1.368	58.716	0.10109	3.042	58.814		0.04618	1.306	60.924	0.10107	2.853	60.886
15	0.00858	0.251	59.841	0.05577	1.632	59.752	45	0.00724	0.201	61.578	0.04738	1.325	61.371
	0.01838	0.539	59.742	0.06469	1.893	59.742		0.01506	0.419	61.532	0.05738	1.605	61.353
	0.02662	0.782	59.692	0.07547	2.207	59.739		0.02245	0.627	61.461	0.06871	1.919	61.371
	0.03569	1.046	59.734	0.08754	2.557	59.749		0.03044	0.850	61.456	0.08208	2.292	61.347
	0.04601	1.348	59.751	0.10170	2.968	59.754		0.03852	1.077	61.387	0.10090	2.817	61.319
25	0.00938	0.268	60.633	0.05522	1.580	60.468							
	0.01843	0.528	60.502	0.06457	1.848	60.449							
	0.02742	0.785	60.519	0.07540	2.156	60.458							
	0.03756	1.075	60.498	0.08819	2.521	60.440							
	0.04661	1.334	60.475	0.10090	2.883	60.438							
						L-Valine (117.15)							
5	0.00849	0.239	88.952	0.05464	1.529	89.027	35	0.00796	0.207	91.578	0.05780	1.504	91.376
	0.01772	0.497	89.078	0.06568	1.835	89.045		0.01769	0.458	91.592	0.06765	1.760	91.364
	0.02722	0.765	88.999	0.07783	2.173	89.043		0.02799	0.725	91.553	0.07826	2.036	91.330
	0.03629	1.017	89.034	0.08924	2.490	89.033		0.03815	0.993	91.431	0.08941	2.324	91.335
	0.04516	1.265	89.034	0.10056	2.802	89.042		0.04809	1.251	91.402	0.10160	2.639	91.327
15	0.00824	0.225	89.886	0.05718	1.550	89.959	45	0.00825	0.213	91.936	0.05055	1.302	91.909
	0.01668	0.454	89.976	0.06887	1.866	89.953		0.01699	0.438	91.957	0.05955	1.534	91.901
	0.02571	0.699	89.966	0.08082	2.186	89.965		0.02607	0.672	91.959	0.07164	1.842	91.917
	0.03576	0.970	89.990	0.09226	2.492	89.971		0.03397	0.876	91.934	0.08535	2.193	91.903
	0.04626	1.256	89.945	0.10242	2.765	89.964		0.04178	1.077	91.914	0.10023	2.571	91.912
25	0.00730	0.197	90.284	0.05764	1.514	90.937							
	0.01735	0.465	90.496	0.06701	1.758	90.952							
	0.02726	0.723	90.753	0.07643	2.002	90.971							
	0.03760	0.993	90.841	0.08739	2.288	90.950							
	0.04776	1.258	90.884	0.10066	2.634	90.929							
						L-Leucine (131.18)							
5	0.00740	0.192	105.243	0.04466	1.143	105.463	35	0.00868	0.197	108.975	0.05514	1.262	108.664
	0.01438	0.368	105.553	0.05076	1.299	105.448		0.01694	0.385	108.944	0.06326	1.447	108.654
	0.02066	0.526	105.646	0.05794	1.483	105.432		0.02496	0.567	108.892	0.07191	1.645	108.642
	0.02698	0.687	105.637	0.06608	1.691	105.410		0.03265	0.746	108.776	0.08071	1.845	108.627
	0.03323	0.848	105.575	0.07602	1.946	105.376		0.04009	0.917	108.726	0.08960	2.044	108.661
	0.03887	0.996	105.463	0.08414	2.151	105.390		0.04758	1.088	108.715	0.09750	2.224	108.637
15	0.00791	0.194	106.706	0.05096	1.251	106.571	45	0.00612	0.137	109.551	0.05848	1.313	109.434
	0.01481	0.364	106.623	0.05996	1.471	106.557		0.01235	0.280	109.358	0.06691	1.501	109.425
	0.02135	0.525	106.608	0.06936	1.700	106.563		0.01917	0.432	109.420	0.07460	1.671	109.447
	0.02777	0.683	106.580	0.07799	1.910	106.567		0.02592	0.584	109.424	0.08193	1.833	109.452
	0.03476	0.855	106.574	0.08817	2.156	106.572		0.03318	0.749	109.377	0.08960	2.003	109.457
	0.04241	1.043	106.554					0.04126	0.929	109.411	0.09617	2.146	109.477
25	0.00883	0.209	107.696	0.04904	1.156	107.734		0.04967	1.116	109.432			
	0.01696	0.402	107.693	0.05530	1.303	107.719							
	0.02427	0.574	107.703	0.06193	1.459	107.713							
	0.03092	0.730	107.736	0.06930	1.632	107.710							
	0.03719	0.878	107.739	0.07779	1.830	107.704							
	0.04314	1.017	107.754	0.08731	2.053	107.698							
						L-Isoleucine (131.18)							
5	0.00668	0.185	103.548	0.05460	1.495	103.653	15	0.00753	0.199	104.840	0.05227	1.376	104.778
	0.01463	0.403	103.628	0.06679	1.827	103.636		0.01561	0.412	104.882	0.06283	1.654	104.759
	0.02404	0.661	103.626	0.07899	2.158	103.634		0.02382	0.628	104.798	0.07569	1.989	104.758
	0.03372	0.925	103.646	0.09008	2.459	103.635		0.03259	0.859	104.787	0.08937	2.345	104.761
	0.04344	1.191	103.646	0.09996	2.725	103.634		0.04201	1.107	104.781	0.10272	2.693	104.749

Table 1 (Continued)

t/°C	m/ (mol·kg⁻¹)	10³ (ϱ − ϱ₁)/ (g·cm⁻³)	φv/ (cm³·mol⁻¹)	m/ (mol·kg⁻¹)	10³ (ϱ − ϱ₁)/ (g·cm⁻³)	φv/ (cm³·mol⁻¹)	t/°C	m/ (mol·kg⁻¹)	10³ (ϱ − ϱ₁)/ (g·cm⁻³)	φv/ (cm³·mol⁻¹)	m/ (mol·kg⁻¹)	10³ (ϱ − ϱ₁)/ (g·cm⁻³)	φv/ (cm³·mol⁻¹)
						L-Isoleucine (131.18)							
25	0.00644	0.164	105.941	0.05008	1.281	105.709	45	0.00446	0.109	107.531	0.05593	1.375	107.263
	0.01348	0.346	105.719	0.06091	1.554	105.733		0.01079	0.265	107.359	0.06709	1.647	107.257
	0.02119	0.543	105.719	0.07396	1.887	105.700		0.01979	0.486	107.389	0.07742	1.900	107.244
	0.03035	0.778	105.713	0.08794	2.241	105.702		0.02767	0.680	107.331	0.08732	2.140	107.246
	0.03995	1.023	105.711	0.10092	2.568	105.702		0.03575	0.879	107.299	0.10186	2.492	107.252
35	0.00679	0.170	106.627	0.05008	1.254	106.496		0.04502	1.107	107.282			
	0.01400	0.350	106.612	0.06183	1.546	106.496							
	0.02159	0.540	106.589	0.07488	1.870	106.492							
	0.03003	0.753	106.516	0.08981	2.240	106.489							
	0.03958	0.991	106.510	0.10274	2.559	106.486							
						DL-Methionine (149.21)							
5	0.02774	1.323	101.379	0.07116	3.360	101.658	35	0.03419	1.488	105.914	0.07835	3.394	105.902
	0.03505	1.667	101.473	0.08802	4.146	101.687		0.04368	1.901	105.860	0.09123	3.946	105.915
	0.04424	2.099	101.561	0.10300	4.841	101.718		0.05404	2.348	105.889	0.10300	4.449	105.913
	0.05591	2.647	101.604					0.06624	2.875	105.873			
15	0.02747	1.244	103.841	0.07085	3.207	103.674	45	0.02502	1.076	106.705	0.06649	2.843	106.766
	0.03484	1.579	103.796	0.08792	3.976	103.626		0.02954	1.270	106.685	0.07517	3.207	106.823
	0.04393	1.989	103.770	0.10300	4.654	103.595		0.03526	1.515	106.719	0.08423	3.588	106.852
	0.05579	2.526	103.715					0.04232	1.818	106.674	0.09353	3.975	106.917
25	0.02855	1.268	104.858	0.07098	3.135	104.890		0.04999	2.144	106.718	0.10300	4.369	106.958
	0.03639	1.614	104.873	0.08689	3.831	104.893		0.05809	2.488	106.741			
	0.04546	2.015	104.865	0.10300	4.532	104.909							
	0.05709	2.527	104.854										
						L-Phenylalanine (165.19)							
5	0.02771	1.295	118.313	0.06710	3.108	118.505	35	0.02725	1.164	122.821	0.06609	2.801	122.936
	0.03469	1.617	118.374	0.08051	3.719	118.553		0.03397	1.447	122.881	0.08111	3.429	122.975
	0.04354	2.025	118.447	0.09282	4.280	118.577		0.04252	1.810	122.888	0.09282	3.915	123.013
	0.05449	2.530	118.464					0.05359	2.276	122.910			
15	0.02680	1.200	120.336	0.06565	2.931	120.252	45	0.02729	1.142	123.994	0.06709	2.794	124.005
	0.03356	1.501	120.349	0.07988	3.561	120.246		0.03428	1.434	123.977	0.08147	3.385	124.020
	0.04214	1.883	120.338	0.09282	4.137	120.191		0.04300	1.797	123.984	0.09282	3.844	124.101
	0.05293	2.364	120.300					0.05418	2.259	124.018			
25	0.02665	1.165	121.544	0.06586	2.859	121.659							
	0.03342	1.460	121.551	0.08062	3.491	121.692							
	0.04201	1.831	121.608	0.09282	4.012	121.705							
	0.05281	2.298	121.628										
						L-Proline (115.13)							
5	0.03126	1.081	80.452	0.07707	2.649	80.545	35	0.03142	1.008	83.264	0.07726	2.468	83.289
	0.03911	1.352	80.461	0.09289	3.187	80.569		0.03922	1.257	83.267	0.09194	2.932	83.299
	0.04908	1.693	80.508	0.10615	3.637	80.575		0.04927	1.578	83.273	0.10615	3.378	83.336
	0.06197	2.133	80.534					0.06208	1.985	83.288			
15	0.03082	1.033	81.558	0.07673	2.557	81.635	45	0.03177	1.004	83.958	0.07697	2.428	83.886
	0.03859	1.292	81.599	0.09270	3.085	81.643		0.03996	1.264	83.890	0.09205	2.899	83.900
	0.04860	1.625	81.605	0.10615	3.528	81.649		0.05032	1.590	83.898	0.10615	3.336	83.939
	0.06138	2.049	81.624					0.06290	1.987	83.875			
25	0.03147	1.029	82.503	0.07741	2.518	82.543							
	0.03935	1.285	82.505	0.09295	3.020	82.540							
	0.04952	1.615	82.531	0.10615	3.443	82.555							
	0.06252	2.036	82.541										
						L-Tryptophan (204.23)							
5	0.01717	1.106	139.651	0.03522	2.257	139.821	35	0.01532	0.917	144.789	0.03451	2.055	144.873
	0.02069	1.332	139.697	0.04076	2.610	139.843		0.01975	1.180	144.815	0.04024	2.392	144.955
	0.02483	1.596	139.722	0.04588	2.936	139.819		0.02418	1.443	144.865	0.04588	2.723	144.992
	0.02968	1.905	139.795					0.02895	1.726	144.846			
15	0.01500	0.942	141.391	0.03448	2.159	141.393	45	0.01569	0.929	145.724	0.03503	2.057	146.036
	0.01931	1.212	141.376	0.04024	2.517	141.399		0.01988	1.174	145.830	0.04056	2.378	146.110
	0.02396	1.502	141.397	0.04588	2.867	141.403		0.02448	1.445	145.863	0.04588	2.680	146.281
	0.02891	1.811	141.406					0.02962	1.743	145.958			
25	0.01527	0.931	143.378	0.03440	2.090	143.428							
	0.01960	1.193	143.451	0.04012	2.435	143.438							
	0.02420	1.472	143.421	0.04588	2.781	143.464							
	0.02906	1.766	143.438										
						L-Tyrosine (181.19)							
5	0.00125	0.079	118.476	0.00170	0.107	118.256	15	0.00125	0.074	121.991	0.00170	0.101	121.552
	0.00135	0.085	118.470	0.00180	0.113	118.452		0.00133	0.079	122.368	0.00180	0.110	120.313
	0.00143	0.091	117.978	0.00192	0.119	119.057		0.00142	0.083	122.588	0.00191	0.118	119.464
	0.00152	0.095	118.431	0.00204	0.129	118.134		0.00151	0.088	122.843	0.00203	0.127	118.477
	0.00161	0.100	118.998	0.00216	0.136	118.450		0.00160	0.095	121.645	0.00216	0.137	117.979

Table 1 (Continued)

t/°C	m/(mol·kg^{-1})	10^3 ($\varrho - \varrho_1$)/(g·cm^{-3})	ϕ_v/(cm^3·mol^{-1})	m/(mol·kg^{-1})	10^3 ($\varrho - \varrho_1$)/(g·cm^{-3})	ϕ_v/(cm^3·mol^{-1})	t/°C	m/(mol·kg^{-1})	10^3 ($\varrho - \varrho_1$)/(g·cm^{-3})	ϕ_v/(cm^3·mol^{-1})	m/(mol·kg^{-1})	10^3 ($\varrho - \varrho_1$)/(g·cm^{-3})	ϕ_v/(cm^3·mol^{-1})
						L-Tyrosine (181.19)							
25	0.00122	0.070	123.746	0.00168	0.095	124.609	45	0.00120	0.065	127.673	0.00163	0.089	127.233
	0.00130	0.075	123.885	0.00178	0.101	124.523		0.00127	0.069	127.843	0.00174	0.096	126.843
	0.00139	0.080	124.075	0.00189	0.107	124.846		0.00135	0.073	127.361	0.00188	0.102	127.651
	0.00148	0.084	124.421	0.00202	0.115	124.318		0.00143	0.078	127.245	0.00203	0.110	127.498
	0.00158	0.090	124.097	0.00216	0.122	124.790		0.00152	0.084	126.660	0.00216	0.115	128.807
35	0.00122	0.068	126.261	0.00167	0.091	126.720							
	0.00130	0.072	126.051	0.00177	0.099	126.052							
	0.00139	0.076	126.847	0.00189	0.104	126.439							
	0.00147	0.081	126.752	0.00203	0.110	127.110							
	0.00156	0.087	126.156	0.00216	0.116	127.859							

[a] Molecular masses are in parentheses.

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

t/°C	m/(mol·kg^{-1})	($u - u_1$)/(m·s^{-1})	ϕ_k/(cm^3·mol^{-1}·GPa^{-1})	m/(mol·kg^{-1})	($u - u_1$)/(m·s^{-1})	ϕ_k/(cm^3·mol^{-1}·GPa^{-1})	t/°C	m/(mol·kg^{-1})	($u - u_1$)/(m·s^{-1})	ϕ_k/(cm^3·mol^{-1}·GPa^{-1})	m/(mol·kg^{-1})	($u - u_1$)/(m·s^{-1})	ϕ_k/(cm^3·mol^{-1}·GPa^{-1})
						Glycine (75.07)[a]							
5	0.00804	0.445	−34.655	0.04983	2.792	−34.978	35	0.00990	0.492	−23.378	0.06146	3.077	−23.540
	0.01547	0.869	−35.211	0.05840	3.275	−34.968		0.01918	0.953	−23.373	0.07174	3.584	−23.474
	0.02390	1.341	−35.138	0.07018	3.930	−34.876		0.02850	1.422	−23.486	0.08269	4.126	−23.426
	0.03361	1.879	−34.951	0.08416	4.706	−34.767		0.03705	1.844	−23.399	0.09658	4.817	−23.398
	0.04186	2.349	−35.057	0.10343	5.775	−34.639		0.04542	2.273	−23.542	0.10896	5.430	−23.366
15	0.00815	0.467	−32.027	0.04970	2.809	−31.405		0.05339	2.668	−23.495			
	0.01548	0.875	−31.497	0.06069	3.429	−31.363	45	0.01070	0.506	−21.341	0.05359	2.554	−21.451
	0.02410	1.364	−31.526	0.07341	4.137	−31.235		0.02013	0.943	−21.092	0.06192	2.948	−21.398
	0.03279	1.851	−31.409	0.08738	4.925	−31.200		0.02799	1.336	−21.564	0.07253	3.473	−21.526
	0.04082	2.312	−31.513	0.10342	5.825	−31.123		0.03703	1.750	−21.266	0.08515	4.050	−21.320
25	0.00947	0.493	−26.273	0.05400	2.833	−26.421		0.04470	2.130	−21.463	0.10091	4.795	−21.247
	0.01786	0.931	−26.285	0.06316	3.335	−26.603							
	0.02637	1.379	−26.377	0.07337	3.860	−26.468							
	0.03563	1.870	−26.466	0.08601	4.517	−26.387							
	0.04519	2.365	−26.351	0.10064	5.289	−26.385							
						L-Alanine (89.09)							
5	0.00802	0.635	−40.681	0.05592	4.318	−39.106	35	0.00679	0.408	−20.525	0.05295	3.226	−21.030
	0.01655	1.285	−39.602	0.06679	5.151	−38.985		0.01562	0.933	−20.377	0.06392	3.902	−21.094
	0.02543	1.971	−39.468	0.07762	5.985	−38.913		0.02471	1.493	−20.757	0.07641	4.661	−21.055
	0.03500	2.709	−39.340	0.08889	6.843	−38.778		0.03327	2.013	−20.803	0.08835	5.379	−20.982
	0.04535	3.510	−39.279	0.10186	7.826	−38.607		0.04303	2.614	−20.938	0.10141	6.183	−21.025
15	0.00779	0.552	−30.916	0.05126	3.630	−30.806	45	0.00910	0.516	−17.821	0.05065	2.917	−18.293
	0.01568	1.116	−31.129	0.06166	4.348	−30.592		0.01782	1.016	−17.958	0.05909	3.387	−18.144
	0.02427	1.719	−30.876	0.07427	5.228	−30.482		0.02619	1.502	−18.157	0.06798	3.902	−18.189
	0.03284	2.322	−30.776	0.08642	6.093	−30.521		0.03380	1.947	−18.302	0.08152	4.663	−18.084
	0.04215	2.976	−30.694	0.10164	7.149	−30.379		0.04198	2.378	−17.768	0.10035	5.803	−18.434
25	0.00774	0.513	−25.562	0.05350	3.492	−24.933							
	0.01694	1.114	−25.274	0.06466	4.211	−24.838							
	0.02548	1.670	−25.127	0.07709	5.029	−24.889							
	0.03371	2.211	−25.136	0.08776	5.717	−24.820							
	0.04283	2.794	−24.918	0.10124	6.589	−24.779							
						L-Valine (117.15)							
5	0.00771	0.908	−51.225	0.05506	6.499	−51.135	35	0.00664	0.600	−23.717	0.05707	5.105	−23.200
	0.01620	1.918	−51.596	0.06617	7.799	−50.954		0.01431	1.291	−23.622	0.06825	6.095	−23.125
	0.02508	2.965	−51.425	0.07745	9.128	−50.887		0.02312	2.074	−23.336	0.07923	7.063	−23.034
	0.03428	4.044	−51.213	0.08919	10.486	−50.630		0.03437	3.080	−23.305	0.08970	7.981	−22.943
	0.04436	5.231	−51.118	0.10040	11.787	−50.458		0.04580	4.102	−23.270	0.10000	8.894	−22.920
15	0.00728	0.768	−37.845	0.05687	6.080	−38.612	45	0.00660	0.537	−17.691	0.05298	4.338	−17.963
	0.01589	1.700	−38.809	0.06707	7.168	−38.553		0.01552	1.254	−17.370	0.06419	5.248	−17.890
	0.02597	2.778	−38.736	0.07738	8.269	−38.506		0.02438	1.991	−17.871	0.07496	6.122	−17.831
	0.03621	3.873	−38.711	0.08801	9.392	−38.377		0.03359	2.765	−18.222	0.08656	7.069	−17.822
	0.04597	4.909	−38.584	0.10075	10.751	−38.329		0.04286	3.521	−18.134	0.10055	8.188	−17.680
25	0.00790	0.778	−30.314	0.05755	5.592	−29.387							
	0.01750	1.706	−29.748	0.06826	6.632	−29.344							
	0.02698	2.630	−29.687	0.07855	7.631	−29.303							
	0.03669	3.571	−29.560	0.08909	8.651	−29.236							
	0.04679	4.553	−29.506	0.10029	9.728	−29.137							
						L-Leucine (131.18)							
5	0.00680	1.003	−62.391	0.04129	5.961	−60.006	15	0.00699	0.903	−44.028	0.05154	6.590	−42.986
	0.01330	1.947	−61.506	0.04860	7.007	−59.838		0.01420	1.829	−43.756	0.05909	7.551	−42.911
	0.01986	2.885	−60.722	0.05603	8.064	−59.641		0.02159	2.781	−43.710	0.06652	8.493	−42.807
	0.02669	3.875	−60.653	0.06355	9.136	−59.495		0.02889	3.712	−43.469	0.07430	9.471	−42.649
	0.03386	4.901	−60.273	0.07344	10.541	−59.292		0.03623	4.649	−43.334	0.08283	10.552	−42.565
								0.04370	5.604	−43.253			

Table 2 (Continued)

t/°C	m/ (mol·kg⁻¹)	(u − u₁)/ (m·s⁻¹)	φₖ/ (cm³·mol⁻¹·GPa⁻¹)	m/ (mol·kg⁻¹)	(u − u₁)/ (m·s⁻¹)	φₖ/ (cm³·mol⁻¹·GPa⁻¹)	t/°C	m/ (mol·kg⁻¹)	(u − u₁)/ (m·s⁻¹)	φₖ/ (cm³·mol⁻¹·GPa⁻¹)	m/ (mol·kg⁻¹)	(u − u₁)/ (m·s⁻¹)	φₖ/ (cm³·mol⁻¹·GPa⁻¹)
						L-Leucine (131.18)							
25	0.00669	0.775	−31.853	0.05399	6.167	−30.869	45	0.00635	0.597	−16.004	0.05455	5.080	−15.387
	0.01405	1.613	−31.295	0.06136	7.001	−30.769		0.01386	1.301	−15.869	0.06341	5.874	−15.109
	0.02153	2.475	−31.341	0.06923	7.891	−30.694		0.02326	2.189	−15.989	0.07159	6.606	−14.892
	0.02963	3.397	−31.160	0.07680	8.738	−30.557		0.03414	3.192	−15.631	0.07847	7.232	−14.826
	0.03806	4.362	−31.112	0.08458	9.615	−30.486		0.04446	4.145	−15.473	0.08489	7.808	−14.710
	0.04627	5.294	−30.989										
35	0.00680	0.696	−21.687	0.05436	5.540	−21.487							
	0.01426	1.457	−21.589	0.06169	6.287	−21.483							
	0.02226	2.276	−21.661	0.06882	7.011	−21.472							
	0.03032	3.108	−21.810	0.07576	7.732	−21.582							
	0.03844	3.937	−21.769	0.08315	8.489	−21.602							
	0.04669	4.774	−21.683										
						L-Isoleucine (131.18)							
5	0.00844	1.195	−60.197	0.05849	8.183	−58.631	35	0.00912	0.929	−23.392	0.05538	5.628	−23.216
	0.01725	2.436	−59.851	0.06883	9.620	−58.466		0.01732	1.763	−23.341	0.06610	6.714	−23.182
	0.02657	3.737	−59.367	0.07853	10.965	−58.301		0.02577	2.621	−23.293	0.07731	7.844	−23.106
	0.03647	5.117	−59.080	0.08795	12.271	−58.168		0.03502	3.561	−23.268	0.08848	8.972	−23.057
	0.04678	6.552	−58.825	0.10160	14.162	−57.992		0.04505	4.578	−23.233	0.10036	10.171	−23.013
15	0.00891	1.120	−43.500	0.05471	6.841	−42.853	45	0.00869	0.793	−16.136	0.05162	4.769	−16.814
	0.01736	2.182	−43.391	0.06582	8.223	−42.743		0.01726	1.583	−16.411	0.06240	5.764	−16.794
	0.02599	3.259	−43.169	0.07806	9.748	−42.666		0.02551	2.346	−16.569	0.07424	6.858	−16.800
	0.03487	4.366	−43.046	0.09049	11.295	−42.580		0.03322	3.063	−16.691	0.08814	8.127	−16.706
	0.04444	5.561	−42.959	0.10175	12.686	−42.443		0.04173	3.859	−16.846	0.10038	9.245	−16.643
25	0.00905	1.023	−32.060	0.05472	6.160	−31.656							
	0.01796	2.029	−31.985	0.06533	7.337	−31.483							
	0.02685	3.029	−31.863	0.07631	8.561	−31.382							
	0.03567	4.019	−31.767	0.08826	9.897	−31.321							
	0.04484	5.051	−31.730	0.10010	11.211	−31.217							
						DL-Methionine (149.21)							
5	0.04340	5.395	−58.903	0.08228	10.180	−58.087	35	0.04411	3.852	−23.410	0.08466	7.362	−23.091
	0.05053	6.280	−58.814	0.09347	11.539	−57.785		0.05133	4.475	−23.297	0.09479	8.238	−23.034
	0.05978	7.421	−58.617	0.10300	12.671	−57.395		0.06127	5.343	−23.295	0.10300	8.937	−22.937
	0.07049	8.738	−58.369					0.07278	6.340	−23.213			
15	0.04593	5.117	−43.547	0.08307	9.183	−42.918	45	0.03706	2.929	−17.598	0.06854	5.410	−17.376
	0.05362	5.966	−43.437	0.09412	10.386	−42.772		0.04178	3.306	−17.618	0.07755	6.118	−17.306
	0.06204	6.887	−43.256	0.10300	11.360	−42.718		0.04699	3.714	−17.539	0.08770	6.901	−17.146
	0.07179	7.954	−43.093					0.05331	4.216	−17.531	0.09710	7.622	−16.990
25	0.04650	4.559	−31.786	0.08598	8.352	−31.104		0.06087	4.817	−17.523	0.10300	8.084	−16.954
	0.05487	5.368	−31.636	0.09578	9.281	−30.930							
	0.06394	6.242	−31.471	0.10300	9.964	−30.805							
	0.07447	7.240	−31.192										
						L-Phenylalanine (165.19)							
5	0.03914	5.809	−66.755	0.07313	10.773	−65.571	35	0.03945	4.006	−23.811	0.07387	7.497	−23.641
	0.04543	6.732	−66.512	0.08345	12.247	−65.057		0.04589	4.667	−23.871	0.08482	8.605	−23.573
	0.05334	7.887	−66.189	0.09282	13.589	−64.708		0.05377	5.463	−23.785	0.09282	9.405	−23.467
	0.06278	9.269	−65.918					0.06336	6.433	−23.703			
15	0.03849	5.110	−49.119	0.07281	9.601	−48.431	45	0.03903	3.604	−17.168	0.07356	6.763	−16.856
	0.04460	5.919	−49.073	0.08323	10.941	−48.143		0.04529	4.173	−17.039	0.08442	7.741	−16.684
	0.05294	7.013	−48.882	0.09282	12.165	−47.864		0.05382	4.962	−17.054	0.09282	8.482	−16.492
	0.06237	8.237	−48.600					0.06290	5.787	−16.923			
25	0.03926	4.537	−34.505	0.07393	8.483	−33.829							
	0.04564	5.268	−34.392	0.08439	9.660	−33.616							
	0.05372	6.186	−34.187	0.09282	10.603	−33.426							
	0.06345	7.292	−33.999										
						L-Proline (115.13)							
5	0.04345	4.176	−43.542	0.08224	7.857	−42.930	35	0.04317	3.001	−17.937	0.08238	5.721	−17.821
	0.05041	4.836	−43.382	0.09478	9.034	−42.718		0.04997	3.476	17.964	0.09487	6.587	−17.793
	0.05942	5.694	−43.254	0.10615	10.105	−42.568		0.05921	4.117	−17.929	0.10615	7.366	−17.744
	0.07018	6.711	−43.070					0.06999	4.867	−17.900			
15	0.04357	3.759	−32.405	0.08281	7.099	−31.928	45	0.04445	2.933	−15.038	0.08314	5.477	−14.920
	0.05052	4.348	−32.261	0.09518	8.140	−31.763		0.05129	3.388	−15.065	0.09483	6.244	−14.883
	0.05983	5.146	−32.190	0.10615	9.057	−31.598		0.06046	3.984	−14.964	0.10615	6.984	−14.838
	0.07068	6.074	−32.099					0.07109	4.683	−14.936			
25	0.04376	3.360	−23.801	0.08249	6.320	−23.621							
	0.05069	3.892	−23.791	0.09473	7.251	−23.553							
	0.05976	4.589	−23.774	0.10615	8.112	−23.451							
	0.07039	5.398	−23.688										
						L-Tryptophan (204.23)							
5	0.01917	2.841	−65.023	0.03681	5.389	−63.524	15	0.01874	2.463	−46.992	0.03575	4.645	−45.910
	0.02231	3.294	−64.572	0.04179	6.104	−63.225		0.02175	2.852	−46.748	0.04098	5.307	−45.612
	0.02658	3.916	−64.304	0.04588	6.677	−62.810		0.02580	3.370	−46.384	0.04588	5.923	−45.314
	0.03151	4.637	−64.108					0.03053	3.980	−46.232			

Table 2 (Continued)

t/°C	m/(mol·kg⁻¹)	(u − u₁)/(m·s⁻¹)	φₖ/(cm³·mol⁻¹·GPa⁻¹)	m/(mol·kg⁻¹)	(u − u₁)/(m·s⁻¹)	φₖ/(cm³·mol⁻¹·GPa⁻¹)	t/°C	m/(mol·kg⁻¹)	(u − u₁)/(m·s⁻¹)	φₖ/(cm³·mol⁻¹·GPa⁻¹)	m/(mol·kg⁻¹)	(u − u₁)/(m·s⁻¹)	φₖ/(cm³·mol⁻¹·GPa⁻¹)
						L-Tryptophan (204.23)							
25	0.01886	2.219	−33.792	0.03596	4.190	−33.051	45	0.01885	1.735	−15.254	0.03611	3.329	−15.033
	0.02188	2.572	−33.730	0.04126	4.801	−32.916		0.02190	2.025	−15.419	0.04142	3.831	−15.113
	0.02591	3.036	−33.489	0.04588	5.327	−32.743		0.02600	2.397	−15.205	0.04588	4.251	−15.132
	0.03063	3.580	−33.273					0.03082	2.839	−15.095			
35	0.01920	2.039	−24.511	0.03628	3.822	−23.879							
	0.02229	2.360	−24.326	0.04156	4.371	−23.745							
	0.02633	2.782	−24.147	0.04588	4.817	−23.598							
	0.03105	3.273	−23.974										
						L-Tyrosine (181.19)							
5	0.00133	0.212	−82.606	0.00180	0.256	−70.403	35	0.00165	0.138	−17.246	0.00200	0.183	−21.929
	0.00143	0.222	−79.967	0.00190	0.266	−69.266		0.00174	0.153	−19.749	0.00208	0.187	−20.947
	0.00152	0.232	−78.138	0.00199	0.276	−68.395		0.00183	0.164	−20.778	0.00216	0.199	−22.006
	0.00161	0.246	−77.817	0.00208	0.283	−66.430		0.00192	0.176	−21.936			
	0.00171	0.252	−74.454	0.00216	0.272	−59.389	45	0.00142	0.102	−9.370	0.00184	0.148	−14.513
15	0.00141	0.153	−40.961	0.00182	0.224	−49.873		0.00151	0.117	−12.712	0.00192	0.156	−14.988
	0.00150	0.163	−41.332	0.00191	0.238	−51.138		0.00160	0.121	−11.727	0.00200	0.168	−16.500
	0.00158	0.171	−40.461	0.00199	0.252	−52.377		0.00168	0.129	−12.224	0.00208	0.183	−18.871
	0.00166	0.192	−45.225	0.00208	0.259	−51.142		0.00176	0.141	−13.993	0.00216	0.191	−18.912
	0.00175	0.213	−49.538	0.00216	0.267	−50.150							
25	0.00134	0.130	−28.237	0.00181	0.156	−21.543							
	0.00144	0.133	−25.770	0.00190	0.174	−24.942							
	0.00153	0.144	−26.675	0.00199	0.182	−24.742							
	0.00163	0.137	−20.637	0.00208	0.185	−23.524							
	0.00172	0.152	−23.032	0.00216	0.189	−22.413							

[a] Molecular masses are in parentheses.

1. These values were used to calculate the apparent molar volumes, ϕ_v, of the solutes using the following equation:

$$\phi_v = M_2/\varrho - (\varrho - \varrho_1)/(m\varrho\varrho_1) \quad (1)$$

where M_2 is the solute molar mass, m is the molality, ϱ is the density of the solution, and ϱ_1 is the density of the pure solvent. The ϱ_1 values at various temperature were taken from the table given by Kell (Kell, 1975). Values of 0.999964, 0.999100, 0.997045, 0.994032, and 0.990213 g·cm^{-3} were used as the density of pure water at 5, 15, 25, 35, and 45 °C, respectively. The calculated ϕ_v values are also given in Table 1.

The apparent molar adiabatic compressibilities, ϕ_k, of the solutes can be calculated using the equation:

$$\phi_k = M_2\kappa_s/\varrho - (\kappa_{s,1}\varrho - \kappa_s\varrho_1)/(m\varrho\varrho_1) \quad (2)$$

where κ_s and $\kappa_{s,1}$ are the adiabatic compressibilities of solution and pure solvent, respectively, and other symbols are as defined for eq 1. The adiabatic compressibility was determined from the sound velocity and density using the relation:

$$\kappa_s = 1/(u^2\varrho) \quad (3)$$

The sound velocity differences between solution and water $(u - u_1)$ and the ϕ_k values are given in Table 2. The sound velocities in pure water (u_1) were taken from the table reported by Del Grosso and Mader (Del Grosso and Mader, 1972). Values of 1426.162, 1465.931, 1496.687, 1519.808, and 1536.409 m·s^{-1} were used as the sound velocity in pure water at 5, 15, 25, 35, and 45 °C, respectively.

For sufficiently dilute solutions, the variation of the apparent molar quantities (ϕ_q) with molality can be adequately represented by the linear relation:

$$\phi_q = Q_2^\circ + S_q m \quad (4)$$

where Q_2° is the infinite dilution value that is equal to the partial molar quantity at infinite dilution and S_q is the experimental slope.

Eq 4 was fitted to our ϕ_v and ϕ_k data by the least-squares method outlined earlier (Sakurai et al., 1994). The V_2° and K_2° values together with their standard deviations are summarized in Tables 3 and 4, respectively, along with the concentration dependence of these thermodynamic functions S_v and S_κ. For Tyr the values of S_v and S_k could not be determined because of the very low solubility in water. Therefore, V_2° and K_2° values of Tyr are the mean values of ϕ_v and ϕ_k, respectively. For the purpose of comparison, the V_2° and K_2° values available in the literature are also included in Tables 3 and 4, respectively.

In general, the results obtained from the present study are in good agreement with the literature values within experimental uncertainties, except for the K_2° values for Tyr (Kharakoz, 1989). We are unable to give a satisfactory explanation for the origin of these discrepancies. It is worth noting, however, that Kharakoz estimated V_2° values of Tyr on the assumption of group additivity for the calculation of K_2°, whereas we used the V_2° values determined experimentally.

Figure 1 shows the temperature dependence of V_2° of amino acids. The features of V_2° of all amino acids studied in the temperature range 5−45 °C is similar to that of typical electrolytes, i.e., the values of $\partial V_2^\circ/\partial T$ are positive, and the values of $\partial^2 V_2^\circ/\partial T^2$ are negative (Hepler, 1969; Millero, 1971). This result suggests that the effects of the charged end groups of amino acids are the predominant factor for the feature of temperature dependence of V_2° of amino acids.

It is well-known that charged groups influence electrostatically surrounding water molecules, so called electrostriction. As a result, the electrostricted water is much less compressible than bulk water and leads to a large decrease in the compressibility of aqueous solution. Thus, the K_2° values of all amino acids are negative at all temperatures investigated.

The temperature dependence of K_2° of glycine and amino acids having aliphatic side chains is shown in Figure 2.

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

t/°C	V_2^o/ ($cm^3 \cdot mol^{-1}$)	S_v/ ($cm^3 \cdot kg \cdot mol^{-2}$)	V_2^o in references/($cm^3 \cdot mol^{-1}$)
		Glycine	
5	41.07 (0.01)[a]	1.18 (0.11)	
15	42.29 (0.02)	0.79 (0.18)	42.4;[b] 42.46[c]
25	43.19 (0.01)	0.09 (0.13)	43.3;[b] 43.26;[c] 43.19[d] 43.25;[e] 43.23[f]
35	43.81 (0.02)	−0.63 (0.17)	43.8[b]
45	44.00 (0.03)	1.43 (0.33)	
		L-Alanine	
5	58.64 (0.02)	1.88 (0.25)	
15	59.73 (0.01)	0.23 (0.17)	59.9;[b] 59.67[c]
25	60.52 (0.01)	−0.86 (0.17)	60.4;[b] 60.47;[c] 60.47[d] 60.45;[e] 60.50[f]
35	60.96 (0.02)	−0.73 (0.28)	60.9[b]
45	61.46 (0.02)	−1.41 (0.28)	
		L-Valine	
5	89.03 (0.01)	0.15 (0.16)	
15	89.96 (0.01)	0.11 (0.16)	90.08[g]
25	90.81 (0.08)	1.58 (0.93)	90.78;[d] 90.78;[f] 90.80;[g] 90.79[h]
35	91.51 (0.04)	−1.92 (0.44)	
45	91.93 (0.01)	−0.23 (0.16)	
		L-Leucine	
5	105.61 (0.04)	−2.94 (0.61)	
15	106.58 (0.01)	−0.13 (0.21)	106.81[g]
25	107.76 (0.01)	−0.66 (0.19)	107.74;[d] 107.73;[g] 107.57[h]
35	108.80 (0.04)	−1.86 (0.56)	
45	109.37 (0.01)	1.03 (0.18)	
		L-Isoleucine	
5	103.65 (0.01)	−0.15 (0.11)	
15	104.80 (0.01)	−0.51 (0.10)	104.90[g]
25	105.73 (0.02)	−0.29 (0.19)	105.76;[g] 105.45[h]
35	106.54 (0.02)	−0.52 (0.20)	
45	107.32 (0.02)	−0.79 (0.26)	
		DL-Methionine	
5	101.41 (0.05)	3.16 (0.57)	
15	103.89 (0.02)	−2.91 (0.20)	104.0[b]
25	104.83 (0.01)	0.77 (0.17)	105.2;[b] 105.35;[d] 105.3[h]
35	105.85 (0.02)	0.62 (0.29)	
45	106.51 (0.03)	4.20 (0.34)	
		L-Phenylalanine	
5	118.28 (0.03)	3.32 (0.37)	
15	120.43 (0.02)	−2.52 (0.30)	120.3[b]
25	121.50 (0.02)	2.24 (0.24)	121.7;[b] 121.48;[d] 121.92[h]
35	122.77 (0.01)	2.54 (0.18)	
45	123.90 (0.05)	1.89 (0.67)	
		L-Proline	
5	80.43 (0.02)	1.41 (0.22)	
15	81.57 (0.01)	0.80 (0.16)	
25	82.50 (0.01)	0.50 (0.15)	82.5;[b] 82.83;[d] 82.65;[h] 82.87[h]
35	83.22 (0.02)	1.00 (0.22)	
45	83.86 (0.04)	0.62 (0.48)	
		L-Tryptophan	
5	139.62 (0.06)	4.97 (1.54)	
15	141.38 (0.01)	0.41 (0.32)	141.6[b]
25	143.38 (0.03)	1.58 (0.72)	143.7;[b] 143.91;[d] 144.0[h]
35	144.66 (0.04)	7.00 (1.07)	
45	145.43 (0.06)	17.92 (1.73)	
		L-Tyrosine	
5	118.47 (0.29)	−[i]	
15	120.92 (1.74)	−	
25	124.33 (0.37)	−	123[h]
35	126.63 (0.54)	−	
45	127.48 (0.53)	−	

[a] Standard deviations are in parentheses. [b] Kharakoz (1989). [c] Hakin et al. (1994). [d] Millero et al. (1978). [e] Jolicoeur and Boileau (1978). [f] Ogawa et al. (1984). [g] Duke et al. (1994). [h] Jolicoeur et al. (1986). [i] S_v values could not be determined as described in the text.

Table 4. Partial Molar Adiabatic Compressibilities of Amino Acids in Dilute Aqueous Solutions at 5, 15, 25, 35, and 45 °C

t/°C	K_2^o/($cm^3 \cdot mol^{-1} \cdot GPa^{-1}$)	S_k/($cm^3 \cdot kg \cdot mol^{-2} \cdot GPa^{-1}$)	K_2^o in references/ ($cm^3 \cdot mol^{-1} \cdot GPa^{-1}$)
		Glycine	
5	−35.28 (0.05)[a]	6.12 (0.63)	
15	−31.66 (0.04)	5.24 (0.54)	−31.3[b]
25	−26.50 (0.10)	0.91 (1.24)	−26.6;[b] −27.00;[c] −27.16[d]
35	−23.59 (0.05)	1.94 (0.57)	
45	−21.56 (0.12)	2.69 (1.57)	
		L-Alanine	
5	−39.78 (0.07)	11.43 (0.83)	
15	−31.01 (0.07)	6.22 (0.92)	−30.4[b]
25	−25.16 (0.07)	3.87 (0.81)	−25.1;[b] −25.56;[c] −24.74[d]
35	−20.87 (0.11)	−1.78 (1.33)	
45	−17.85 (0.18)	−4.98 (2.34)	
		L-Valine	
5	−51.78 (0.09)	12.75 (1.11)	
15	−38.90 (0.07)	5.60 (0.89)	−37.8[b]
25	−29.82 (0.04)	6.79 (0.55)	−28.8;[b] −30.62;[c] −30.43[d]
35	−23.56 (0.04)	6.59 (0.46)	
45	−18.23 (0.13)	5.15 (1.57)	
		L-Leucine	
5	−61.25 (0.16)	27.49 (2.73)	
15	−43.95 (0.06)	17.16 (0.87)	−43.0[b]
25	−31.59 (0.03)	13.15 (0.49)	−30.5;[b] −31.78[c]
35	−21.70 (0.12)	2.02 (1.85)	
45	−16.35 (0.08)	19.46 (1.15)	
		L-Isoleucine	
5	−59.67 (0.10)	16.99 (1.22)	
15	−43.37 (0.04)	9.05 (0.48)	
25	−32.10 (0.04)	8.95 (0.46)	−30.3[b]
35	−23.43 (0.02)	4.16 (0.22)	
45	−16.83 (0.11)	1.46 (1.33)	
		DL-Methionine	
5	−60.19 (0.15)	26.36 (1.80)	
15	−44.15 (0.09)	14.36 (1.07)	−41.3[b]
25	−32.53 (0.09)	16.79 (1.00)	−30.6;[b] −31.18[c]
35	−23.75 (0.05)	7.74 (0.59)	
45	−18.14 (0.07)	11.47 (0.79)	
		L-Phenylalanine	
5	−68.29 (0.11)	38.41 (1.38)	
15	−50.14 (0.08)	24.21 (1.08)	−46.7[b]
25	−35.28 (0.04)	19.83 (0.47)	−33.7;[b] −34.54[c]
35	−24.18 (0.06)	7.41 (0.75)	
45	−17.70 (0.12)	12.39 (1.52)	
		L-Proline	
5	−44.14 (0.04)	14.91 (0.42)	
15	−32.96 (0.05)	12.65 (0.59)	
25	−24.11 (0.04)	6.10 (0.45)	−23.4;[b] −23.25[c]
35	−18.14 (0.03)	3.68 (0.34)	
45	−15.19 (0.04)	3.28 (0.40)	
		L-Tryptophan	
5	−66.46 (0.16)	78.72 (4.32)	
15	−48.00 (0.08)	58.51 (2.24)	−44.8[b]
25	−34.49 (0.08)	38.44 (2.14)	−30.5;[b] −30.24[c]
35	−24.98 (0.09)	30.14 (2.26)	
45	−15.35 (0.17)	5.89 (4.51)	
		L-Tyrosine	
5	−72.69 (7.14)	−[e]	
15	−47.22 (4.67)	−	−40[b]
25	−24.15 (2.34)	−	−34[b]
35	−20.66 (1.67)	−	
45	−14.38 (3.08)	−	

[a] Standard deviations are in parentheses. [b] Kharakoz (1991). [c] Millero et al. (1978). [d] Ogawa et al. (1984). [e] S_k values could not be determined as described in the text.

With increasing side chain length, the K_2^o values decrease at lower temperature, are practically constant between 30 and 35 °C, and increase at higher temperature. This feature is similar to that observed for a series of *n*-alcohols (Hoiland, 1980; Nakajima et al., 1975; Sakurai et al., 1995).

The large temperature dependence of K_2^o for the amino acids having more hydrophobic side chains results from the

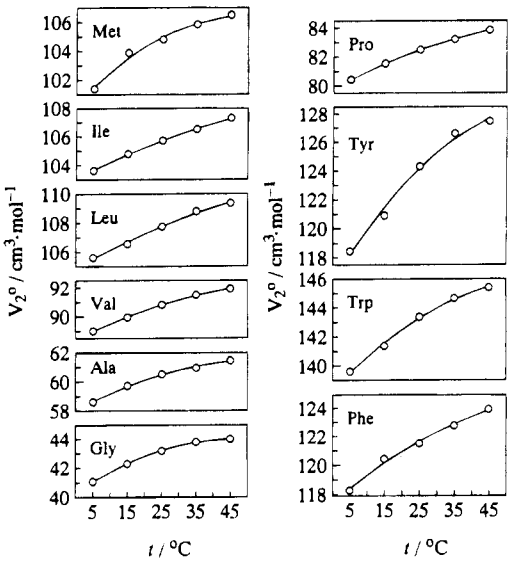

Figure 1. Temperature dependence of the partial molar volumes of amino acids in dilute aqueous solution.

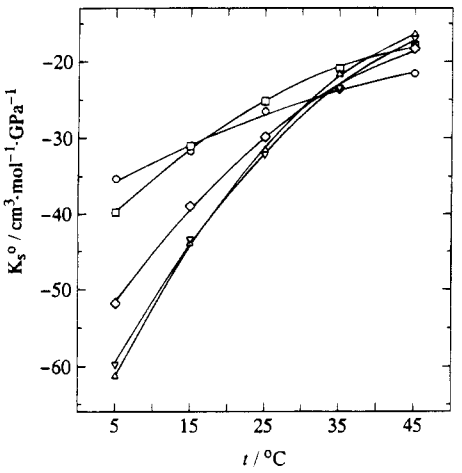

Figure 2. Temperature dependence of the partial molar adiabatic compressibilities of amino acids containing aliphatic side chains in dilute aqueous solution: ○, glycine; □, L-alanine; ◇, L-valine; ▽, L-leucine; and △, L-isoleucine.

fact that the sign of a methylene or methyl group contribution to the partial molar adiabatic compressibility changes with temperature: large negative at lower temperatures and positive at higher temperatures (Nakajima et al., 1975; Sakurai et al., 1995).

The concentration dependence of the partial molar quantities of solutes in aqueous solutions has been interpreted in terms of the solute–solute interactions. Unfortunately, the variation of S_v or S_k with temperature or the solute species (Tables 1 and 2) shows some scatter. This may be due to relatively low concentrations studied here, and hence we could not obtain very credible values of S_v and S_k to give a detailed discussion.

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