# Partial Molar Volumes and Isentropic Compressibilities of *N*-Acetyl Amino Acid Amides in Dilute Aqueous Solutions at (5, 15, 25, 35, and 45) °C

## Masayuki Kikuchi,\* Masao Sakurai, and Katsutoshi Nitta

Division of Biological Sciences, Graduate School of Science, Hokkaido University, Sapporo 060, Japan

The densities and sound velocities in dilute aqueous solutions of nine *N*-acetyl amino acid amides were measured at (5, 15, 25, 35, and 45) °C. The *N*-acetyl amino acid amides used were *N*-acetylglycinamide, *N*-acetyl-L-alaninamide, *N*-acetyl-L-valinamide, *N*-acetyl-L-leucinamide, *N*-acetyl-L-methioninamide, *N*-acetyl-L-prolinamide, *N*-acetyl-L-phenylalaninamide, *N*-acetyl-L-tryptophanamide, and *N*-acetyl-L-tyrosinamide. Partial molar volumes and partial molar isentropic compressibilities of these *N*-acetyl amino acid amides at infinite dilution were evaluated. Furthermore, the side chain contribution to the partial molar quantities of the *N*-acetyl amino acid amides can be derived using a group additivity approach. The results were compared with those of amino acids reported in our previous paper.

#### Introduction

In order to obtain a better understanding of the hydration behavior of proteins, studies have been made on the volumetric properties of amino acids, considered as model compounds, in aqueous solution (Jolicoeur and Boileau, 1978; Jolicoeur *et al.*, 1986; Kharakoz, 1989, 1991; Millero *et al.*, 1978). However, since amino acids are zwitterions in aqueous solutions, the charged end groups may interfere with the hydration of adjacent amino acid side chains. Thus it seems that the amino acids are not necessarily the most suitable compounds to model the amino acid side chain in proteins.

Hydration effects are known to be very sensitive to temperature (Kharakoz, 1989, 1991; Sakurai *et al.*, 1994). While the temperature dependence studies of volumetric properties are useful for a more complete understanding of the solute hydration, the great majority of previous investigations of model compounds has been conducted only at 25 °C.

In view of the above fact, it is of interest to determine the volumetric properties of *N*-acetyl amino acid amides which have no ionic groups as reasonable model compounds and compare the results with those of amino acids.

Volumetric data for amino acids that can be compared have been reported in dilute aqueous solutions at (5, 15, 25, 35, and 45) °C (Kikuchi *et al.*, 1995). In the present paper we report the partial molar volumes and isentropic compressibilities of some *N*-acetyl amino acid amides in dilute aqueous solution over the same experimental temperature range as our previous investigation, (5 to 45) °C.

### **Experimental Section**

The *N*-acetyl amino acid amides used, *N*-acetyl-glycinamide (Ac-Gly-NH<sub>2</sub>), *N*-acetyl-L-alaninamide (Ac-Ala-NH<sub>2</sub>), *N*-acetyl-L-valinamide (Ac-Val-NH<sub>2</sub>), *N*-acetyl-L-leucinamide (Ac-Leu-NH<sub>2</sub>), *N*-acetyl-L-methioninamide (Ac-Met-NH<sub>2</sub>), *N*-acetyl-L-prolinamide (Ac-Pro-NH<sub>2</sub>), *N*-acetyl-Lphenylalaninamide (Ac-Phe-NH<sub>2</sub>), *N*-acetyl-L-tryptophanamide (Ac-Trp-NH<sub>2</sub>), and *N*-acetyl-L-tryptophanamide (Ac-Trp-NH<sub>2</sub>), and *N*-acetyl-L-tyrosinamide (Ac-Tyr-NH<sub>2</sub>), were extra pure reagents obtained commercially: *N*-acetyl-glycinamide was obtained from Aldrich Chemical Co., Inc., Milwaukee, WI; *N*-acetyl-L-tyrosinamide was obtained from Peptide Institute, Inc., Minoh, Japan. The other compounds were obtained from BACHEM Feinchemikalien AG, Bubendorf, Switzerland. These samples were dried in vacuo before the measurements and used without further purification. All solutions were prepared by mass with deionized and distilled water. The solution densities were measured by an oscillating-tube densimeter (DMA 60/ 601, Anton Paar, Austria) with a precision of  $\pm$  (2  $\times$  10<sup>-6</sup>) g·cm<sup>-3</sup>. The sound velocities in the solutions were measured at a frequency of about 5 MHz using a sing-around velocimeter constructed in our laboratory. The precision of the measurements of the sound velocity was estimated to be better than 1  $\text{cm}\cdot\text{s}^{-1}$  for the dilute solution range studied. The temperature of the fluid surrounding the measuring cell of the densimeter or velocimeter was maintained within  $\pm 0.002$  deg by using a laboratory-made temperature controller using Y-cut quartz. 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 Ac-Phe-NH<sub>2</sub>, Ac-Trp-NH<sub>2</sub>, and Ac-Tyr-NH<sub>2</sub>, the measurements of the densities and sound velocities of all *N*-acetyl amino acid amide solutions were carried out over the concentration range *ca*. (0.01–0.1) mol·kg<sup>-1</sup>. Because of the low solubilities of Ac-Phe-NH<sub>2</sub>, Ac-Trp-NH<sub>2</sub>, and Ac-Tyr-NH<sub>2</sub> in water, the maximum concentration of Ac-Phe-NH<sub>2</sub> was about 0.05 mol·kg<sup>-1</sup>, and those of Ac-Trp-NH<sub>2</sub> and Ac-Tyr-NH<sub>2</sub> were about 0.01 mol·kg<sup>-1</sup>. For *N*-acetyl-L-isoleucinamide, owing to the low solubility in water, it was impossible to measure the densities and sound velocities.

#### **Results and Discussion**

The apparent molar volumes,  $V_{\phi}$ , and the apparent molar isentropic compressibilities,  $K_{s,\phi}$ , of the solutes were calculated from the solution densities and the isentropic compressibilities using the following equations:

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

and

$$K_{\mathrm{s},\phi} = M_2 \kappa_{\mathrm{s}} / \rho - (\kappa_{\mathrm{s},1} \rho - \kappa_{\mathrm{s}} \rho_1) / (m \rho \rho_1) \tag{2}$$

In eqs 1 and 2,  $M_2$  is the solute molar mass, *m* is the molality,  $\rho$  is the density of the solution, and  $\rho_1$  is the density of the pure solvent. In eq 2,  $\kappa_s$  and  $\kappa_{s,1}$  are the

Table 1.	Density	Differences and Ap	parent Molar Volu	mes for Aqueous	s Solutions of <b>I</b>	N-Acetyl Acid Aı	nides at (5, 1	15, 25,
35, and 4	5) °C Č	-	-	-		U U		

	, .												
400	<i>m</i> /mol·	$\frac{10^3}{( ho -  ho_1)/}$	$V_{\phi}$	<i>m</i> /	$\frac{10^3}{( ho -  ho_1)/}$	$V_{\phi}$	490	<i>m</i> /	$\frac{10^3}{( ho -  ho_1)/}$	$V_{\phi}$	<i>m</i> /	$\frac{10^3}{( ho -  ho_1)/}$	$V_{\phi}/$
U'C	Kg 1	g·cm <sup>3</sup>	cm <sup>3</sup> ·mol <sup>-1</sup>	mol·kg <sup>1</sup>	g·cm <sup>3</sup>	cm <sup>3</sup> ·mol <sup>-1</sup>	#C	mol·kg 1	g·cm <sup>3</sup>	cm <sup>3</sup> ·mol <sup>-1</sup>	mol·kg <sup>1</sup>	g·cm <sup>3</sup>	cm <sup>3</sup> ·mol <sup>-1</sup>
5	0 011 74	0 325	88.41	0.060.33	N- 1 664	Acetylglycin 88 39	amide 35	$(116.12)^a$ 0.015.04	0 370	91.85	0 082 61	2 040	91.63
0	0.021 22	0.588	88.35	0.071 76	1.978	88.37	00	0.026 68	0.658	91.81	0.093 37	2.307	91.59
	0.031 21	0.863	88.38	0.082 43	2.271	88.36		0.042 08	1.039	91.73	0.103 46	2.557	91.57
	0.040 20	1.111	88.38	0.092 72	2.554	88.35		0.054 92	1.356	91.70	0.114 47	2.830	91.53
15	0.049 37	0.270	89.80	0.103 20	2.840	89.71	45	0.009 50	0.664	92.62	0.125 80	3.021	92.49
	0.020 27	0.533	89.82	0.072 30	1.902	89.69		0.054 73	1.317	92.60	0.138 79	3.332	92.47
	0.030 67	0.809	89.71	0.084 59	2.225	89.67		0.075 23	1.810	92.56	0.151 81	3.645	92.44
	0.039 84	1.051	89.69 89.67	0.095 93	2.522	89.66 89.64		0.093 26	2.242	92.53 92.52	0.164 15	3.940	92.41
25	0.009 61	0.245	90.80	0.071 50	1.816	90.75		0.100 00	21000	02.02			
	0.024 05	0.612	90.79	0.082 80	2.101	90.74							
	0.03726	0.947	90.82 90.78	0.093 85	2.380	90.74 90.72							
	0.040 00	1.552	90.77	0.100 20	2.004	00.72							
					<i>N</i> -	Acetvl-L-alan	ninami	de (130.2)					
5	0.100 59	2.388	106.20	0.053 37	1.272	106.23	35	0.100 59	2.158	109.03	0.051 77	1.117	109.01
	0.088 21	2.096	106.21	0.042 56	1.016	106.22		0.087 92	1.889	109.02	0.041 12	0.888	109.02
	0.075 78	1.803	106.21	0.033 08	0.792	106.17		0.074 94	1.614	109.01	0.032 17	0.695	109.05
15	0.100 59	2.301	107.15	0.051 79	1.194	107.09	45	0.100 59	2.110	109.86	0.051 72	1.096	109.74
	0.088 44	2.026	107.14	0.041 42	0.957	107.06		0.087 11	1.833	109.81	0.041 62	0.884	109.72
	0.075 26	1.727	107.13	0.032 39	0.750	107.04		0.074 09	1.564	109.77	0.032 47	0.690	109.75
25	0.100 59	2.226	107.12	0.053 14	1.184	108.03		0.002 19	1.314	109.78			
	0.088 24	1.956	108.07	0.042 21	0.942	108.03							
	0.075 52	1.676	108.08	0.032 84	0.735	107.99							
	0.063 77	1.418	108.07										
E	0 102 57	0 0 0 0	100.00	0.054.45	1 1 1 0 0	Acetyl-L-vali		le (158.2)	1 0 2 9	120.00	0.054.50	1 099	140.09
5	0.103 57	2.238	136.31	0.034 45	0.937	136.37	30	0.091 16	1.932	140.00	0.034 50	0.810	140.02
	0.078 15	1.691	136.33	0.033 32	0.723	136.41		0.078 30	1.465	140.00	0.033 47	0.629	140.03
15	0.066 04	1.430	136.34	0.050.07	1 107	107.00	45	0.066 02	1.236	140.02	0.050.00	1 0 1 0	141.05
15	0.103 57	2.120	137.54	0.053 97	1.107	137.63	45	0.103 57	1.851	141.27	0.056 20	1.012	141.25
	0.078 28	1.605	137.58	0.042 00	0.680	137.65		0.079 02	1.417	141.26	0.035 16	0.633	141.23
	0.066 09	1.355	137.62					0.067 19	1.208	141.26			
25	0.103 57	2.016	138.80	0.054 19	1.058	138.87							
	0.091 37	1.780	138.84	0.042 67	0.634	138.90							
	0.066 09	1.289	138.87	0.000 00	01011	100101							
					N-A	Acetyl-L-leuci	inamic	le (172.23)					
5	0.097 73	1.880	152.71	0.049 72	0.960	Ĭ52.78	35	0.097 73	1.528	157.19	0.050 69	0.797	157.23
	0.085 40	1.644	152.73	0.039 60	0.766	152.77		0.085 44	1.339	157.18	0.040 49	0.638	157.22
	0.072 96	1.405	152.75	0.030 81	0.597	152.77		0.073 29	0.970	157.21	0.031 40	0.494	137.20
15	0.097 73	1.736	154.32	0.049 81	0.888	154.38	45	0.097 73	1.423	158.85	0.051 21	0.754	158.80
	0.085 60	1.523	154.33	0.039 67	0.707	154.41		0.085 47	1.250	158.81	0.040 87	0.602	158.81
	0.072 78	1.295	154.35	0.030 75	0.549	154.42		0.073 52	1.080	158.78	0.031 65	0.467	138.81
25	0.097 73	1.624	155.76	0.050 52	0.843	155.82		0.002 10	0.011	100.70			
	0.085 81	1.428	155.77	0.040 46	0.677	155.81							
	0.073 33	1.221	155.79	0.031 38	0.524	155.85							
	0.001 03	1.027	155.00		N7 A .								
5	0.094 30	3,750	149.97	0.048 79	1.952	249.99	35	0.094 30	3.317	155.32	0.047 80	1.692	155.35
0	0.082 87	3.301	149.97	0.038 50	1.544	149.97		0.081 96	2.888	155.32	0.037 76	1.339	155.33
	0.070 94	2.830	149.97	0.029 79	1.197	149.94		0.070 26	2.481	155.32	0.029 17	1.035	155.36
15	0.059 48	2.376	149.99	0 0 4 8 00	1 973	151 80	45	0.058 75	2.077	155.34	0 0 4 8 25	1 666	156 60
15	0.034 30	3.134	151.93	0.048 55	1.486	151.85	45	0.034 30	2.833	156.66	0.048 25	1.313	156.69
	0.070 95	2.702	151.91	0.030 09	1.155	151.85		0.070 60	2.436	156.61	0.029 40	1.016	156.79
95	0.059 75	2.279	151.91	0.040.00	1 700	150 71		0.058 98	2.037	156.63			
23	0.094 30	3.435	153.68	0.048 60	1.782	153.71							
	0.071 56	2.615	153.69	0.029 70	1.092	153.71							
	0.059 68	2.185	153.70										
					N-Acet	yl-L-phenyla	lanina	mide (206.	25)				
5	0.048 38	1.909	166.47	0.026 89	1.067	166.39	35	0.048 38	1.661	172.45	0.026 31	0.909	172.34
	0.043 00	1.700	100.44	0.022 05	0.655	100.35		0.043 31	1.494	172.32	0.021 15	0.731	172.35
	0.032 00	1.270	166.37	0.010 11	0.000	100.00		0.031 60	1.092	172.31	5.010 #1	0.000	1, 2.02
15	0.048 38	1.814	168.56	0.027 03	1.017	168.59	45	0.048 38	1.593	174.43	0.026 82	0.890	174.28
	0.043 00	1.613	168.58 168.58	0.022.03	0.830 0.621	168.55		0.043 63	1.442	174.32	0.021 58	0.718	174.23
	0.032 05	1.205	168.57	0.010 47	0.021	100.33		0.032 20	1.069	174.24	0.010 91	0.302	174.32
25	0.048 38	1.734	170.51	0.026 53	0.954	170.53							
	0.042 97	1.541	170.51	0.021 41	0.772	170.46							
	0.031 71	1.140	170.31	0.010 17	0.001	170.00							

Tab	le 1. (Con	tinued)											
		10 <sup>3</sup>			10 <sup>3</sup>				10 <sup>3</sup>			10 <sup>3</sup>	
t∕°C	<i>m</i> /mol∙ kg⁻¹	$( ho -  ho_1)/$ g·cm <sup>-3</sup>	$V_{\phi}/$ cm <sup>3</sup> ·mol <sup>-1</sup>	<i>m</i> / mol∙kg <sup>−1</sup>	$( ho -  ho_1)/$ g·cm <sup>-3</sup>	$V_{\phi}$ / cm <sup>3</sup> ·mol <sup>-1</sup>	t/°C	<i>m</i> / mol·kg <sup>-1</sup>	$( ho -  ho_1)/$ g·cm <sup>-3</sup>	$V_{\phi}$ / cm <sup>3</sup> ·mol <sup>-1</sup>	<i>m</i> / mol·kg <sup>-1</sup>	$( ho -  ho_1)/$ g·cm <sup>-3</sup>	$V_{\phi}/$ cm <sup>3</sup> ·mol <sup>-1</sup>
					N-	Acetyl-L-pro	linami	de (156.2)					
5	0.107 20	3.425	123.82	0.053 09	1.704	123.88	35	0.107 20	3.084	127.62	0.052 50	1.519	127.67
	0.093 29	2.985	123.83	0.041 71	1.340	123.91		0.093 58	2.697	127.62	0.041 36	1.197	127.70
	0.079 62	2.550	123.85	0.032 64	1.049	123.92		0.079 61	2.297	127.64	0.032 45	0.939	127.72
	0.065 94	2.113	123.89					0.065 50	1.893	127.65			
15	0.107 20	3.292	125.16	0.052 60	1.626	125.16	45	0.107 20	3.009	128.72	0.052 90	1.494	128.74
	0.093 55	2.878	125.16	0.041 60	1.287	125.18		0.093 64	2.632	128.73	0.041 15	1.164	128.75
	0.079 56	2.451	125.16	0.032 54	1.009	125.13		0.079 67	2.245	128.71	0.032 35	0.916	128.74
	0.065 41	2.019	125.16					0.065 99	1.863	128.70			
25	0.107 20	3.183	126.39	0.052 75	1.576	126.41							
	0.093 80	2.789	126.39	0.041 64	1.246	126.39							
	0.079 53	2.369	126.39	0.032 61	0.977	126.38							
	0.065 71	1.961	126.39										
					N-Ac	etvl-L-trvpto	phana	mide (245.3	3)				
5	0.013 39	0.768	187.81	0.007 28	0.418	187.83	35	0.013 39	0.683	195.06	0.007 18	0.367	195.02
	0.011 88	0.681	187.81	0.005 79	0.333	187.66		0.011 91	0.608	194.99	0.005 72	0.291	195.20
	0.010 28	0.590	187.86	0.004 44	0.255	187.89		0.010 26	0.524	195.01	0.004 40	0.224	195.15
	0.008 68	0.498	187.88					0.008 62	0.440	194.98			
15	0.013 39	0.732	190.62	0.007 37	0.405	190.46	45	0.013 39	0.669	196.61	0.007 07	0.354	196.56
	0.011 83	0.648	190.57	0.005 92	0.325	190.44		0.011 82	0.592	196.50	0.005 64	0.283	196.46
	0.010 28	0.562	190.64	0.004 53	0.249	190.46		0.010 13	0.507	196.57	0.004 36	0.218	196.63
	0.008 77	0.480	190.60					0.008 51	0.427	196.54			
25	0.013 39	0.706	192.84	0.007 22	0.380	192.96							
	0.011 90	0.628	192.85	0.005 74	0.302	193.02							
	0.010 28	0.543	192.72	0.004 37	0.229	193.16							
	0.008 63	0.455	192.88										
					NL A	cetyl-i -tyro	sinami	da (999 91)					
5	0 011 06	0.582	169 49	0 007 01	0.369	169 55	35	0 011 06	0.520	175 89	0 006 29	0 294	176 15
0	0.010 15	0.534	169 57	0.007.01	0.316	169 51	00	0.009.96	0.520	175.00	0.000 20	0.204	175.84
	0.009.11	0.479	169.63	0.003 81	0.254	169 50		0.008 77	0.400	175.82	0.003 22	0.197	175.04
	0.008.03	0.473	169.67	0.004 01	0.204	100.00		0.007 50	0 354	175.02	0.004 10	0.107	170.00
15	0.011.06	0.556	171 99	0 006 98	0.350	172 14	45	0.011.06	0.507	177 58	0 007 00	0.321	177 59
10	0.010.10	0.508	171.00	0.006.02	0.304	171.89	10	0.010.10	0.463	177.54	0.005.92	0.271	177.61
	0.009.04	0.300	171.92	0.000 02	0 244	171.89		0.009.07	0.400	177.57	0.003 32	0.219	177.71
	0.007.96	0.401	171.00	0.001 01	0.211	171.00		0.008.01	0.369	177 47	0.00170	0.210	1,,,,1
25	0.011.06	0.537	173.92	0.006.91	0.337	173.88		5.000 01	0.000	1,,,1			
20	0.010 16	0.495	173.82	0.005 87	0.285	173.97							
	0.009 11	0.444	173.86	0.004 71	0.229	173.85							
	0.007 99	0.388	174.02	5.001.11	0.220	1.0.00							

<sup>a</sup> Molecular masses (g/mol) are in parentheses.

isentropic compressibilities of solution and pure solvent, respectively. The isentropic compressibility was determined from the sound velocity, *u*, and density using the following relation:

$$\kappa_{\rm s} = 1/(u^2 \,\rho) \tag{3}$$

The density differences between solution and pure water  $(\rho - \rho_1)$  at (5, 15, 25, 35, and 45) °C are given in Table 1. The  $\rho_1$  values at various temperatures were taken from the table given by Kell (1975). Values of (0.999 964, 0.999 100, 0.997 045, 0.994 032, and 0.990 213) g·cm<sup>-3</sup> were used as the density of pure water at (5, 15, 25, 35, and 45) °C, respectively. These values were used to calculate the apparent molar volumes,  $V_{\phi}$ , of the solutes using eq 1. The calculated  $V_{\phi}$  values are also given in Table 1.

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

The density values of the solution used for sound velocity measurements were calculated from  $V_2^\circ$  (partial molar volume at the infinite dilution) and  $S_v$  (experimental slope) values obtained by using eq 4 (see below) in the same manner reported previously (Sakurai *et al.*, 1994, 1995). These values were used to calculate the apparent molar isentropic compressibilities,  $K_{s,\phi}$ , of the solutes using eqs 2 and 3. The calculated  $K_{s,\phi}$  values are also given in Table 2. For sufficiently dilute solutions, the variation of the apparent molar quantities,  $Q_{\phi}$ , with molality can be adequately represented by the linear relation

$$Q_{\phi} = Q_{\phi}^{\circ} + S_{q}m \tag{4}$$

where  $Q_{\phi}^{*}$  is the infinite dilution value that is equal to the partial molar quantity at infinite dilution ( $Q_{2}^{\circ}$ ) and  $S_{q}$  is the experimental slope.

Equation 4 was fitted to our  $V_{\phi}$  and  $K_{s,\phi}$  data by the leastsquares method outlined earlier (Sakurai et al., 1994). The  $V_2^{\circ}$  and  $K_{s,2}^{\circ}$  values together with their standard deviations are summarized in Table 3 along with the concentration dependence of these thermodynamic functions  $S_v$  and  $S_k$ . The previously available  $V_2^{\circ}$  values at 25 °C are (90.56, 108.06, 139.00, and 126.51) cm<sup>3</sup>·mol<sup>-1</sup> for Ac-Gly-NH<sub>2</sub>, Ac-Ala-NH<sub>2</sub>, Ac-Val-NH<sub>2</sub>, and Ac-Pro-NH<sub>2</sub>, respectively (Leslie and Lilley, 1985). The previously available  $K_{s,2}^{\circ}$  values at 25 °C are (-1.99 and -0.72) cm<sup>3</sup>·mol<sup>-1</sup>·GPa<sup>-1</sup> for Ac-Gly-NH<sub>2</sub> and Ac-Ala-NH<sub>2</sub>, respectively (Hedwig and Hoiland, 1995). To our knowledge, no comparable  $V_2^{\circ}$  and  $K_{s,2}^{\circ}$  data can be found in the literature, except for the above values. For  $V_2^{\circ}$  values, the results obtained from the present study are in good agreement with those available in the literature. However, the corresponding comparison for  $K_{s,2}^{\circ}$ values reveals several differences. We currently have no explanation for these discrepancies in  $K_{s,2}^{\circ}$  values. For Ac-Trp-NH<sub>2</sub> and Ac-Tyr-NH<sub>2</sub>, the absolute values of  $S_k$  and its standard deviations are extraordinarily large. These are because these compounds have low solubilities in water, described in the Experimental Section, and as

Table 2.Sound Velocity Differences and Apparent Molar Isentropic Compressibilities for Aqueous Solutions of<br/>N-Acetyl Amino Acid Amides at (5, 15, 25, 35, and 45) °C

			Ks d			$K_{\rm s, 0}/\rm cm^{3}$ ·				$K_{s,\phi}$			$K_{\rm s}$ /cm <sup>3</sup>
	<i>m</i> /	$(u - u_1)/(u -$	cm <sup>3</sup> ·mol <sup>-1</sup> ·	<i>m</i> /	$(u - u_1)/(u -$	mol <sup>-1</sup> .		<i>m</i> /	$(u - u_1)/$	cm <sup>3</sup> ⋅mol <sup>-1</sup> ・	<i>m</i> /	$(u - u_1)/$	mol <sup>-1</sup> .
t/°C	mol∙kg <sup>−1</sup>	$m \cdot s^{-1}$	GPa <sup>-1</sup>	mol∙kg <sup>−1</sup>	$m \cdot s^{-1}$	GPa <sup>-1</sup>	t/°C	mol∙kg <sup>−1</sup>	$m \cdot s^{-1}$	GPa <sup>-1</sup>	mol∙kg <sup>-1</sup>	$m \cdot s^{-1}$	GPa <sup>-1</sup>
					N-Ac	etylglycin	amide	e (116.12) <sup>a</sup>					
5	0.010 32	0.730	-18.90	0.055 33	3.892	-18.62	35	0.012 58	0.542	4.25	0.061 67	2.695	3.77
	0.018 09	1.279	-18.89	0.065 73	4.613	-18.52		0.022 11	0.967	3.86	0.076 20	3.331	3.72
	0.026 37	1.858	-18.74	0.077 11	5.408	-18.47		0.029 70	1.291	4.00	0.086 15	3.774	3.64
	0.034 88	2.462	-18.81	0.089 05	6.227	-18.33		0.036 36	1.588	3.86	0.099 38	4.342	3.67
15	0.045 55	3.203	-18.63	0.101 13	7.056	-18.22	45	0.049 31	2.155	3.81	0.112 49	4.912	3.65
15	0.014 03	0.840	-8.89	0.003 91	3.810	-8.48 -8.40	45	0.008 /0	0.320	8.44 8.26	0.032 03	1.900	7.01
	0.025 55	2 118	-8.90	0.073.01	4.389	-8.49 -8.44		0.017 17	0.033	7 70	0.003 31	2.404	7.87
	0.046 81	2.793	-8.50	0.091 64	5.458	-8.47		0.021 20	1.185	8.02	0.096 35	3.632	7.77
	0.054 99	3.284	-8.54	0.101 14	6.014	-8.41		0.041 11	1.557	7.77	0.111 74	4.210	7.75
25	0.012 86	0.660	-1.61	0.068 13	3.466	-1.40							
	0.022 22	1.124	-1.19	0.077 10	3.919	-1.39							
	0.033 84	1.697	-0.92	0.086 71	4.415	-1.45							
	0.044 92	2.279	-1.30	0.095 57	4.862	-1.43							
	0.055 53	2.823	-1.37	0.104 23	5.296	-1.40							
					N-Ace	tvl-i -alar	inam	ide (130-2)					
5	0.100 59	8.867	-20.26	0.056 91	5.060	-20.82	35	0.100 59	5.594	5.78	0.057 37	3.189	5.82
	0.090 33	7.986	-20.44	0.048 07	4.281	-20.93		0.090 17	5.017	5.77	0.048 34	2.686	5.83
	0.078 78	6.980	-20.58	0.041 41	3.693	-21.01		0.078 90	4.382	5.83	0.041 69	2.318	5.81
	0.067 30	5.972	-20.68					0.067 56	3.749	5.86			
15	0.100 59	7.666	-9.35	0.056 89	4.370	-9.78	45	0.100 59	4.754	11.07	0.056 94	2.702	10.92
	0.090 01	6.877	-9.48	0.047 96	3.698	-9.98		0.090 02	4.255	11.05	0.048 03	2.279	10.91
	0.078 62	6.013	-9.54	0.041 35	3.198	-10.14		0.078 57	3.721	10.99	0.041 47	1.966	10.93
	0.067 22	5.150	-9.64					0.067 13	3.184	10.94			
25	0.100 59	6.601	-1.10	0.057 27	3.788	-1.43							
	0.089 94	5.913	-1.18	0.048 57	3.219	-1.51							
	0.078 48	5.1/1	-1.27	0.042 04	2.791	-1.58							
	0.007 39	4.447	-1.34										
					N-Ac	etyl-L-vali	inami	de (158.2)					
5	0.103 57	12.818	-28.94	0.058 07	7.258	-29.77	35	0.103 57	7.921	8.34	0.058 39	4.505	8.06
	0.092 46	11.470	-29.14	0.048 88	6.121	-29.94		0.092 85	7.111	8.31	0.049 29	3.810	8.01
	0.080 53	10.012	-29.32	0.042 17	5.287	-30.04		0.080 88	6.213	8.20	0.042 52	3.296	7.90
	0.068 64	8.557	-29.56		0.007	10.07	4.5	0.068 95	5.309	8.13	0.050.00	0.050	
15	0.103 57	11.017	-13.32	0.059 20	6.367	-13.97	45	0.103 57	6.732	15.75	0.058 89	3.859	15.55
	0.092 79	9.900	-13.49	0.049 87	0.072 1619	-14.04 -14.15		0.092 70	0.030 5 204	15.72	0.049 09	3.200 2 202	15.58
	0.061 30	7 490	-13.39 -13.78	0.043 02	4.042	-14.15		0.061 30	J.304 4 565	15.63	0.042 03	2.000	15.50
25	0.103 57	9.341	-1.00	0.059 28	5.398	-1.40		0.000 07	4.000	15.05			
~0	0.092 95	8.408	-1.13	0.050 10	4.570	-1.48							
	0.081 71	7.405	-1.20	0.043 24	3.952	-1.56							
	0.069 89	6.350	-1.31										
						المعام المعا		J. (179.99	<b>`</b>				
5	0 007 73	1/ 828	-38.83	0.055.96	7V-Ace 8 5 8 5	tyi-L-ieuci	25	de (172.23 0.007 73	) 8 002	8 60	0.055.17	5 074	8 39
5	0.037 73	13 201	-39.15	0.033 30	7 979	-40.00	33	0.037 73	7 964	8.63	0.033 17	1 279	8 27
	0.076 40	11.662	-39.49	0.040 86	6.301	-40.62		0.076 26	6.976	8.54	0.040 06	3.695	8.22
	0.065 69	10.047	-39.71					0.065 03	5.967	8.41			
15	0.097 73	12.422	-17.40	0.055 33	7.121	-18.33	45	0.097 73	7.453	18.33	0.055 78	4.310	17.84
	0.087 39	11.147	-17.67	0.046 77	6.034	-18.53		0.087 16	6.673	18.18	0.046 93	3.639	17.71
	0.076 62	9.806	-17.92	0.040 30	5.207	-18.63		0.076 56	5.890	17.99	0.040 43	3.141	17.64
	0.065 44	8.396	-18.10					0.065 81	5.072	17.93			
25	0.097 73	10.460	-2.26	0.055 21	5.977	-2.88							
	0.087 05	9.349	-2.45	0.046 62	5.063	-3.05							
	0.075 93	8.176	-2.59	0.040 22	4.377	-3.17							
	0.065 05	7.023	-2.73										
					N-Acety	/l-L-methi	onina	mide (190.	.3)				
5	0.094 30	11.888	-32.75	0.052 81	6.745	-33.99	35	0.094 30	7.377	6.68	0.052 55	4.148	6.35
	0.084 04	10.637	-33.12	0.044 71	5.724	-34.22		0.084 44	6.626	6.57	0.044 22	3.499	6.25
	0.073 00	9.266	-33.40	0.038 75	4.975	-34.49		0.073 09	5.744	6.51	0.038 15	3.020	6.25
	0.062 28	7.935	-33.75					0.062 17	4.897	6.42			
15	0.094 30	10.307	-16.64	0.052 02	5.751	-17.49	45	0.094 30	6.039	15.70	0.053 94	3.494	15.31
	0.083 91	9.205	-16.91	0.043 84	4.863	-17.74		0.084 58	5.422	15.67	0.045 48	2.953	15.24
	0.072 67	8.000	-17.16	0.037 87	4.202	-17.76		0.074 03	4.762	15.55	0.039 31	2.549	15.28
9 E	0.001.81	0.819	-17.32	0.059.70	4 704	9.01		0.063 49	4.098	15.43			
20	0.094 30	0.404 7 569	-1.39 -1.50	0.032 /9	4.704 7 027	-2.01 -2.16							
	0.073 29	6 574	-1 71	0.038 51	3 494	-2.28							
	0.062 40	5.615	-1.86	0.000 01	5,101	~.~0							

Tab	le 2. (Con	tinued)											
			$K_{s,\phi}$			$K_{s,\phi}/cm^3$ ·				$K_{\mathrm{s},\phi}$			$K_{\rm s,\phi}/{\rm cm^3}$
	<i>m</i> /	$(u - u_1)/$	cm³⋅mol <sup>−1</sup> ∙	<i>m</i> /	$(u - u_1)/(u - u_1)$	mol <sup>-1</sup> .		<i>m</i> /	$(u - u_1)/$	cm³∙mol <sup>−1</sup> •	<i>m</i> /	$(u - u_1)/$	mol <sup>-1</sup> .
t/°C	mol∙kg <sup>−1</sup>	$\mathbf{m} \cdot \mathbf{s}^{-1}$	GPa <sup>-1</sup>	mol∙kg <sup>−1</sup>	$\mathbf{m} \cdot \mathbf{s}^{-1}$	GPa <sup>-1</sup>	t/°C	mol∙kg <sup>−1</sup>	$\mathbf{m} \cdot \mathbf{s}^{-1}$	GPa <sup>-1</sup>	mol∙kg <sup>−1</sup>	$\mathbf{m} \cdot \mathbf{s}^{-1}$	GPa <sup>-1</sup>
					N-Acetyl-	L-phenyla	lanin	amide (206	6.25)				
5	0.048 38	6.905	-35.96	0.027 67	3.987 <sup>ँ</sup>	-37.06	35	0.048 38	4.325	8.17	0.028 09	2.502	8.32
	0.043 59	6.243	-36.34	0.023 27	3.358	-37.26		0.043 96	3.929	8.17	0.023 53	2.085	8.60
	0.038 14	5.470	-36.51	0.020 05	2.902	-37.56		0.038 70	3.449	8.31	0.020 23	1.790	8.68
	0.032 63	4.694	-36.87					0.033 21	2.958	8.34			
15	0.048 38	6.013	-18.14	0.027 61	3.455	-18.70	45	0.048 38	3.459	19.78	0.027 76	1.974	19.93
	0.043 73	5.440	-18.22	0.023 16	2.906	-18.90		0.043 90	3.149	19.63	0.023 31	1.653	20.03
	0.038 19	4.763	-18.42	0.019 92	2.506	-19.12		0.038 45	2.745	19.80	0.020 10	1.426	20.00
	0.032 62	4.077	-18.59					0.032 84	2.338	19.90			
25	0.048 38	5.092	-3.15	0.027 73	2.936	-3.49							
	0.043 78	4.619	-3.28	0.023 34	2.479	-3.68							
	0.038 33	4.045	-3.30	0.020 12	2.144	-3.88							
	0.032 75	3.468	-3.51										
					N-Ac	etvl-L-prol	inam	ide (156.2)					
5	0.107 20	12.154	-32.93	0.060 12	6.888	-33.80	35	0.107 20	7.659	1.45	0.060 26	4.313	1.45
	0.095 80	10.896	-33.19	0.050 66	5.819	-34.02		0.095 94	6.857	1.45	0.050 78	3.637	1.43
	0.083 12	9.481	-33.42	0.043 78	5.036	-34.15		0.083 22	5.948	1.47	0.043 82	3.139	1.44
	0.071 05	8.129	-33.68					0.071 18	5.090	1.47			
15	0.107 20	10.462	-18.20	0.060 14	5.927	-18.84	45	0.107 20	6.472	8.59	0.060 84	3.694	8.45
	0.095 59	9.356	-18.39	0.050 68	4.999	-18.92		0.096 22	5.815	8.56	0.051 39	3.125	8.40
	0.083 33	8.176	-18.55	0.043 73	4.316	-18.95		0.083 86	5.076	8.53	0.044 41	2.698	8.44
	0.071 08	6.984	-18.65					0.071 64	4.341	8.50			
25	0.107 20	8.798	-6.23	0.060 23	4.988	-6.66							
	0.095 76	7.880	-6.36	0.050 79	4.213	-6.74							
	0.083 42	6.881	-6.47	0.043 81	3.639	-6.81							
	0.071 19	5.883	-6.56										
					N-Acety	l-1 -trypto	nhana	mide (245	(3)				
5	0 013 63	1 933	-33.64	0 007 98	1 158	-35.95	35	0 013 63	1 181	12 41	0 007 95	0 707	11 12
Ŭ	0.012.32	1 755	-34.08	0.006 78	0.990	-36.53	00	0.012.33	1.082	11.81	0.006 74	0.611	10.09
	0.010.85	1.760	-35.19	0.005 85	0.865	-37.76		0.012.00	0.944	12.27	0.005 82	0.527	10.05
	0.009.33	1.350	-35.60	0.000 00	0.000	01.10		0.009.33	0.829	11 17	0.000 02	0.021	10.10
15	0.013.63	1 644	-1344	0 007 81	0 957	-14 74	45	0.013.63	1 016	20.29	0 007 97	0 590	20.58
10	0.012.23	1 476	-13.59	0.006.59	0.807	-14.73	10	0.012.39	0.914	20.20	0.006.76	0.508	19.93
	0.010.71	1 291	-13.50	0.005.68	0 700	-15.32		0.010.88	0.820	19 77	0.005.84	0.000	20.06
	0.009.22	1 117	-13.88	0.000 00	0.100	10.02		0.009.36	0.703	19.93	0.000 01	0.107	20.00
25	0.013.63	1 428	-0.35	0 007 98	0 860	-2.11		0.000 00	0.700	10.00			
~0	0.012 33	1.294	-0.47	0.006 75	0.726	-1.94							
	0.010.84	1 1 4 2	-0.65	0.005.84	0.623	-1.37							
	0.009 33	1.005	-2.02	0.000 01	0.020	1.07							
					MAco	wl_t_twroe	inom	ida (999 9/	1)				
5	0 011 06	1 256	-20.81	0 007 01	0 794	-20.57	35	0.011.06	0 726	17 98	0 006 48	0 413	19 14
Ŭ	0.010.19	1 165	-21.32	0.006.02	0.676	-19.93	00	0.010.00	0.661	17.00	0.005 52	0.348	19.52
	0.009.18	1 047	-21.02	0.005.13	0.572	-19.00		0.008 79	0 581	17.73	0.004 73	0.290	20.48
	0.008.07	0.915	-20.73	0.000 10	0.072	10.12		0.007 58	0.001	18.05	0.00170	0.200	20.10
15	0.011.06	1.038	-3.12	0.006 88	0.640	-2.61	45	0.011.06	0.668	21.92	0.006 40	0.371	23 33
10	0.010 12	0.946	-2.86	0.005 90	0.547	-2.48	10	0.010 02	0.605	21.92	0.005 39	0.308	23 77
	0 009 04	0.843	-2.69	0.005.05	0 466	-2.09		0.008.78	0.519	22.65	0 004 65	0.269	23 39
	0.007 93	0.740	-2.75	5.000 00	0.100	2.00		0.007 53	0.433	23 52	5.051 00	0.000	~0.00
25	0.011.06	0.901	7 03	0.006 71	0.548	6 90		5.557 00	0.100	~0.0~			
~0	0 010 19	0.834	6 47	0 005 74	0 467	7 11							
	0.008 97	0.730	7 08	0.004 91	0.396	7 48							
	0.007 82	0.637	7.01	5.001.01	0.000								

<sup>a</sup> Molecular masses (g/mol) are in parentheses.

the concentration ranges in this measurement are limited.

The temperature dependence of the partial molar volumes is equal to the partial molar expansibility  $E_2^{\circ}$  (= $(\partial V_2^{\circ}/\partial T)_p$ ). Table 4 shows the partial molar expansibilities of *N*-acetyl amino acid amides and amino acids (Kikuchi *et al.*, 1995) in dilute aqueous solution at 25 °C. The  $E_2^{\circ}$  values were estimated by the least-squares fitting to a quadratic equation. With the exception of tyrosine and *N*-acetyl tyrosinamide, Table 4 shows that  $E_2^{\circ}$  values for the *N*-acetyl amino acid amide derivative are larger than those for the amino acid derivative. The values of  $(\partial^2 V_2^{\circ}/\partial T^2)_p$  for *N*-acetyl amino acid amides are negative, similar to those of amino acids.

The  $K_{s,2}^{\circ}$  values for all the *N*-acetyl amino acid amides are small or negative within the temperature range (5 to

25) °C. *N*-Acetyl amino acid amides have two amide groups which are able to form hydrogen bonds with water. It has been considered that the hydrogen bonding leads to a decrease in the compressibility (Conway and Ayranci, 1988). Therefore, the small or negative  $K_{s,2}^{\circ}$  values of *N*-acetyl amino acid amides result from the hydrogen bonding interaction between the amide groups and water.

The  $K_{s,2}^{\circ}$  values for *N*-acetyl amino acid amides having aliphatic side chains are plotted in Figure 1 as a function of temperature. The feature of the temperature dependence of  $K_{s,2}^{\circ}$  for these compounds is as follows: with increasing side chain length, the  $K_{s,2}^{\circ}$  values decrease at lower temperatures, are practically constant between (30 and 35) °C, and increase at higher temperatures. This feature is similar to that observed for a series of amino

Table 3.	Partial	Molar Vo	olumes a	and Is	sentrop	oic	
Compress	sibilities	of N-Ac	etyl Ami	ino A	cid Am	ides	in
Dilute Aq	ueous S	olutions	at (5, 15	5, 25, 2	25, and	45)	°C

		$S_{\rm v}$	$K_{\rm s}^{\rm o}$	$S_{\mathbf{k}}$
	$V_2^{\circ}/$	cm <sup>3</sup> ·kg·	cm <sup>3</sup> ∙mol <sup>-1</sup> ∙	cm <sup>3</sup> ·kg·mol <sup>-2</sup> ·
t/°C	cm³∙mol <sup>−1</sup>	mol <sup>-2</sup>	GPa <sup>-1</sup>	GPa <sup>−1</sup>
		MAcotuloluci	inomido	
5	88 <i>1</i> 1(0 01) <sup>a</sup>	-0.54(0.15)	-19.05(0.04)	8 06(0 53)
15	80.76(0.02)	-1.07(0.23)	-8.68(0.04)	2 63(1 12)
25	00.84(0.02)	-1.11(0.12)	-1.10(0.11)	-254(121)
25 25	90.84(0.01) 01.97(0.01)	-1.11(0.13) 2 85 (0.19)	-1.19(0.11)	-2.34(1.31)
33 45	91.07(0.01) 02 70(0.01)	-2.63(0.12) -1.68(0.08)	7 06(0.00)	-2.93(0.02) -1.97(0.02)
45	92.70(0.01)	-1.08(0.08)	7.90(0.08)	-1.67(0.93)
		N-Acetyl-L-ala	ninamide	
5	106.22(0.02)	-0.13(0.24)	-21.54(0.05)	12.43(0.60)
15	107.03(0.02)	1.31(0.27)	-10.48(0.11)	11.34(1.29)
25	108.01(0.03)	0.80(0.32)	-1.88(0.02)	7.69(0.26)
35	109.00(0.03)	0.28(0.32)	5.90(0.05)	-1.19(0.63)
45	109.65(0.03)	2.09(0.34)	10.76(0.04)	3.15(0.45)
		N-Acetyl-L-va	linamide	
5	136.45(0.01)	-1.58(0.10)	-30.81(0.03)	18.12(0.36)
15	137.74(0.01)	-1.92(0.12)	-14.75(0.05)	13.79(0.60)
25	138.96(0.01)	-1.52(0.10)	-1.93(0.03)	8.80(0.34)
35	140.07(0.02)	-0.71(0.18)	7.67(0.04)	6.73(0.48)
45	141.27(0.03)	-0.06(0.31)	15.38(0.03)	3.64(0.40)
	(,	N7.4 ( 1 - 1	• • • •	
٣	150.04(0.00)	N-Acetyl-L-leu	cinamide	00 50/1 00
5 17	152.84(0.02)	-1.26(0.24)	-41.81(0.10)	30.50(1.20)
15	154.47(0.01)	-1.55(0.17)	-19.54(0.05)	21.59(0.69)
25	155.88(0.01)	-1.13(0.12)	-3.74(0.04)	15.02(0.54)
35	157.27(0.02)	-0.81(0.22)	7.87(0.03)	8.54(0.42)
45	158.75(0.04)	0.86(0.51)	17.15(0.07)	11.89(0.85)
	Λ	-Acetyl-L-meth	ioninamide	
5	149.99(0.02)	-0.19(0.27)	-35.61(0.06)	30.02(0.81)
15	151.86(0.02)	0.82(0.29)	-18.61(0.08)	20.53(1.03)
25	153.73(0.01)	-0.43(0.09)	-2.84(0.04)	15.27(0.49)
35	155.36(0.01)	-0.45(0.15)	5.93(0.04)	7.93(0.48)
45	156.61(0.10)	0.94(1.40)	14.87(0.07)	9.08(0.89)
	N-7	Acetyl-L-phenyl	alaninamide	
5	166.23(0.05)	5.10(1.33)	-38.56(0.12)	52,63(3,06)
15	168.57(0.03)	-0.04(0.71)	-19.63(0.09)	31.30(2.24)
25	170.52(0.05)	-0.15(1.19)	-4.18(0.12)	21.37(3.03)
35	172.23(0.09)	3.54(2.28)	8.87(0.13)	-14.98(3.24)
45	174.09(0.11)	5.99(2.86)	20.24(0.16)	-11.15(4.10)
	,	M A satural x mus	linemide	
F	199.07(0.09)	1 20(0 20)		10 1(0 66)
15	123.97(0.02) 195.17(0.01)	-1.30(0.20)	-33.00(0.00)	19.1(0.00) 19.4(0.67)
10	123.17(0.01) 126 41(0.01)	-0.07(0.17)	-19.30(0.00)	12.4(0.07)
20 25	120.41(0.01) 127.72(0.02)	-0.12(0.12) 1.05(0.21)	-7.21(0.03)	8.93(0.31)
35	127.73(0.02) 128 74(0.02)	-1.03(0.21) -0.10(0.24)	1.40(0.03) 8 20(0.02)	0.02(0.30)
45	120.74(0.02)	-0.19(0.24)	8.29(0.02)	2.04(0.20)
	N	-Acetyl-L-trypto	ophanamide	
5	187.83(0.10)	-0.55(9.07)	-39.96(0.49)	465(43.6)
15	190.39(0.10)	18.6(8.73)	-16.03(0.54)	201(48.5)
25	193.09(0.16)	-21.5(14.2)	-3.70(0.83)	250(74.1)
35	195.11(0.11)	-6.85(9.95)	8.71(0.72)	275(64.0)
45	196.50(0.10)	6.08(8.89)	19.70(0.73)	49.2(64.7)
		N-Acetvl-L-trve	osinamide	
5	169.63(0.16)	-7.26(17.2)	-18.96(0.82)	-204(88.8)
15	171.95(0.17)	1.75(18.7)	-1.63(0.23)	-129(25.4)
25	173.97(0.15)	-7.77(16.7)	7.48(0.57)	-61.3(62.4)
35	175.97(0.22)	-5.85(24.5)	20.93(1.02)	-304(112)
45	177.65(0.12)	-8.99(12.9)	25.49(0.59)	-329(64.3)
-	· · · /			· · · · · · · · · · · · · · · · · · ·

<sup>a</sup> Standard deviations are in parentheses.

acids and *n*-alcohols (Hoiland, 1980; Kikuchi *et al.*, 1995; Nakajima *et al.*, 1975; Sakurai *et al.*, 1995). The large temperature dependence of  $K_{s,2}^{\circ}$  for the *N*-acetyl amino acid amides having more hydrophobic side chains results from the fact that the sign of a methylene or methyl group contribution to the partial molar isentropic compressibility changes with temperature: large negative at lower temperatures and positive at higher temperatures (Nakajima *et al.*, 1975; Sakurai *et al.*, 1995).

The side chain contributions to the partial molar quantity  $(Q_2^{\circ})$  of the various *N*-acetyl amino acid amides can be derived from the difference between the properties of each

Table 4. Partial Molar Expansibilities of *N*-Acetyl Amino Acid Amides and Amino Acids in Dilute Aqueous Solutions at 25 °C

	$10^2 E_2^{\circ}$ /cm <sup>3</sup> ·mol <sup>-1</sup> ·K <sup>-1</sup>						
side chain	<i>N</i> -acetyl amino acid amide derivative	amino acid derivative <sup>a</sup>					
Gly	10(1) <sup>b</sup>	7(1)					
Ală	8(2)	6(2)					
Val	11(1)	7(1)					
Leu	14(1)	9(3)					
Met	16(2)	12(6)					
Pro	12(2)	8(1)					
Phe	19(3)	13(5)					
Trp	22(4)	14(4)					
Tyr	20(1)	23(11)					

<sup>*a*</sup> Based on  $V_2^{\circ}$  data for the amino acids from Kikuchi *et al.* (1995). <sup>*b*</sup> Standard deviations are in parentheses.



**Figure 1.** Temperature dependence of the partial molar isentropic compressibilities of *N*-acetyl amino acid amides containing aliphatic side chains in dilute aqueous solution: (circle) *N*-acetyl-glycinamide; (square) *N*-acetyl-L-alaninamide; (diamond) *N*-acetyl-L-valinamide; (triangle) *N*-acetyl-L-leucinamide. The solid lines represent the results of the approximation by the second polynominal.

N-acetyl amino acid amide and N-acetylglycinamide.

 $Q_2^{\circ}(\mathrm{Rn}) = Q_2^{\circ}(N$ -acetyl amino acid amide) –  $Q_2^{\circ}(N$ -acetylglycinamide) (5)

where  $Q_2^{\circ}(Rn)$  defines the side chain contribution to  $Q_2^{\circ}$  of the *N*-acetyl amino acid amide relative to the -H group of *N*-acetylglycinamide.

Values of  $V_2^{\circ}(Rn)$  and  $K_{s,2}^{\circ}(Rn)$  calculated using the  $V_2^{\circ}$ and  $K_{s,2}^{\circ}$  results for the *N*-acetyl amino acid amides are given in Table 5. For the purpose of comparison,  $V_2^{\circ}(Ra)$ and  $K_{s,2}^{\circ}(Ra)$  values, which were obtained from  $V_2^{\circ}$  and  $K_{s,2}^{\circ}$  data for amino acids (Kikuchi *et al.*, 1995) in the same manner as above, are also included in Table 5. Table 5 shows that there are differences between  $Q_2^{\circ}(Rn)$  and  $Q_2^{\circ}$ (Ra) values.

With the exception of the alanyl and prolyl side chains,  $Q_2^{\circ}(Ra)$  values are smaller than  $Q_2^{\circ}(Rn)$  values at various temperatures. It seems that these differences arise from the different interactions between the ionic groups in amino acids and the amide groups in *N*-acetyl amino acid amides with water. The amino acids in aqueous solution have two charged groups which influence electrostatically the surrounding water molecules. Electrostriction leads to a decrease in volume and compressibility (Desnoyers *et al.*, 1965; Kharakoz, 1991; Millero, 1971). Consequently, the

side				$K_{\rm s,2}^{\rm o}({\rm Rn})/$	$K_{\rm s,2}^{\circ}({\rm Ra})^{a}/$
chain		$V_2^{\circ}(\text{Rn})/$	$V_2^{\circ}(\mathrm{Ra})^a/$	cm³∙mol <sup>−1</sup> ∙	cm <sup>3</sup> ·mol <sup>-1</sup> ·
(R)	t/°C	cm³∙mol <sup>−1</sup>	cm³∙mol <sup>−1</sup>	GPa <sup>-1</sup>	GPa <sup>-1</sup>
Ala	5	17.81	17.57	-2.49	-4.50
	15	17.27	17.44	-1.80	0.65
	25	17.17	17.33	-0.69	1.34
	35	17.13	17.15	1.94	2.72
	45	16.95	17.46	2.80	3.71
Val	5	48.04	47.96	-11.76	-16.50
	15	47.98	47.67	-6.07	-7.24
	25	48.12	47.62	-0.74	-3.32
	35	48.20	47.70	3.71	0.03
	45	48.57	47.93	7.42	3.33
Leu	5	64.43	64.54	-22.76	-25.97
	15	64.71	64.29	-10.86	-12.29
	25	65.04	64.57	-2.55	-5.09
	35	65.40	64.99	3.91	1.89
	45	66.05	65.37	9.19	5.21
Met	5	61.58	60.34	-16.56	-24.91
	15	62.10	61.60	-9.93	-12.49
	25	62.89	61.64	-1.65	-6.03
	35	63.49	62.04	1.97	-0.16
	45	63.91	62.51	6.91	3.42
Phe	5	77.82	77.21	-19.51	-33.01
	15	78.81	78.14	-10.95	-18.48
	25	79.68	78.31	-2.99	-8.78
	35	80.36	78.96	4.91	-0.59
	45	81.39	79.90	12.28	3.86
Pro	5	35.56	39.36	-15.95	-8.86
	15	35.41	39.28	-10.88	-1.30
	25	35.57	39.31	-6.02	2.39
	35	35.86	39.41	-2.50	5.45
	45	36.04	39.86	0.33	6.37
Trp	5	99.42	98.55	-20.91	-31.18
•	15	100.63	99.09	-7.35	-16.34
	25	102.25	100.19	-2.51	-7.99
	35	103.24	100.85	4.75	-1.39
	45	103.80	101.43	11.74	6.21
Tyr	5	81.22	77.40	0.09	-37.41
-	15	82.19	78.63	7.05	-15.56
	25	83.13	81.14	8.67	2.35
	35	84.10	82.82	16.97	2.93
	45	84.95	83.48	17.53	7.18

<sup>*a*</sup> Based on  $V_2^{\circ}$  and  $K_2^{\circ}$  data for the amino acids from Kikuchi *et al.* (1995).

results suggest that the influence of the electrostriction of the charged groups in amino acids for the hydration of adjacent amino acid side chains appears to be greater than that of hydrogen bonding interaction of amide groups in *N*-acetyl amino acid amides.

For the alanyl and prolyl side chains, contrary to the features of difference between the values of  $Q_2^{\circ}(Rn)$  and  $Q_2^{\circ}(Ra)$  described above,  $Q_2^{\circ}(Ra)$  values are larger. In particular, the feature for the prolyl side chain is remarkable. However, at present we are unable to give a satisfactory explanation for the origin of these unique characteristics.

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#### **Literature Cited**

- Conway, B. E.; Ayranci, E. Structural Effects in The Partial Molar Volumes and Isentropic Compressibilities of Organic Bases and Their Conjugate Ions. J. Chem. Thermodyn. **1988**, 20, 9–27.
- Del Grosso, V. A.; Mader, C. W. Speed of Sound in Pure Water. J. Acoust. Soc. Am. 1972, 52, 1442-1446.
- Desnoyers, J. E.; Verrall, R. E.; Conway, B. E. Electrostriction in Aqueous Solutions of Electrolytes. *J. Chem. Phys.* **1965**, *43*, 243– 250.
- Hedwig, G. R.; Hoiland, H. Partial Molar Isentropic Pressure Coefficients of some N-acetyl Amino Acid and Peptide Amides at Infinite Dilution in aqueous solutions at the Temperature 298.15 K. J. Chem. Thermodyn. 1995, 27, 745–750.
- Hoiland, H. Partial Molal Volumes, Expansibilities, Compressibilities for Aqueous Alcohol Solutions Between 5 °C and 40 °C. J. Solution Chem. 1980, 9, 857–866.
- Jolicoeur, C.; Boileau, J. Apparent Molal Volumes and Heat Capacities of Low Molecular Weight Peptides in Water at 25 °C. Can. J. Chem. 1978, 56, 2707–2713.
- Jolicoeur, C.; Riedl, B.; Desrochers, D.; Lemelin, L. L.; Zamojska, R.; Enea, O. Solvation of Amino Acid Residues in Water and Urea-Water Mixtures: Volumes and Heat Capacities of 20 Amino Acids in Water and in 8 Molar Urea at 25 °C. J. Solution Chem. 1986, 15, 109–128.
- Kell, G. S. Density, Thermal Expansivity, and Compressibility of Liquid Water from 0° to 150 °C: Correlations and Tables for Atmospheric Pressure and Saturation Reviewed and Expressed on 1968 Temperature Scale. J. Chem. Eng. Data 1975, 20, 97–105.
- Kharakoz, D. P. Volumetric Properties of Proteins and Their Analogs in Diluted Water Solutions. 1. Partial Volumes of Amino Acids at 15–55 °C. Biophys. Chem. 1989, 34, 115–125.
- Kharakoz, D. P. Volumetric Properties of Proteins and Their Analogues in Diluted Water Solutions. 2. Partial Adiabatic Compressibilities of Amino Acids at 15–70 °C. J. Phys. Chem. 1991, 95, 5634–5642.
- Kikuchi, M.; Sakurai, M.; Nitta, K. Partial Molar Volumes and Adiabatic Compressibilities of Amino Acids in Dilute Aqueous Solutions at 5, 15, 25, 35, and 45 °C. J. Chem. Eng. Data 1995, 40, 935–942.
- Leslie, T. E.; Lilley, T. H. Aqueous Solutions Containing Amino Acids and Peptides. Part 20. Volumetric Behavior of Some Terminally Substituted Amino Acids and Peptides at 298.15 K. *Biopolymers* 1985, 24, 695–710.
- Millero, F. J. The Molal Volumes of Electrolytes. *Chem. Rev.* 1971, 71, 147–176.
- Millero, F. J.; Surdo, A. L.; Shin, C. The Apparent Molal Volumes and Adiabatic Compressibilities of Aqueous Amino Acids at 25 °C. *J. Phys. Chem.* **1978**, *82*, 784–792.
- Nakajima, T.; Komatsu, T.; Nakagawa, T. Apparent Molal Volumes and Adiabatic Compressibilities of *n*-Alkanols and  $\alpha, \omega$ -Alkane Diols in Dilute Aqueous Solutions at 5, 25, and 45 °C. II. Apparent Molal Adiabatic Compressibilities. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 788– 790.
- Sakurai, M.; Nakagawa, T. Densities of Dilute Solutions of Water in Benzene and in Methanol at 278.15, 288.15, 298.15, 308.15, and 318.15 K. Partial Molar Volumes V<sub>w</sub> and Values of ∂V<sub>w</sub>/∂T for Water in Benzene and in Methanol. J. Chem. Thermodyn. **1982**, 14, 269– 274.
- Sakurai, M.; Nakamura, K.; Takenaka, N. Apparent Molar Volumes and Apparent Molar Adiabatic Compressions of Water in Some Alcohols. Bull. Chem. Soc. Jpn. 1994, 67, 352–359.
- Sakurai, M.; Nakamura, K.; Nitta, K. Sound Velocities and Apparent Molar Adiabatic Compressions of Alcohols in Dilute Aqueous Solutions. J. Chem. Eng. Data 1995, 40, 301–310.

Received for review April 24, 1996. Accepted August 13, 1996.®

#### JE960147Z

<sup>®</sup> Abstract published in Advance ACS Abstracts, October 1, 1996.