Adiabatic Compressibilities and Related Parameters of some Amino Acids in Aqueous Solutions

J.S. Sandhu* and Urmila Kashyap

Department of Chemistry, Punjabi University, PATIALA 147 002

Adiabatic compressibilities and other related parameters have been calculated from the experimentally determined Ultrasonic velocities of aqueous solutions of some amino acids. The large negative values of apparent molar adiabatic compressibilities (ϕ_k) suggest that these amino acids are highly hydrated. The temperature dependence of ϕ_k hints towards decrease in hydration.

The compressibility data have been reported for a number of amino acids in aqueous solutions by various workers [1-5], but the temperature dependence has not received attention so far except the one by Lark *et.al.* [4] for glycine. In our earlier communication [6], we have reported temperature dependence of the viscosities of amino acids in aqueous solutions. In order to understand the interactions of these amino acids in aqueous solutions better, adiabatic copressibilities and related parameters are reported in this communication.

EXPERIMENTAL

The amino acids chosen are glycine (GLY), α-alanine (α-ALA), ß-amino-n-butyric acid (ß-ABA), α-amino-*i*-valeric acid (VAL), and α-amino-*n*-valeric acid (NOR). These amino acids are selected to observe the effect of increasing number of methylene groups and branching the alkyl chain.

The amino acid samples were of the purest commercially available quality. The sources and the method of drying of these amino acids have been mentioned in an earlier communication [6].

Ultrasonic velocities were measured using a ultrasonic interferometer F-81 (Mittal Enterprises) operating at a fixed frequency of 2 MHz. The temperature of the liquid was maintained constant to an accuracy of ±0.01°C by circulating water from a thermostat. The system was calibrated with pure water. The observed value of sound velocity (1496.67 $m.sec^{-1}$ at 298.15°K) is in good agreement with the literature value (1496.63 $m.sec^{-1}$) [7]. The reproducibility in measurements was found to be ±0.05 $m.sec.^{-1}$.

The apparatus used for the density measurements and the experimental procedure are similar to those described earlier [6]. The reproducibility in density measurements was found to be $\pm 3 \times 10^{-5}$ $g.cm^{-3}$.

RESULTS AND DISCUSSION

Various acoustic parameters have been calculated as follows:

Adiabatic compressibility (ß) has been calculated from the Ultrasonic velocity (u) using the equation:

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$$\beta = \frac{1}{u^2\rho} \quad \ldots (1)$$

where u and ρ are the ultrasonic velicity and density of the solution.

Molar sound velocity (R) has been calculated using the effective molecular weight (M) with the relation [8]:

$$R = (M/\rho)\, u^{1/3} \quad \ldots (2)$$

where

$$M = \frac{n_1 M_1 + n_2 M_2}{n_1 + n_2} \quad \ldots (3)$$

n_1 and n_2 are the number of moles of solute and solvent respectively and M_1 and M_2 are their molecular weights.

Specific accoustic impedance (Z) has been calculated using the equation:

$$Z = u\rho \quad \ldots (4)$$

Inter-molecular free length (L) has been obtained from the relation:

$$\beta = k.\, L^p \quad \ldots (5)$$

where k and p are temperature dependent constants [9].

Apparent molar adiabatic compressibilities (ϕ_k) of the amino acid solutions have been determined from the density (ρ) and adiabatic compressibility (β) of the solution using the equation:

$$\rho_k = \left(\frac{1000}{C}\right)\beta - \left(\frac{1000\,\rho}{C} - M\right)\frac{\beta_o}{\rho_o} \quad \ldots (6)$$

where ρ_o is the density of water, C the molarity, M the molecular weight of the solute and β_o is the adiabatic compressibility for water.

The results have been presented in Table 1. Each of these parameters have been plotted as a function of concentration. The plots for each parameter are found to be linear at a given temperature (plots not given). It is evident from Table 1 that the adiabatic compressibility decreases with increase in concentration of the amino acids as is observed in most of the electrolyte solutions. It shows that the solutions are becoming less compressible on adding the amino acids. The plots of R and Z *vs* concentrations have positive slopes, while those of L *vs* concentration have negative slopes. The compressibility of the amino acid solution decreases with concentration and hence, free length is found to decrease with increase in concentration of the amino acids.

The increase in the length of side chains of the amino acids has little effect on the values of above parameters. Similar behaviour at 298.15°K has been reported for the aqueous solutions of GLY, ALA and VAL by Chattopadhyay and Lahiri [10]. However, the temperature shows a significant effect; there is a marked increase in the values as the temperature is raised from 298.15° to 318.15°K.

The ϕ_k of the amino acids is a linear function of molar concentration. It may further be noted from Table 1 that the increase in concentration and temperature has the same effect on ϕ_k values. The values of ϕ_k are least-square fitted to the equation:

$$\phi_k = \phi_k^{\circ} + S_k C \quad \ldots (7)$$

Table 1

The values of Parameters of Amino acids

C mol.dm^{-3}	u m.sec^{-1}	$\beta \times 10^{6}$ bar^{-1}	$\phi_k \times 10^{4}$ cm^3.bar^{-1} mol^{-1}	R	Zx10^{5} cgs units	Lx10^{6} cm.mol^{-1}
GLY 298.15°K						
0.06213	1500.1	44.48	-27.35	207.0	1.499	0.4267
0.12409	1503.4	44.20	-26.55	207.4	1.505	0.4254
0.21535	1508.4	43.78	-26.57	208.1	1.514	0.4235
0.31852	1514.1	43.31	-26.31	208.9	1.525	0.4213
0.37694	1517.5	43.04	-26.31	209.4	1.531	0.4201
0.45112	1521.6	42.71	-26.08	209.9	1.539	0.4186
0.51945	1525.4	42.41	-25.81	210.4	1.546	0.4172
308.15°K						
0.06199	1523.5	43.26	-22.85	208.7	1.517	0.4261
0.12323	1526.6	43.00	-22.97	209.2	1.523	0.4249
0.21468	1531.0	42.63	-22.31	209.8	1.532	0.4232
0.31750	1536.2	42.21	-22.02	210.6	1.542	0.4213
0.37571	1539.2	41.97	-22.96	211.0	1.548	0.4202
0.45103	1543.0	41.67	-21.63	211.6	1.555	0.4188
0.51776	1546.3	41.41	-23.36	212.1	1.562	0.4175
318.15°K						
0.06235	1539.8	42.51	-19.59	210.2	1.528	0.4329
0.12369	1542.7	42.27	-19.73	210.7	1.533	0.4318
0.21386	1546.7	41.93	-19.28	211.4	1.542	0.4302
0.31627	1551.6	41.54	-19.14	212.1	1.552	0.4284
0.37424	1554.1	41.33	-18.79	212.5	1.557	0.4274
0.45029	1557.5	41.06	-18.33	213.1	1.564	0.4261
0.51571	1560.6	40.82	-18.14	213.6	1.570	0.4250
α-ALA 298.15°K						
0.06439	1500.9	44.44	-24.22	207.3	1.599	0.4265
0.11103	1504.1	44.19	-25.09	207.8	1.504	0.4254
0.22090	1511.0	43.65	-23.54	209.1	1.516	0.4229
0.34969	1519.7	43.00	-23.29	210.6	1.530	0.4199
0.45522	1526.7	42.49	-22.60	211.8	1.541	0.4175
0.56188	1535.4	41.99	-22.08	212.9	1.553	0.4152
308.15°K						
0.06323	1524.3	43.22	-20.90	209.0	1.518	0.4259
0.11103	1527.1	43.00	-20.29	209.5	1.523	0.4249
0.22025	1533.8	42.50	-19.57	210.8	1.534	0.4226
0.34859	1541.4	41.93	-18.79	212.2	1.547	0.4200
0.45386	1547.5	41.48	-18.19	213.4	1.558	0.4179
0.56003	1554.4	41.00	-18.07	214.6	1.569	0.4156
318.15°K						
0.06515	1540.8	42.46	-18.24	210.5	1.529	0.4326
0.11025	1543.4	42.26	-18.12	211.0	1.533	0.4317
0.21943	1549.5	41.80	-16.95	212.3	1.544	0.4296
0.34728	1556.5	41.28	-16.79	213.7	1.556	0.4271
0.45216	1562.5	40.84	-15.91	214.9	1.567	0.4250
0.55811	1568.5	40.41	-15.51	216.0	1.578	0.4230
β-ABA 298.15°K						
0.06194	1501.0	44.44	-19.31	207.4	1.499	0.4265
0.10557	1504.2	44.20	-20.07	208.1	1.504	0.4254
0.21141	1512.0	43.62	-20.25	209.7	1.516	0.4228
0.31445	1519.2	43.09	-19.21	211.2	1.527	0.4203
0.41592	1527.1	42.54	-19.16	212.8	1.539	0.4178
0.51456	1534.9	42.01	-18.98	214.3	1.551	0.4153
0.60902	1542.5	41.50	-19.00	215.7	1.562	0.4129

Table 1 Contd.

308.15°K						
0.06310	1524.5	43.21	-15.65	209.2	1.518	0.4259
0.10524	1527.4	43.00	-16.00	209.8	1.523	0.4249
0.21078	1534.2	42.50	-14.91	211.4	1.534	0.4226
0.31352	1541.1	42.01	-14.56	212.9	1.545	0.4203
0.41466	1548.1	41.52	-14.62	214.4	1.556	0.4181
0.51302	1554.7	41.07	-13.98	215.9	1.566	0.4159
0.62440	1562.4	40.55	-13.75	217.5	1.578	0.4135
318.15°K						
0.06148	1540.7	42.47	-12.41	210.7	1.528	0.4327
0.10485	1543.5	42.37	-12.59	211.4	1.533	0.4318
0.20999	1550.0	41.80	-11.98	219.9	1.543	0.4296
0.31228	1556.4	41.34	-12.10	214.4	1.554	0.4274
0.41306	1562.8	40.90	-11.60	215.9	1.564	0.4253
0.51109	1570.0	40.43	-12.12	217.4	1.576	0.4231
0.62945	1577.3	39.93	-11.54	219.1	1.588	0.4207
VAL 298.15°K						
0.04908	1501.6	44.42	-30.88	207.5	1.499	0.4264
0.09917	1506.8	44.06	-31.08	208.4	1.506	0.4248
0.15566	1512.2	43.68	-29.33	209.5	1.514	0.4231
0.21324	1517.6	43.30	-28.25	210.6	1.522	0.4213
0.27341	1523.7	42.89	-28.08	211.8	1.530	0.4194
308.15°K						
0.04893	1524.8	43.21	-23.88	209.2	1.518	0.4259
0.09886	1529.5	42.89	-24.17	210.1	1.524	0.4244
0.1509	1534.8	42.53	-24.13	211.2	1.532	0.4227
0.21257	1539.4	42.22	-21.21	212.3	1.539	0.4213
0.27255	1544.9	41.85	-21.42	213.4	1.547	0.4196
318.15°K						
0.04874	1541.2	42.46	-20.17	210.7	1.528	0.4326
0.09848	1545.3	42.18	-18.61	211.7	1.534	0.4313
0.15459	1549.5	41.89	-16.31	212.7	1.541	0.4300
0.21278	1554.2	41.57	-16.50	213.8	1.548	0.4285
0.27149	1558.6	41.28	-14.69	214.9	1.554	0.4271
NOR 298.15°K						
0.04319	1501.1	44.46	-30.71	207.4	1.498	0.4266
0.11117	1507.8	43.99	-29.31	208.7	1.508	0.4245
0.14853	1511.5	43.73	-29.08	209.4	1.513	0.4233
0.22207	1518.7	43.24	-27.72	210.8	1.523	0.4210
0.29298	1526.6	42.77	-27.17	212.2	1.532	0.4188
0.36383	1532.5	42.31	-26.56	213.5	1.542	0.4167
308.15°K						
0.04378	1524.4	43.24	-23.87	209.1	1.517	0.4260
0.11082	1530.4	42.83	-22.15	210.4	1.526	0.4241
0.14807	1533.8	42.60	-21.87	211.1	1.530	0.4231
0.22139	1540.2	42.17	-20.74	212.5	1.540	0.4211
0.29204	1546.8	41.74	-20.60	213.9	1.549	0.4191
0.36264	1552.3	41.37	-18.96	215.2	1.557	0.4173
318.15°K						
0.04452	1540.6	42.50	-16.44	210.6	1.527	0.4328
0.11040	1543.9	42.14	-15.47	211.9	1.535	0.4312
0.14749	1549.3	41.92	-16.30	212.6	1.540	0.4301
0.22053	1555.1	41.53	-15.47	214.0	1.548	0.4283
0.29091	1559.9	41.20	-13.40	215.3	1.556	0.4268
0.36118	1565.7	40.83	-13.14	216.4	1.564	0.4250

Table 2

The values of limiting Apparent Molar Adiabatic Compressibilities (ϕ_k°)± standard deviations (σ_k) of Amino acids

Literature values is included where available with reference

$[\phi_k^\circ \pm \sigma_k] \times 10^4$ cm^3.mol^{-1}.bar^{-1}		
298.15°K	308.15°K	318.15°K
GLY		
-27.2 ± 0.2	-23.2 ± 0.1	-20.0 ± 0.1
-27.19 [1]	-22.4 [4]	
-27.00 [2] (0.44)		
-25.0 ± 0.6 [3]		
-27.3 ± 0.12 [4]		
-27.0 ± 0.36 [5]		
α-ALA		
-25.0 ± 0.3	-21.0 ± 0.2	-18.6 ± 0.1
-26.80 [1]		
-25.3 ± 0.13 [2]		
-21.6 ± 0.5 [3]		
24.74 ± 0.18 [5]		
ß-ABA		
-20.0 ± 0.3	-16.0± 0.2	-12.5 ± 0.2
-18.7 ± 0.6[3]		
VAL		
-31.9 ± 0.5	-25.2 ± 0.9	-20.9 ± 0.7
30.62 ± 0.23 [2]		
-24.0 ± 0.2 [3]		
-30.43 ± 0.10 [5]		
NOR		
-30.9 ± 0.2	-24.0 ± 0.4	-17.2 ± 0.5

where ϕ_k° is the apparent molar adiabatic compressibility at infinite dilution and S_k is the experimental slope. The ϕ_k° values along with the standard errors, σ_k of the fit are listed in Table 2. The Table 2 also includes the literature values [1-5] for comparison. The compressibility data for NOR has not been reported in the literature, so comparison could not be done. It is evident from Table 2 that the ϕ_k° value of NOR is less negative than that of VAL. This may be due to the presence of unbranched side chain in NOR unlike the branched isopropyl side chain in VAL.

All the amino acids investigated have negative values of ϕ_k° and fall within the values for charged nitrogen compounds and carboxylate or hydroxy carboxylate ions. The negative values appear to be due to the presence of charged centres, particularly the carboxylate ions [3]. The large negative values of ϕ_k° indicate that they are highly hydrated [11]. Since the values of ϕ_k° are becoming less negative with temperature, it indicates that the hydration is decreasing with rise in temperature, which is in accordance with the earlier conclusion drawn from viscosity studies [6].

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