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Partial Molar Volumes, Expansibilities, and Compressibilities of α,ω-Aminocarboxylic Acids in Aqueous Solutions between 18 and 55 °C

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We have determined the apparent molar volumes, expansibilities, and adiabatic compressibilities of a homologous series of eight α,ω-aminocarboxylic acids within the temperature range 18–55 °C. We interpret the resulting data in terms of the hydration of the component aliphatic and charged atomic groups. From temperature-dependent studies, we find the total electrostriction of the noninteracting amino and carboxyl groups at 25 °C to be equal to −26 cm^3 mol^{-1}. We also evaluated the temperature dependences of both the density and the coefficient of adiabatic compressibility and interpreted these data in terms of hydrophobically and electrostatically perturbed solvent domains in the hydration shells of the aliphatic and charged atomic groups. We discuss the implications of our results for developing an understanding of the forces that stabilize/destabilize biologically important structures.

1. Introduction

Hydrophobic and charged atomic groups are components of almost every biologically important system. It is generally acknowledged that the hydration of such atomic groups plays an important role in the conformational stability of biopolymers.[1-3] Consequently, characterization of the hydration properties of both hydrophobic and charged groups should provide insights into the role of solute–solvent interactions associated with fundamental biopolymers phenomena such as folding–unfolding transitions, ligand interactions, etc.

Volumetric properties of solutes, such as the partial molar volume, compressibility, and expansibility, are known to be sensitive to the degree and nature of solute hydration.[4-10] Consequently, as part of efforts over the past two decades to understand hydration phenomena, a variety of volumetric measurements have been conducted on simple model compounds containing hydrophobic and/or charged atomic groups, including alcohols and diols,[6,11-15] mono- and dicarboxylic acids,[16-20] α-amino acids,[4,5,8,9,21-24] and α,ω-aminocarboxylic acids.[5,25-29]

At neutral pH, α,ω-aminocarboxylic acids exist as zwitterions containing two oppositely charged carboxyl and amino groups separated by a nonbranched chain of CH_2 groups: NH_3^+–$(CH_2)_n$–COO^-. There are obvious advantages for choosing α,ω-amino acids as model systems for studying hydration effects of charged and hydrophobic atomic groups: (i) they do not contain other atomic groups which might influence the hydration of the aliphatic and/or charged groups; (ii) the distance between the carboxyl and amino groups can be varied systematically by changing the number of aliphatic CH_2 groups in the molecule, thereby allowing one to study the interaction of the charged ends as a function of the distance between them; (iii) the presence of the two charged groups at the termini of the hydrophobic chain provides sufficient solubility of long homologs, a prerequisite for volumetric measurements.

A survey of the literature reveals reasonably good agreement between published values of partial molar volumes of α,ω-amino acids at 25 °C reported by different groups.[5,25-27,29] Shahidi and Farrell[27] have published the most complete data set on the partial molar volumes of α,ω-aminocarboxylic acids (from glycine to 11-aminoundecanoic acid) at 25 °C. These authors report an apparent decrease in the overall volume of the water caused by solute–solvent interactions associated with the independent hydration of the charged end groups. Such a contraction of water in the vicinity of charged groups due to solute–solvent interactions is called electrostriction. By comparing the partial molar volumes of α,ω-amino acid zwitterions with the corresponding uncharged hydroxyamides, these authors report average values of 16.2 ± 0.6 cm^3/mol[27] and 18.5 ± 0.4 cm^3/mol[25] for the total apparent electrostriction induced by hydration of the noninteracting charged end groups. The individual electrostriction contribution of the isolated NH_3^+ and COO^- groups has been estimated by Shahidi[28] to be 14.5 ± 1.7 and 4.5 ± 0.6 cm^3/mol, respectively. On the basis of these values of electrostriction, it has been proposed that when the charged groups are separated by five[25] or six[27] methylene groups, the two oppositely charged termini do not interfere with the hydration of each other or the hydration of the rest of the molecule.

Despite the significance of these previous studies, a complete understanding of such hydration phenomena requires determination of the partial molar expansibility and compressibility, in addition to the volume measurements. Such measurements are scarce. In fact, to our knowledge, the only previous report of partial molar expansibility and compressibility data on α,ω-amino acids is that of Cabani et al.[5] in which a series of short α,ω-amino acids from glycine to 6-aminohexanoic acid was investigated. However, the data derived from this study were insufficient to derive either the individual contributions of the independently hydrated CH_2 groups or the contribution of the noninteracting oppositely charged amino and carboxyl termini. Furthermore, since hydration effects in solutions are known to be strongly sensitive to temperature,[8,9] temperature-dependent studies of the partial molar volume, compressibility, and expansibility are required to develop a more complete understanding of solute hydration. Despite this recognition, few, if any, temperature dependence studies of the partial molar characteristics of α,ω-amino acids have been reported.

To address the deficiencies noted above and to gain a better understanding of the hydration of biologically ubiquitous charged and uncharged groups, we report here temperature-dependent determinations of the partial molar volume, expansibility, and compressibility of eight α,ω-amino acids within the temperature range 18–55 °C. We interpret the resulting data in terms of the hydration of the CH_2 methylene group and hydration of the charged amino and carboxyl groups.

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TABLE I: Relative Molar Increments of Sound Velocity, $[U]$, as a Function of Temperature, T, for the α,ω-Amino Acids

compound	$[U]$ (cm^3 mol^{-1}) 18 °C	25 °C	40 °C	55 °C
glycine	37.3 ± 0.2	35.3 ± 0.1	32.2 ± 0.2	30.1 ± 0.2
β-alanine	45.6 ± 0.2	43.0 ± 0.2	38.6 ± 0.3	36.1 ± 0.3
4-aminobutanoic acid	59.0 ± 0.2	55.1 ± 0.2	48.4 ± 0.3	46.0 ± 0.4
5-aminopentanoic acid	73.7 ± 0.3	67.9 ± 0.3	58.7 ± 0.4	55.5 ± 0.4
6-aminohexanoic acid	87.0 ± 0.3	79.9 ± 0.3	70.5 ± 0.4	63.9 ± 0.4
7-aminoheptanoic acid	99.3 ± 0.3	91.4 ± 0.3	78.4 ± 0.4	69.5 ± 0.4
8-aminooctanoic acid	111.2 ± 0.3	101.7 ± 0.4	85.5 ± 0.4	75.9 ± 0.4
11-aminoundecanoic acid	146.6 ± 0.6	132.0 ± 0.6	107.6 ± 0.6	92.9 ± 0.6

TABLE II: Apparent Molar Volumes, $\bar{V}$, as a Function of Temperature, T, for the α,ω-Amino Acids

compound	$\bar{V}$ (cm^3 mol^{-1}) 18 °C	25 °C	40 °C	55 °C
glycine	42.7 ± 0.2	43.2 ± 0.1	44.0 ± 0.2	44.2 ± 0.2
β-alanine	57.6 ± 0.3	58.3 ± 0.2	59.1 ± 0.3	59.2 ± 0.3
4-aminobutanoic acid	72.4 ± 0.3	73.1 ± 0.2	74.1 ± 0.3	73.7 ± 0.3
5-aminopentanoic acid	87.3 ± 0.3	88.3 ± 0.3	89.1 ± 0.4	88.7 ± 0.4
6-aminohexanoic acid	103.1 ± 0.3	104.3 ± 0.3	105.2 ± 0.4	105.2 ± 0.4
7-aminoheptanoic acid	118.6 ± 0.4	120.0 ± 0.4	121.3 ± 0.4	121.4 ± 0.4
8-aminooctanoic acid	134.2 ± 0.4	135.6 ± 0.4	136.9 ± 0.5	137.7 ± 0.4
11-aminoundecanoic acid	180.1 ± 0.6	182.6 ± 0.6	184.5 ± 0.7	186.9 ± 0.7

2. Experimental Section

All the α,ω-amino acids used in the studies reported here were of the highest purity commercially available and were used without further purification. Specifically, glycine, β-alanine, 4-aminobutanoic acid, 5-aminopentanoic acid, 6-aminohexanoic acid, 7-aminoheptanoic acid, 8-aminooctanoic acid, and 11-aminoundecanoic acid were purchased from Fluka (Buchs, Switzerland). Some of these α,ω-amino acids, namely 5-aminopentanoic acid, 7-aminoheptanoic acid, 8-aminooctanoic acid, and 11-aminoundecanoic acid, also were obtained from Sigma Chemical to evaluate if the sample varied with the source. Within the experimental accuracy of our measurements, no difference was detected between the two sets of data on the same compound from different sources.

Solutions of α,ω-amino acids were prepared with triply-distilled water which was degassed by boiling. The specific conductivity of the water used was less than 10^{-6} ohm^{-1} cm^{-1}. The concentrations of the samples were determined by weighing 10–20 mg of a solute material with a precision of ±0.03 mg and dissolving the sample in a known amount of water. Glycine, β-alanine, and 4-aminobutanoic acid were dried at 110 °C for 12 h prior to weighing. All other α,ω-amino acids were dried at room temperature under vacuum in the presence of phosphorus pentoxide for 72 h prior to weighing. To prevent formation of air bubbles, all solutions were preheated to 5 °C above the measuring temperature before placing them into the ultrasonic or densimetric cells.

All densities were measured using a vibrating tube densimeter (DMA-60, Anton Paar, Austria) with a precision of $\pm 1.5 \times 10^{-6}$ g/cm^3 at 18, 25, 40, and 55 °C. The apparent molar volume, ϕV, was calculated from the standard equation

$$\phi V = M/\rho - (\rho - \rho_0)/(\rho_0 \rho m) \qquad (1)$$

where M is the molecular weight of the solute, m is the molal concentration, and ρ and ρ_0 are the densities of the solution and solvent, respectively. Values for the density of water were taken from the work of Kell.[30]

The solution sound velocity values required to calculate the apparent molar adiabatic compressibility, ϕK_s, of a solute were measured at 18, 25, 40, and 55 °C using the resonator method[31-33] at a frequency of about 7.5 MHz. Ultrasonic resonator cells with sample volumes of 0.8 cm^3 were thermostated with an accuracy of ±0.01 °C, and a previously described differential technique was employed for all measurements.[32] In this technique, the difference between the sound velocities in the solution, U, and the neat solvent, U_0, was evaluated from the difference between the resonance frequencies of the ultrasonic cell filled with the solution, f_n, and the cell filled with solvent, f_{n0}, using the relationship[32]

$$(U - U_0)/U_0 = (f_n - f_{n0})/f_{n0}$$

where n denotes the number of the resonance used for the measurements. Theoretical analyses[34,35] have shown that for the type of resonators used in our studies the relative accuracy of the sound velocity measurements is about $\pm 10^{-4}$% at frequencies near 7.5 MHz.

Apparent molar adiabatic compressibility values for the solutes were calculated from the densimetric and ultrasonic data using the expression[9]

$$\phi K_s = \beta_{s0}(2\phi V - 2[U] - M/\rho_0) \qquad (2)$$

where β_{s0} is the coefficient of adiabatic compressibility of water, $[U]$ is the relative molar increment for the sound velocity of a solute and is equal to $(U - U_0)/(U_0 C)$, and C is the molar concentration. The coefficient of the adiabatic compressibility of water, β_{s0}, required to evaluate ϕK_s from eq 2 was calculated from the data on density[30] and sound velocity,[36] since $\beta_{s0} = (\rho_0 U_0^2)^{-1}$.

For each evaluation of ϕV or ϕK_s, three to five independent measurements were carried out within a concentration range of 1–3 mg/mL for all of the α,ω-amino acids, except 11-aminoundecanoic acid, for which concentrations close to 1 mg/mL were used due to its low solubility.

3. Results

Tables I–III show the relative molar increments of sound velocity, $[U]$, apparent molar volumes, ϕV, and apparent molar adiabatic compressibilities, ϕK_s, of eight α,ω-amino acids at 18, 25, 40, and 55 °C, respectively. Errors were estimated by taking into account uncertainties due to the concentration determination, temperature drifts, and apparatus limitations. The concentration dependences of the apparent molar volumes and compressibilities of the eight α,ω-amino acids are known to be negligible in the range of concentrations used in the present work.[5,27] Within the limits of experimental error, the apparent molar volumes, ϕV, and adiabatic compressibilities, ϕK_s, we have determined in the concentration range 1–3 mg/mL coincide with the values of the partial molar volume, $\bar{V}$, and the adiabatic compressibility, $\bar{K}_s$, obtained by extrapolation to infinite dilution.

The temperature dependences of the partial molar volumes, $\bar{V}$, and adiabatic compressibilities, $\bar{K}_s$, that we have measured can

TABLE III: Apparent Molar Adiabatic Compressibilities, $\bar{K}_s$, as a Function of Temperature, T, for the α,ω-Amino Acids

compound	$\bar{K}_s$ (10^{-4} cm^3 mol^{-1} bar^{-1})			
	18 °C	25 °C	40 °C	55 °C
glycine	−29.6 ± 0.4	−26.6 ± 0.2	−22.4 ± 0.4	−20.4 ± 0.4
β-alanine	−30.0 ± 0.4	−26.3 ± 0.4	−21.0 ± 0.5	−18.7 ± 0.5
4-aminobutanoic acid	−35.1 ± 0.4	−30.2 ± 0.4	−22.8 ± 0.6	−20.9 ± 0.6
5-aminopentanoic acid	−41.4 ± 0.5	−34.3 ± 0.5	−24.7 ± 0.7	−22.2 ± 0.7
6-aminohexanoic acid	−45.6 ± 0.5	−37.1 ± 0.5	−27.1 ± 0.8	−21.4 ± 0.7
7-aminoheptanoic acid	−49.1 ± 0.6	−39.6 ± 0.6	−26.1 ± 0.8	−18.4 ± 0.7
8-aminooctanoic acid	−52.1 ± 0.8	−41.1 ± 0.7	−24.9 ± 0.8	−16.1 ± 0.7
11-aminoundecanoic acid	−61.9 ± 1.0	−45.1 ± 1.0	−21.2 ± 1.2	−6.9 ± 1.2

TABLE IV: Partial Molar Expansibility, $\bar{E}$, as a Function of Temperature, T, for the α,ω-Amino Acids

compound	$\bar{E}$ (10^{-2} cm^3 mol^{-1} K^{-1})			
	18 °C	25 °C	40 °C	55 °C
glycine	8.5 ± 1.0	6.8 ± 1.0	3.2 ± 1.0	0 ± 1.0
β-alanine	10.6 ± 1.0	8.2 ± 1.0	3.1 ± 1.0	−2.0 ± 1.0
4-aminobutanoic acid	13.6 ± 1.5	9.8 ± 1.5	1.8 ± 1.5	−6.3 ± 1.5
5-aminopentanoic acid	14.9 ± 2.0	10.6 ± 2.0	1.5 ± 2.0	−7.6 ± 2.0
6-aminohexanoic acid	15.8 ± 2.0	11.9 ± 2.0	3.4 ± 2.0	−5.0 ± 2.0
7-aminoheptanoic acid	19.6 ± 3.0	15.0 ± 3.0	5.0 ± 3.0	−5.0 ± 3.0
8-aminooctanoic acid	17.2 ± 3.0	14.1 ± 3.0	7.5 ± 3.0	1.0 ± 3.0
11-aminoundecanoic acid	24.6 ± 4.0	21.8 ± 4.0	15.9 ± 4.0	9.9 ± 4.0

TABLE V: Temperature Slopes of the Partial Molar Adiabatic Compressibilities, $\Delta\bar{K}_s/\Delta T$, as a Function of Temperature, T, for the α,ω-Amino Acids

compound	$\Delta\bar{K}_s/\Delta T$ (10^{-5} cm^3 mol^{-1} bar^{-1} K^{-1})			
	18 °C	25 °C	40 °C	55 °C
glycine	4.4 ± 0.2	3.7 ± 0.2	2.1 ± 0.2	0.6 ± 0.2
β-alanine	5.6 ± 0.2	4.7 ± 0.2	2.6 ± 0.2	0.5 ± 0.2
4-aminobutanoic acid	8.1 ± 0.3	6.5 ± 0.3	3.1 ± 0.3	−0.4 ± 0.3
5-aminopentanoic acid	11.1 ± 0.3	8.9 ± 0.3	4.1 ± 0.3	−0.8 ± 0.3
6-aminohexanoic acid	11.4 ± 0.3	9.5 ± 0.3	5.4 ± 0.3	1.3 ± 0.3
7-aminoheptanoic acid	13.8 ± 0.4	11.7 ± 0.4	7.2 ± 0.4	2.7 ± 0.4
8-aminooctanoic acid	16.3 ± 0.4	13.8 ± 0.4	8.4 ± 0.4	3.0 ± 0.4
11-aminoundecanoic acid	24.1 ± 0.6	20.6 ± 0.6	12.9 ± 0.6	5.3 ± 0.6

TABLE VI: Comparison with Literature Values of the Partial Molar Volume, $\bar{V}$, Adiabatic Compressibility, $\bar{K}_s$, and Expansibility, $\bar{E}$, at 25 °C for the α,ω-Amino Acids

compound	$\bar{V}$ (cm^3 mol^{-1})		$\bar{K}$ (10^{-4} cm^3 mol^{-1} bar^{-1})		$\bar{E}$ (10^{-2} cm^3 mol^{-1} K^{-1})	
glycine	43.2[a]	43.33[b] 43.26[c] 43.5[d]	−26.6[a]	−25.0[g]	6.8[a]	10.0[g]
β-alanine	58.3[a]	58.71[c] 58.25[f]	−26.3[a]	−21.5[g]	8.2[a]	8.9[g]
4-aminobutanoic acid	73.1[a]	73.26[b] 73.5[d] 73.02[e]	−30.2[a]	−27.0[g]	9.8[a]	7.3[g]
5-aminopentanoic acid	88.3[a]	87.65[b] 88.3[d] 87.58[e]	−34.3[a]	−27.3[g]	10.6[a]	6.4[g]
6-aminohexanoic acid	104.3[a]	104.31[b] 104.20[c] 104.7[d] 104.02[e]	−37.1[a]	−29.2[g]	11.9[a]	9.2[g]
7-aminoheptanoic acid	120.0[a]	120.0[d]				
8-aminooctanoic acid	135.6[a]	136.1[d]				
11-aminoundecanoic acid	182.6[a]	182.6[d]				

[a] This study. [b] Reference 25. [c] Reference 29. [d] Reference 27. [e] Reference 26. [f] Reference 37. [g] Reference 5.

be approximated well (with a correlation coefficient higher than 0.99) by second-order polynomial functions. The temperature derivatives of $\bar{V}$ and $\bar{K}_s$ then were determined by analytical differentiation of the approximating functions at the required temperatures. Tables IV and V present resulting data as the temperature slope of the partial molar volume (equal to the partial molar expansibility, since $\bar{E} = (\partial\bar{V}/\partial T)_p$) and the temperature slope of the partial molar adiabatic compressibility, $\Delta\bar{K}_s/\Delta T$, respectively.

Table VI compares our data on $\bar{V}$, $\bar{K}_s$, and $\bar{E}$ at 25 °C with the few previous literature reports that exist. While good agreement is found between our data and published data for the partial molar volumes of the α,ω-amino acids, note that poor agreement is observed in the partial molar expansibility and adiabatic compressibility data. The origin of this discrepancy is not clear but may reflect the higher accuracy of the method of measurement used in this work.

4. Discussion

4.1. Partial Molar Volume. The measured partial molar volume can be considered to be a sum of the geometric volume of the solute molecule and changes in the solvent due to its interaction with the solute. This simple semiempirical approach

has been widely used for interpreting partial molar volume data for a broad range of solutes.[4,38-40] Scaled particle theory[41-44] uses geometric considerations to describe the dissolution of a solute and allows one to evaluate intrinsic and hydration contributions to the partial molar volume of a solute. It is noteworthy that scaled particle theory can be used most directly when the solute molecule is spherical in shape. For solutes of other shapes adjustable parameters are required.

Based on scaled particle theory,[41-44] the dissolution of a solute can be considered to be a two-step process:[42] creation of a cavity in the solvent large enough to enclose the solute molecule; placement of the solute molecule into the cavity so that it can interact with the solvent. The partial molar volume of a solute at infinite dilution, $\bar{V}$, represents contributions from each step[42]

$$\bar{V} = V_c + V_I + \beta_{T0}RT \tag{3}$$

where V_c is the partial molar volume of cavity formation; V_I is the volume change associated with the solute–solvent interactions, the "interaction volume"; β_{T0} is the coefficient of isothermal compressibility of the solvent, R is the universal gas constant, and T is the absolute temperature. The term $\beta_{T0}RT$ describes the volume effect of the ideal part of solute dissolution.

The cavity volume, V_c, in eq 3 consists of two terms: $V_c = V_M + V_v$, where V_M is the geometric volume occupied by the solute molecule itself and V_V is the "empty" volume (the volume of the void space surrounding the solute molecule[45,46]), which is due to the thermal motion of solute and solvent molecules and, as noted by Stillinger,[43] "would result even for a point particle (not interacting with the solvent molecules) on account of its kinetic contribution to the pressure". As a first approximation, for low molecular weight substances, the value of the V_M can be taken equal to the van der Waals volume, V_W.

Another conceptual approach for qualitative interpretations of partial molar volume data in terms of hydration[4] uses the relationship

$$\bar{V} = V_M + \Delta V_h = V_M + n_h(\bar{V}_h - \bar{V}_0) \tag{4}$$

where ΔV_h is the volume effect of hydration, $\bar{V}_0$ and $\bar{V}_h$ are the partial molar volumes of water in the bulk state and in the hydration shell of a solute, respectively, and n_h is the "hydration number", that is, the number of water molecules in the hydration shell of a solute.

Equation 4 is based on the so-called "continuous medium" model of a solution,[47] where the hydration shell of a solute is considered as a homogeneous media. This simple model of a solution can be useful for a qualitative analysis of the hydration properties of solutes. Note if one assumes that $\Delta V_h = V_V + V_I + \beta_{T0}RT$, then eqs 3 and 4 are equivalent.

To estimate the "empty" volume, V_V, in eq 3, two different approaches have been proposed in literature. The first approach is based on calculating the partial molar Gibbs free energy required to create a cavity in the solvent according to scaled particle theory.[42,44] In this connection, the relationship between the volume of the cavity, V_C, and the radius of the molecular core, r_M, of a solute is given by[44]

$$V_c = (4\pi N_A/3)r_M^3 + A_1 r_M^2 + A_2 r_M + A_3 \tag{5}$$

where N_A is Avogadro's number and A_1, A_2, and A_3 are the constants. Previous expressions, obtained by Pierotti[42] for calculating the cavity volume, V_C, also can be cast in the form of eq 5.

The second approach for estimating the "empty" volume, V_V, in eq 3 is based on the assumption that the average separation of the solvent from solute molecules (the thickness of the void space), Δ, is the same for molecules of different "chemical character".[45,46] Values between 0.50 and 0.57 Å have been estimated for Δ at 25 °C.[45,46,48,49] Thus, both the cavity volume, V_C, and the "empty" or void volume, V_V, can be estimated from geometrical considerations. For the simplest case, when the solute molecules can be approximated by hard spheres with radius r_M, the following expression for V_C has been used:[45]

$$V_C = (4\pi N_A/3)(r_M + \Delta)^3 \tag{6}$$

The common disadvantage of both approaches noted above is that their application to real solutions implies approximating the shape of the solute molecules either by a sphere[42,44,45] or by some other simple geometric figure.[46] Most molecules, especially flexible molecules such as α,ω-amino acids, cannot be adequately approximated by a simple single geometric shape because of their large number of conformational degrees of freedom. Thus, for real solutes, the two approaches noted above have limited application.

To address, in part, the limitations just noted, we propose two modifications of the original approaches. First, to avoid the need to apply the spherical approximation for the shape of a solute molecule, eq 5 needs to be transformed as shown below in eq 7 so that the cavity volume, V_C, is related not to the radius of a solute molecule, r_M, but rather to its accessible surface area, S_M, and geometric volume, V_M.

$$V_C = V_M + B_1 S_M + B_2 S_M^{1/2} + B_3 \tag{7}$$

where the constants B_1 and B_2 can be determined from experimental data (see below). The volume, V_M, and the accessible surface area, S_M, of a solute molecule in eq 7 can be approximated by its van der Waals volume, V_W, and the surface area, S_W, respectively. Since the coefficients B_1 and B_2 are adjustable parameters determined from experimental data, they allow one to take into account the effect of the shape of a solute molecule. We assume that, in general, these coefficients are essentially the same only for a homologous series of solutes but could differ significantly for different classes of substances.

The second modification is associated with the fact that the constant B_3 is not dependent on the type of solute and can be obtained readily from the scaled particle theory, for the case $r_M = 0$. The value of B_3 represents the volume of the cavity containing a point particle with zero volume, and therefore, it should be independent of the shape of the solute molecules considered, thereby remaining the same for all the approximations used. Actually, B_3 coincides with the term A_3 in eq 5 and depends only on the value of Δ, which can be assumed to be constant for a given temperature and pressure.[45,46] Indeed, B_3 is equal to $4\pi N_A\Delta^3/3$, as it can be obtained from eq 6, if one takes the value of r_M equal to 0.

The coefficients B_1 and B_2 in eq 7 for α,ω-amino acids can be determined if the difference between the partial molar volumes and the van der Waals volumes, $(\bar{V} - V_W)$, is plotted versus the van der Waals surface area, S_W (see Figure 1). Both the van der Waals volume of the molecules and their van der Waals surface areas were calculated according to Bondi.[50]

We have analyzed our data using the modifications described above. Inspection of Figure 1 reveals that the dependences of $(\bar{V} - V_W)$ on S_W at each temperature can be approximated by two straight lines before and beyond the point corresponding to 5-aminopentanoic acid. The break point in Figure 1 suggests that the character of the solute–solvent interactions "before and beyond" 5-aminopentanoic acid is different. We propose that when the distance between the two charged termini is less than that which corresponds to four carbon atoms, then the hydration shells of the NH_3^+ and COO^- groups overlap. Our interpretation of the data involves the reasonable assumption that the overall hydration of such short α,ω-amino acids (fewer than four methylene groups) is determined mostly (if not completely) by electrostatic solute–solvent interactions. Thus, the observed change in the partial molar volume of such short α,ω-amino acids upon increasing the number of aliphatic CH_2 groups up to four results from an increase in the van der Waals volume of the

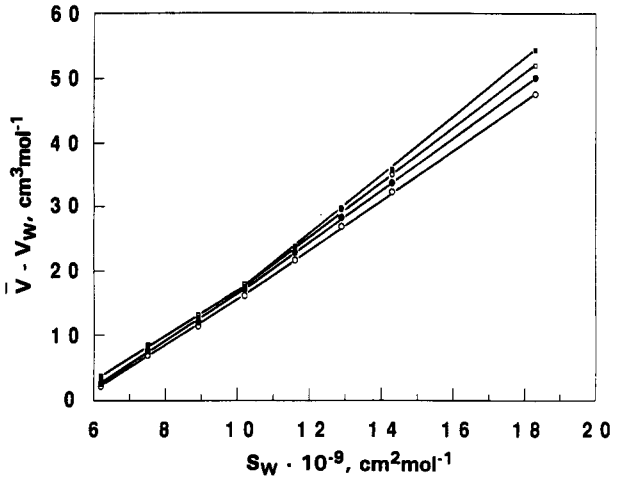

Figure 1. Difference between the partial molar volume of the α,ω-amino acids, $\bar{V}$, and their van der Waals volume, V_W, as a function of the van der Waals surface area, S_W, at 18 (○), 25 (●), 40 (□), and 55 °C (■).

TABLE VII: Values for the Coefficients B_1 and B_3 in Eq 7 as a Function of Temperature, T, for the α,ω-Amino Acids

T, °C	18	25	40	55
B_1, 10^{-9} cm	3.87	4.05	4.19	4.54
B_3, cm^3 mol^{-1}	0.9	0.6	0.4	0.3

molecule and an increase in the "geometric size" of the hydration shells of the charged atomic groups due to a reduction in their overlap. In such short α,ω-amino acids, we propose that any water molecules to which the CH_2 groups are accessible are predominantly under the strong influence of the charged termini, thereby minimizing the impact of the CH_2 groups on hydration. Consequently, in "short" α,ω-amino acids, any contribution of methylene group hydrophobic hydration to the partial molar volume is negligible.

Based on the data in Figure 1, when four or more carbon atoms separate the oppositely charged amino and carboxyl terminal groups (after 5-aminopentanoic acid), the interaction between these groups via overlapping hydration shells either has been obliterated or does not cause a measurable effect on the volume. In the case of such "long" α,ω-amino acids, we propose that CH_2 groups become accessible to solvent molecules which are not under the influence of the charged termini. Consequently, in "long" α,ω-amino acids, the methylene groups begin to exert an independent and significant influence on the characteristics of the adjacent water molecules. Thus, any incremental increase in the partial molar volume of the "long" α,ω-amino acids reflects exclusively the contribution of the independently hydrated CH_2 groups.

A comparison of the hydration effects of the CH_2 group relative to the hydration effects associated with the charged termini reveals that one can neglect the contribution of the CH_2 group to the value of V_I in eq 3.[8,42,46] Thus, after 5-aminopentanoic acid, an increase in the value of $(\bar{V} - V_W)$ with increasing solvent accessible nonpolar surface area can be ascribed solely to an increase in the value of V_V. As is seen from Figure 1, the dependence $(\bar{V} - V_W)$ on S_W beyond 5-aminopentanoic acid is linear, which indicates that the coefficient B_2 in eq 7 for α,ω-amino acids is equal to 0, and the value of B_1 can be found as the slope $\Delta(\bar{V} - V_W)/\Delta S_W$. Table VII presents the coefficients B_1 and B_3 in eq 7 at 18, 25, 40, and 55 °C. The values of B_3 have been calculated using the equations for the cavity volume, V_C, presented by Pierotti[42] for the case of point solute particles with a radius equal to 0. The interaction volumes, V_I, of the α,ω-amino acids calculated from eqs 3 and 7 using the estimated coefficients B_1 and B_3 are listed in Table VIII and plotted vs the number of methylene groups in Figure 2. Note that our estimation of V_I for glycine agrees well with that estimated by Kharakoz[8] (Table VIII). By contrast, our value for electrostriction associated with the independently

TABLE VIII: Values of V_I, the Volume Change Associated with Solute–Solvent Interactions for the α,ω-Amino Acids at Various Temperatures, T

	V_I (cm^3 mol^{-1})			
compound	18 °C	25 °C	40 °C	55 °C
glycine	−23.8	−24.1 (−27[a])	−24.0	−25.8 (−29[a])
β-alanine	−24.1	−24.4	−24.6	−26.7
4-aminobutanoic acid	−25.0	−25.6	−25.7	−29.1
5-aminopentanoic acid	−25.4	−25.9	−26.3	−30.2
6-aminohexanoic acid	−25.2	−25.7	−26.3	−30.3
7-aminoheptanoic acid	−25.0	−25.6	−26.0	−30.3
8-aminooctanoic acid	−25.0	−25.9	−26.4	−30.0
11-aminoundecanoic acid	−25.3	−25.8	−26.3	−30.2

[a] Estimated values of V_I, from Kharakoz.[8]

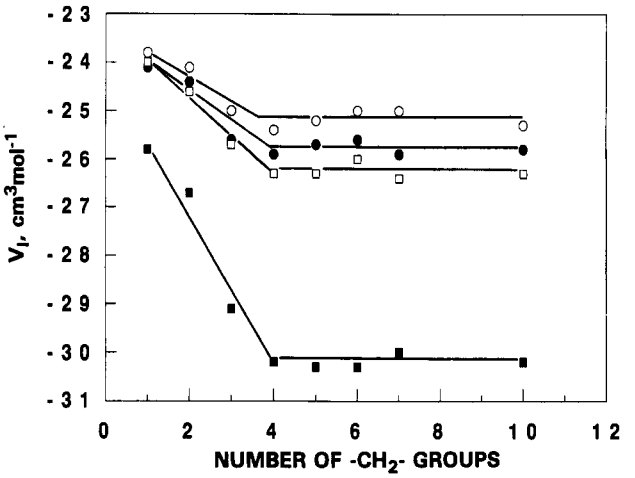

Figure 2. Dependence of the interaction volume, V_I, on the number of methylene groups in the α,ω-amino acid at 18 (○), 25 (●), 40 (□), and 55 °C (■).

hydrated amino and carboxyl groups is higher than the 18.5 and 16.2 cm^3 mol^{-1} values reported by Cabani et al.[25] and Shahidi and Farrell,[27] respectively, which were obtained by comparing partial molar volumes of α,ω-amino acid zwitterions with the corresponding uncharged hydroxyamides. The latter discrepancy may reflect the fact that the comparison method used by these investigators[25,27] does not take into account the volume effects of hydration of the polar groups of the hydroxyamides.

Figure 2 shows that the interaction volume, V_I, becomes constant for the α,ω-amino acids beyond 5-aminopentanoic acid, when four or more CH_2 groups separate the charged end groups. This result is consistent with a model in which the oppositely charged amino and carboxyl groups cease to interfere with their individual hydration shells when they are separated by at least four CH_2 groups. This number is lower than the value of five reported by Cabani et al.[25] and the value of six reported by Shahidi and Farrell.[27] At present, we are not able to provide an explanation for these discrepancies.

On the basis of the information provided above, we conclude that the average value of V_I for the "longer" α,ω-amino acids is a measure of the total electrostriction of the independently hydrated NH_3^+ and COO^- groups. Thus, 5-aminopentanoic acid can be considered as a zwitterionic molecule with a distance between the charged atomic groups corresponding to the geometric sizes of hydration shells of the amino and carboxyl groups. Estimation of the intercharge distance in 5-aminopentanoic acid based on dielectric constant measurements (and evalution of the dipole moments of the zwitterion) yields values between 5.7 and 6.2 Å,[51] distances which correspond roughly to 2–2.5 water molecule diameters. (The effective diameter of a water molecule is taken to be equal to 2.75 Å.[42]) This result suggests that even for such strong solute–solvent interactions, like those between water molecules and the charged terminal groups in the α,ω-

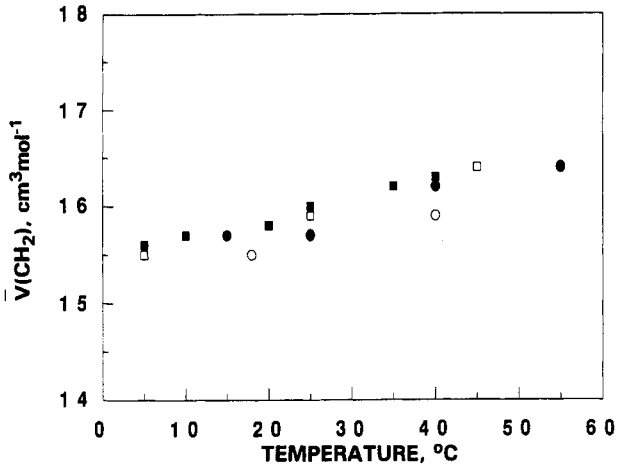

Figure 3. Temperature dependence of the contribution of the CH_2 group to the partial molar volume of different solutes: α,ω-amino acids from this work (○); α-amino acids with the nonbranched aliphatic side chain (●);[8] α,ω-diols (□);[12] primary and secondary alcohols (■).[6]

amino acids, the hydrating water molecules appear localized mostly within the first coordination sphere. Thus, we propose that the hydration shell of a solute basically comprises the water molecules directly contacting the solute molecule, i.e., those included within the first coordination sphere. This result is in accordance with the previous estimations of the size of hydration shell of a solute,[10,52] namely, that hydration-induced changes in the properties of water in the vicinity of an atomic group extend to a distance of 3–4 Å, which corresponds to 1–1.5 layers of water molecules.

Our measurements suggest that overlap of the hydration shells of NH_3^+ and COO^- groups in glycine results in a decrease in the absolute value of the electrostriction by 1.4 ± 0.5 cm^3 mol^{-1} at 18 °C and 4.4 ± 0.5 cm^3 mol^{-1} at 55 °C. The value determined at 25 °C, 1.7 ± 0.5 cm^3 mol^{-1}, is lower than estimates of 3.7 ± 0.9 and 3.8 ± 1.2 cm^3 mol^{-1} derived from the data of Shahidi and Farrell[27] and Cabani et al.,[25] respectively. This disparity may be significant or may fall within the propagated error. Clearly, additional studies are needed to differentiate between these two possibilities.

The volume contribution of a single methylene group, $\bar{V}(CH_2)$, can be derived as an increment of the partial molar volume of the α,ω-amino acids per one CH_2 group. We obtain a value of 15.7 cm^3 mol^{-1} at 25 °C, which coincides well with that obtained from the partial molar volume data of α-amino acids – 15.7 cm^3 mol^{-1} [8] and 15.8 cm^3 mol^{-1},[22] alcohols – 16.0 cm^3 mol^{-1},[6] α,ω-alkane diols – 15.9 cm^3 mol^{-1},[12] amino and diamino alkanes – 15.9 cm^3 mol^{-1},[19] alkanes – 15.8 cm^3 mol^{-1}.[53] A comparison of the temperature dependences of the contributions of independently hydrated methylene groups to the partial molar volume of different solutes (aliphatic α-amino acids, alcohols, α,ω-alkane diols) is shown in Figure 3. The good agreement between our values of $\bar{V}(CH_2)$ and published values of $\bar{V}(CH_2)$ obtained from studies on different compounds suggests that the volume contribution of the independently hydrated methylene group is not sensitive to the nature of the solute containing the methylene group.

4.2. Partial Molar Expansibility. Differentiating eqs 3 and 7 with respect to temperature, one obtains the following relationship for the partial molar expansibility:

$$\bar{E} = (\partial\bar{V}/\partial T)_P = (\partial V_C/\partial T)_P + (\partial V_I/\partial T)_P + (\partial(\beta_{T0}RT)/\partial T)_P = (\partial V_W/\partial T)_P + S_W(\partial B_1/\partial T)_P + S_W^{1/2}(\partial B_2/\partial T)_P + (\partial B_3/\partial T)_P + (\partial V_I/\partial T)_P + (\partial(\beta_{T0}RT)/\partial T)_P \quad (8)$$

Neglecting the temperature dependence of the van der Waals volume, V_W, and taking into account that the coefficient B_2 is

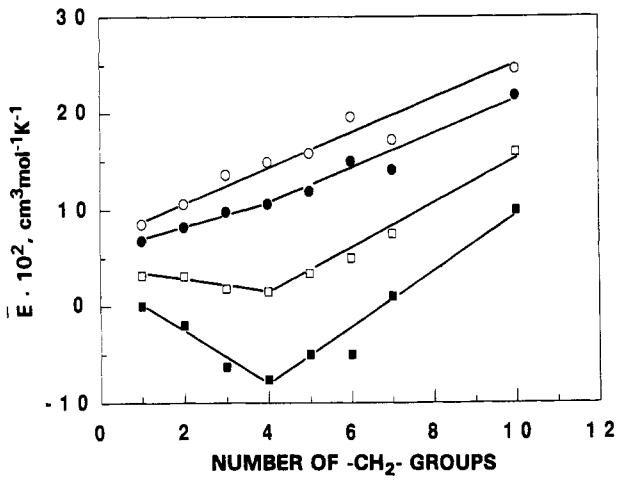

Figure 4. Dependence of the partial molar thermal expansibility of the α,ω-amino acids on the number of methylene groups at 18 (○), 25 (●), 40 (□), and 55 °C (■).

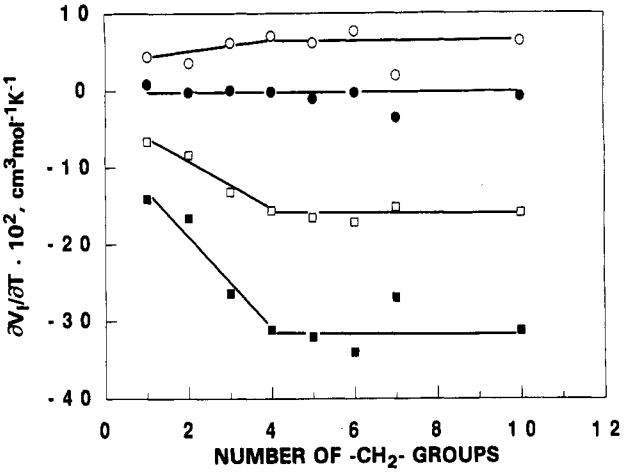

Figure 5. Dependence of the temperature slopes of the interaction volume, V_I, of the α,ω-amino acids on the number of methylene groups at 18 (○), 25 (●), 40 (□), and 55 °C (■).

equal to 0, eq 8 can be rewritten as

$$\bar{E} = S_W(\partial B_1/\partial T)_P + (\partial B_3/\partial T)_P + (\partial V_I/\partial T)_P + (\partial(\beta_{T0}RT)/\partial T)_P \quad (9)$$

Figure 4 shows the dependence on the number of methylene groups of the partial molar thermal expansibility, $\bar{E}$, of the α,ω-amino acids at 18, 25, 40, and 55 °C. Note that at higher temperatures pronounced breaks are observed at points which correspond to 5-aminopentanoic acid. (Recall a similar break point for the dependence of the partial molar volume on the number of methylene groups.) Interestingly, the break disappears at lower temperatures. The first two terms of eq 9, which correspond to the temperature slope of the void volume V_V, increase monotonically at any temperature with an increase in the number of CH_2 groups. The dependences of $\partial V_I/\partial T$ on the number of CH_2 groups are shown in Figure 5. Note that near room temperatures (18–25 °C) the slope $\partial V_I/\partial T$ for the α,ω-amino acids changes sign, with the absolute values of $\partial V_I/\partial T$ being small. (At 25 °C, $\partial V_I/\partial T$ for all the α,ω-amino acids studied is approximately equal to 0.) As a result, the effect of interactions between the amino and carboxyl end groups on $\partial V_I/\partial T$ falls within the limits of our measurement. In this case, the observed change in the partial molar expansibility with the number of CH_2 groups is caused mostly by increasing the value of $\partial V_V/\partial T$, and no breaks are observed on the dependence of $\bar{E}$ on the number of methylene groups.

By contrast, at higher temperatures, when $\partial V_I/\partial T$ approaches

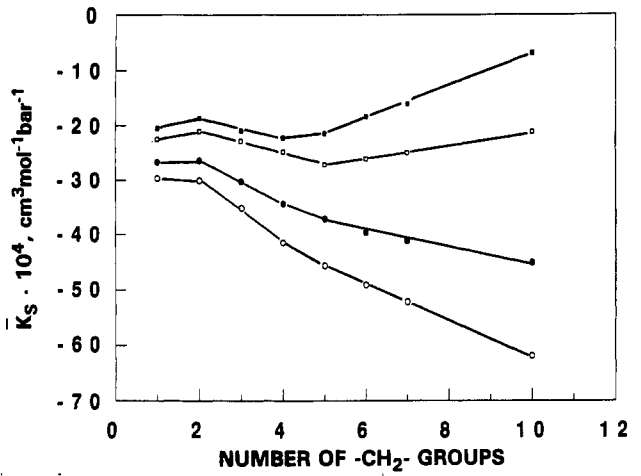

Figure 6. Dependence of the partial molar adiabatic compressibility of the α,ω-amino acids on the number of methylene groups at 18 (○), 25 (●), 40 (□), and 55 °C (■).

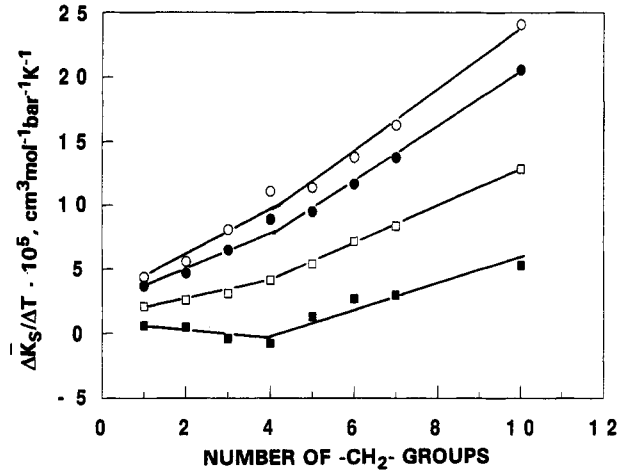

Figure 7. Dependence of the temperature slopes of the partial molar adiabatic compressibility of the α,ω-amino acids on the number of methylene groups at 18 (○), 25 (●), 40 (□), and 55 °C (■).

large negative values, its contribution to the partial molar expansibility becomes significantly. Since the effect of overlapping the hydration shells of the charged groups on the temperature slope of V_I is large and quite measurable, the breaks in the dependences of E on the number of CH_2 groups appear at higher temperatures.

4.3. Partial Molar Adiabatic Compressibility. In the framework of a "continuous medium" model of solutions, the partial molar adiabatic compressibility, $\bar{K}_S$, of a solute can be described, as was done for volume, as the sum of intrinsic and hydration contributions:

$$\bar{K}_S = K_M + \Delta K_h = K_M + n_h(\bar{K}_h - \bar{K}_0) \qquad (10)$$

where K_M is the intrinsic compressibility of a solute molecule; ΔK_h is the compressibility effect of hydration; $\bar{K}_0$ and $\bar{K}_h$ are the partial molar adiabatic compressibilities of water in the bulk state and in the hydration shell of a solute, respectively; and n_h, the hydration number, has the same meaning as in eq 4.

For low molecular weight compounds, the intrinsic compressibility, K_M, is mostly determined by the compressibility of covalent bonds and external electron shells and therefore can be neglected to yield

$$\bar{K}_S = n_h(K_h - K_0) \qquad (11)$$

Inspection of eq 11 reveals that only hydration changes contribute to the partial molar compressibility of low molecular substances. A similar relationship for the temperature slope of the partial molar compressibility, $\Delta\bar{K}_S/\Delta T$, can be derived by differentiating eq 11 to yield

$$\Delta\bar{K}_S/\Delta T = n_h[(\partial\bar{K}_h/\partial T)_P - (\partial\bar{K}_0/\partial T)_P] \qquad (12)$$

Figures 6 and 7 show the dependences on the number of CH_2 groups of the partial molar adiabatic compressibilities, $\bar{K}_S$, of the α,ω-amino acids and their temperature slopes, $\Delta\bar{K}_S/\Delta T$, respectively. A comparison of Figures 4 and 7 reveals that the temperature slopes of the partial molar volume and compressibility describe the hydration of α,ω-amino acids in a qualitatively similar manner. Specifically, a decrease of the overlapping hydration shells of the amino and carboxyl groups from glycine to 5-aminopentanoic acid leads to a linear change in the values of both $\bar{E}$ and $\Delta\bar{K}_S/\Delta T$. The intercharge interaction ceases to be reflected in the values of both $\bar{E}$ and $\Delta\bar{K}_S/\Delta T$ starting from a point corresponding to 5-aminopentanoic acid. Note that the methylene group increases both the partial molar expansibility and temperature slope of $\bar{K}_S$ within the temperature range studied.

The dependence of the partial molar adiabatic compressibility on the number of methylene groups has a more complex form,

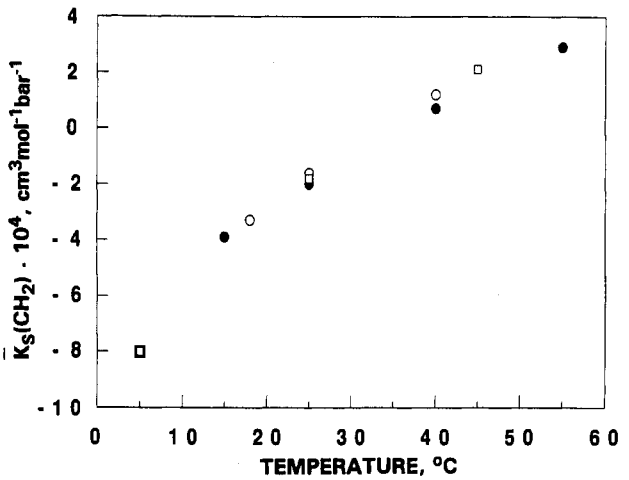

Figure 8. Temperature dependence of the contribution of the CH_2 group to the partial molar adiabatic compressibility of different solutes: α,ω-amino acids from this work (○); α-amino acids with the nonbranched aliphatic side chain (●);[9] primary alcohols and α,ω-diols (□).[11]

as reflected in Figure 6. The interaction between the charged end groups continues to influence the value of $\bar{K}_S$ up to a point corresponding to 6-aminohexanoic acid. This observation may indicate that compressibility "feels" the hydration structure of a solute further than volume, expansibility, or the temperature slope of compressibility. The intercharge distance in 6-aminohexanoic acid determined from dielectric constant measurements is between 6.3 and 7.1 Å,[51] which corresponds to 2.3–2.6 diameters of water molecule. Thus, based on compressibility data, the hydration shell of the charged group in α,ω-aminocarboxylic acids involves 1.2–1.3 effective layers of water molecules, which coincides with our earlier estimations of the "thickness" of hydration shell of other solute molecules.[10,52]

Figure 8 shows the contribution of independently hydrated CH_2 groups to the temperature dependences of the partial molar adiabatic compressibility of α,ω-amino acids (this work), α-amino acids with nonbranched aliphatic side chains,[9] and alcohols and diols.[11] As in the case of volume, we find that independently hydrated methylene groups have the same contribution to the partial molar adiabatic compressibilities of substances which belong to structurally diverse classes. Inspection of Figure 8 reveals that the contribution of the methylene group, $\bar{K}_S(CH_2)$, is negative at low temperatures and becomes positive at temperatures above 30 °C. At 25 °C, the contribution of a CH_2 group to the partial molar adiabatic compressibility of an α,ω-amino acid is negative and equal to -1.6×10^{-4} cm^3 mol^{-1} bar^{-1}. As can be seen from eq 11, a negative value of $\bar{K}_S(CH_2)$ at low

temperatures means that water in the hydration shells of CH_2 group is less compressible than water in the bulk state. By contrast, at higher temperatures the compressibility of bulk water is less than that in the hydration shell of methylene group.

The negative values we have determined for the partial molar adiabatic compressibilities of the α,ω-amino acids within the entire temperature range studied are a result of the large negative contribution of the charged atomic groups. A gradual increase in the amount of water molecules in the hydration shell of the charged atomic groups should lead to a decrease in the partial molar adiabatic compressibility, as we observe upon proceeding from β-alanine to 4-aminobutanoic acid and further to 5-aminopentanoic acid and 6-aminohexanoic acid (except at 55 °C). We propose that in 6-aminohexanoic acid, by contrast to shorter α,ω-amino acids, the methylene groups become partly accessible to the solvent molecules which are not under the influence of the charged termini and begin to influence the partial molar adiabatic compressibility. (This interpretation is consistent with the partial molar volume data discussed in section 4.1.) This solvent exposure of the CH_2 group leads to the shift we observe in the position of 6-aminohexanoic acid in Figure 6, at each temperature studied, from the straight line corresponding to β-alanine, 4-aminobutanoic acid, and 5-aminopentanoic acid. As a result of the positive compressibility contribution of the CH_2 group, at 55 °C, the partial molar adiabatic compressibility of 6-aminohexanoic acid becomes higher than that of 5-aminopentanoic acid. We have assumed that the contribution of the noninteracting amino and carboxyl terminal groups to the partial molar adiabatic compressibility is roughly equal to the partial molar adiabatic compressibility of 5-aminopentanoic acid. This contribution can be seen from Table III to be equal to -34×10^{-4} cm^3 mol^{-1} bar^{-1} at 25 °C.

An intriguing feature of the data is that β-alanine exhibits almost the same partial molar compressibility as glycine at low temperatures (18 and 25 °C) and even exhibits a larger compressibility at high temperatures (40 and 55 °C). This behavior is unexpected, because, based on conventional wisdom, the overlap of the hydration shells of the charged end groups in glycine should be higher than that in β-alanine. Perhaps in the hydration shell of glycine, the dipoles of water molecules between the closely situated charged end groups interact simultaneously with both the positively charged amino and the negatively charged carboxyl groups. In such a model, the water molecules would become highly oriented, and as a result, the compressibility of the water in the hydration shell of glycine would be further reduced. Clearly, additional studies are required to address the unexpected similarity we observe in the partial molar compressibilities of β-alanine and glycine.

4.4. Hydration Characteristics of Aliphatic and Charged Atomic Groups. As explained below, one can estimate the volumetric characteristics (density and coefficients of adiabatic compressibility as well as their temperature dependences) of the water in the hydration shell of an aliphatic CH_2 group and a charged amino and/or carboxyl group from eqs 4 and 11. It should be noted here that eqs 4 and 11 assume the hydration shell of a solute to be homogeneous. Therefore, the values of the partial molar volume, $\bar{V}_h$, in eq 4 and the partial molar adiabatic compressibility, $\bar{K}_h$, in eq 11 of "water in the hydration shell of a solute" are related not only to the adjacent water molecules but also to the "void space" around a solute molecule (see section 4.1). Thus, our estimate of the partial molar volume and adiabatic compressibility of "water in the hydration shells" of the aliphatic CH_2 group and the charged termini involves positive contributions due to the volume and compressibility of the "void space" around these atomic groups.

The "hydration number", n_h, for an aliphatic CH_2 group has been estimated by Nakajima and Hashimoto from geometric considerations to be equal to 4 (the number of water molecules

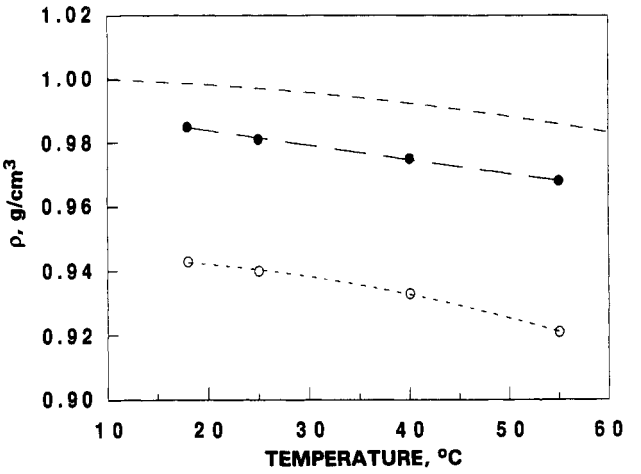

Figure 9. Temperature dependence of the density of the water in the hydration shells of methylene (○), charged groups (●), and bulk water (dashed line).

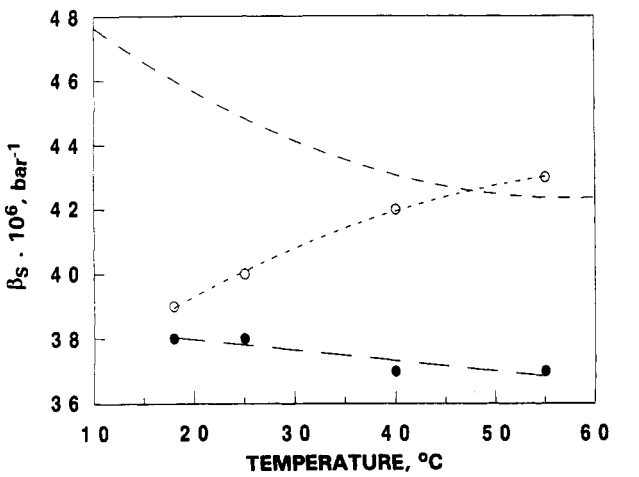

Figure 10. Temperature dependence of the coefficients of adiabatic compressibility of the water in the hydration shells of methylene (○), charged groups (●), and bulk water (dashed line).

in the first coordination shell).[54] Using this number and our experimentally determined contributions of a methylene group to the values of $\bar{V}$ and $\bar{K}_S$ for α,ω-amino acids, the partial molar volume, $\bar{V}_h$, and the adiabatic compressibility, $\bar{K}_h$, of the water in the hydration shell of a CH_2 group can be calculated from eqs 4 and 11, respectively. Our analysis is discussed below.

To compare different substances, it is better to examine their densities and coefficients of adiabatic compressibility rather than their partial molar volumes and compressibilities. Therefore, we have reformulated the values of $\bar{V}_h$ and $\bar{K}_h$ in terms of the density, $\rho_h(CH_2)$, and the coefficient of adiabatic compressibility, $\beta_h(CH_2)$, of the water in the hydration shell of the CH_2 group using $\rho_h(CH_2) = M_W/\bar{V}_h$ (M_W = 18.02 is the molecular weight of water) and $\beta_h(CH_2) = \bar{K}_h/\bar{V}_h$ (see Figures 9 and 10). Note that the density of the water in the hydration shell of a methylene group is lower by 5–6% than that of bulk water, while being characterized by more or less the same temperature dependence within the temperature range 18–55 °C. By contrast, the temperature dependences of the coefficients of adiabatic compressibility of water in the hydration shell of a methylene group, $\beta_h(CH_2)$, and that of bulk water, β_{s0}, are different. Inspection of Figure 10 reveals that the coefficient of adiabatic compressibility of bulk water, β_{s0}, decreases with temperature, while $\beta_h(CH_2)$ increases. In addition, the second temperature derivative of β_{s0} is positive, while the value of $(\partial^2\beta_h(CH_2)/\partial T^2)_P$ is negative.

The data on both the partial molar volume and compressibility (as well as their temperature derivatives) of α,ω-amino acids reveal that the hydration shells of glycine, β-alanine, 4-amino-

TABLE IX: Hydration Numbers, n_h, of the α,ω-Amino Acids Determined from Eqs 13 and 14

compound	n_h eq 13	n_h eq 14
glycine	14	16
β-alanine	19	22
4-aminobutanoic acid	31	34
5-aminopentanoic acid	43	39

butanoic acid, and 5-aminopentanoic acid are dictated mainly by solvation of the oppositely charged amino and carboxyl groups. Hence, hydration characteristics of these compounds can be considered as the hydration characteristics of the charged groups. To determine the "hydration number", n_h, for these α,ω-amino acids, we have applied a previously described approach,[8,52] in which it is postulated and assumed that strong electrostatic solute–solvent interactions in the vicinity of charged groups cause water to cease manifesting the "abnormal" properties inherent to bulk water. As a result, water in the hydration shell of charged atomic groups exhibits a linear temperature dependence of volume, as any "normal" liquid; in other words, the second temperature derivative of water in the hydration shell of charged groups, $(\partial^2\bar{V}_h/\partial T^2)_P$, is equal to 0. Furthermore, the "hydration number", n_h, which is determined predominantly by the number of water molecules in the first coordination sphere, does not depend on temperature.

In the context of this model, eq 4 can be differentiated, while recognizing that the temperature dependence of the intrinsic volume, V_m, of low molecular weight solutes is negligible. In this way, the following relationship can be derived:[8]

$$(\partial^2\bar{V}/\partial T^2)_P = -n_h(\bar{V}_0/\partial T^2)_P \qquad (13)$$

The "hydration number", n_h, then can be evaluated, if the second temperature derivative of the partial molar volume is determined.

The same assumptions can be applied to compressibility;[9] namely, the second temperature derivative of the partial molar compressibility, $(\partial^2\bar{K}_h/\partial T^2)_P$, of water in the hydration shell of charged groups is equal to 0, as it is for other normal liquids. Differentiating eq 11, one obtains the following expression:[9]

$$(\partial^2\bar{K}_s/\partial T^2)_P = -n_h(\partial^2\bar{K}_0/\partial T^2)_P \qquad (14)$$

Thus, the "hydration number", n_h, also can be derived from the second temperature derivative of the partial molar compressibility.

Table IX shows "hydration numbers" that we have calculated using eqs 13 and 14 for four of the α,ω-amino acids studied here. In this analysis, we have assumed that the hydration of these solutes is dominated by the influences of the oppositely charged end groups (see sections 4.1 and 4.3). Note the good agreement we observe (Table IX) between the values of n_h, calculated from the second temperature derivatives of the partial molar volumes (eq 13), and the partial molar compressibilities (eq 14). This agreement lends credence to the assumptions involved in our data analyses.

Partial molar volumes, $\bar{V}_h$, and compressibilities, $\bar{K}_h$, of water in the hydration shells of glycine, β-alanine, 4-aminobutanoic acid, and 5-aminopentanoic acid were calculated from eqs 4 and 11 using average values of n_h from Table IX. Average values of $\bar{V}_h$ and $\bar{K}_h$ for the four α,ω-amino acids noted above and listed in Table IX were taken as hydration characteristics of the charged atomic groups. Plots of the density and the coefficient of adiabatic compressibility of the water in the hydration shell of the charged groups versus temperature are shown in Figures 9 and 10, respectively. Inspection of Figure 9 reveals that the density of water in the hydration shell of the charged groups is higher than it is in the hydration shell of the CH_2 group, with this differential linearly decreasing with temperature. Inspection of Figure 10 reveals that the coefficient of adiabatic compressibility of water in the hydration shell of the charged groups is lower by about 15% than it is in bulk water, with this differential only weakly depending on temperature, in contrast to the behavior of the coefficient of adiabatic compressibility of water in the hydration shell of a methylene group, $\beta_h(CH_2)$.

In short, Figures 9 and 10 reveal essential differences between the hydration characteristics of charged and nonpolar groups. However, one should keep in mind that the analysis described above was made within the framework of a very simple "continuous medium" solution model as described by eqs 4 and 10. Consequently, the results plotted in Figures 9 and 10 should be considered as qualitative rather than quantitative descriptions of hydration characteristics of aliphatic and charged atomic groups.

5. Concluding Remarks

We have determined the partial molar volumes, expansibilities, and adiabatic compressibilities (as well as the temperature dependence of the latter) for eight α,ω-aminocarboxylic acids in aqueous solution within the temperature range 18–55 °C. Based on these data, the following results have been obtained and/or generalizations proposed:

1. For the shorter homologues (containing fewer than four methylene groups) the oppositely charged amino and carboxyl groups interact via overlapping hydration spheres. This interaction ceases when the charged ends are separated by a distance of about 6 Å, which corresponds to about 2–2.5 water molecules diameters. Thus, the solute hydration shell is composed primarily of water molecules directly contacting the solute molecule, thereby corresponding to 1–1.5 layers of water.

2. Compressibility appears to "sense" the solute hydration structure at a greater radius from the solute than does either the volume, expansibility, or the temperature dependence of compressibility.

3. At 25 °C, the total electrostriction for the noninteracting charged amino and carboxyl groups equals −26 $cm^3\ mol^{-1}$ and slightly depends on temperature.

4. At temperatures higher than 40 °C, the absolute value for the total electrostriction for noninteracting charged terminal groups begins to increase sharply, reaching a value of −30 $cm^3\ mol^{-1}$ at 55 °C.

5. The hydration shells of the "short" α,ω-amino acids (glycine, β-alanine, 4-aminopropanoic acid, and 5-aminopentanoic acid) are dictated predominantly by solvation of the oppositely charged terminal groups to the near exclusion of the intervening methylene groups. By contrast, the aliphatic CH_2 groups participate in the formation of the hydration shells of the "longer" α,ω-amino acids.

6. The contribution of the noninteracting charged carboxyl and amino terminal groups to the partial molar adiabatic compressibility is defined by the partial molar adiabatic compressibility of 5-aminopentanoic acid, which is equal to -34×10^{-4} $cm^3\ mol^{-1}\ bar^{-1}$ at 25 °C, and increases with temperature.

7. At 25 °C, the volume contribution of a CH_2 group in α,ω-amino acids is 15.7 $cm^3\ mol^{-1}$, and the compressibility contribution is -1.6×10^{-4} $cm^3\ mol^{-1}\ bar^{-1}$.

8. Independently hydrated CH_2 groups have the same contributions to the overall partial molar characteristics of a substance for solutes that come from structurally diverse classes.

9. At low temperatures, water that hydrates CH_2 groups in α,ω-amino acids is less compressible than bulk water, while at high temperatures the opposite is true.

10. At low temperatures, β-alanine has almost the same partial molar compressibility as glycine, while exhibiting an even larger compressibility at higher temperatures.

11. Water in the hydration shells of aliphatic groups differs from water that hydrates charged groups, not only in the absolute values of the density and the coefficient of adiabatic compressibility but also in the temperature dependences of these characteristics.

In the aggregate, these results provide a detailed quantitative description of both global and local solute hydration properties. Such characterizations should prove useful in developing an understanding of the role that solvent plays in the stabilization/destabilization of biologically important molecules.

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