

THE APPARENT MOLAL HEAT CAPACITIES AND VOLUMES OF THE AMINO ACIDS AND THEIR UNCHARGED ISOMERS^{1,2}

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Studies of the specific heats and densities of aqueous solutions of glycine, glycolamide, *dl*- α -alanine, β -alanine, and lactamide show that the apparent molal heat capacities of these solutes are linear functions of the concentration in dilute solutions, and that the apparent molal volumes are linear functions of the concentration over the whole experimental range. An extension of the Fuoss theory of dipolar solute interaction predicts that these properties of such non-electrolytes in dilute solution should be linear functions of the concentration (instead of the square root of the concentration, as for electrolytes) and allows us to calculate the limiting slopes. These values are within a factor of 10 of the observed values.

The fact that the apparent molal heat capacities and volumes of the amino acids at infinite dilution are appreciably smaller than those of their uncharged isomers has been explained from an electrostatic point of view, based on Kirkwood's treatment of these dipolar solutes. The difference calculated on this basis is about one-third of that observed experimentally, and further refinements in the treatment might give quantitative agreement.

I. INTRODUCTION

Several years ago a systematic study of the heat capacities, heats of dilution, and densities of aqueous solutions of the amino acids and their uncharged isomers was begun in this Laboratory in an effort to determine the effect of the charged groups on these thermodynamic properties of the solutions. Earlier work (9, 10) on the specific heats and densities of aqueous solutions of glycine and glycolamide indicated that the apparent molal heat capacities were linear functions of the molality in the dilute region (up to about 1 *m*), and the apparent molal volumes were linear functions of the molarity throughout the range of concentration from about 0.1 or 0.2 *m* to the nearly saturated solution. The same relationships were recently found (8) for the heat capacities and volumes of *dl*- α -alanine, β -alanine, and lactamide. The experimental data for glycine, glycolamide, α -alanine, β -alanine, and lactamide may be conveniently summarized by means of figures 1 to 4. For a further discussion of the experimental data and techniques the reader is referred to the articles (8, 9, 10) cited above. With the experimental data on these five compounds we are now in a position to test certain theoretical approaches to the study of the non-electrolytic solution.

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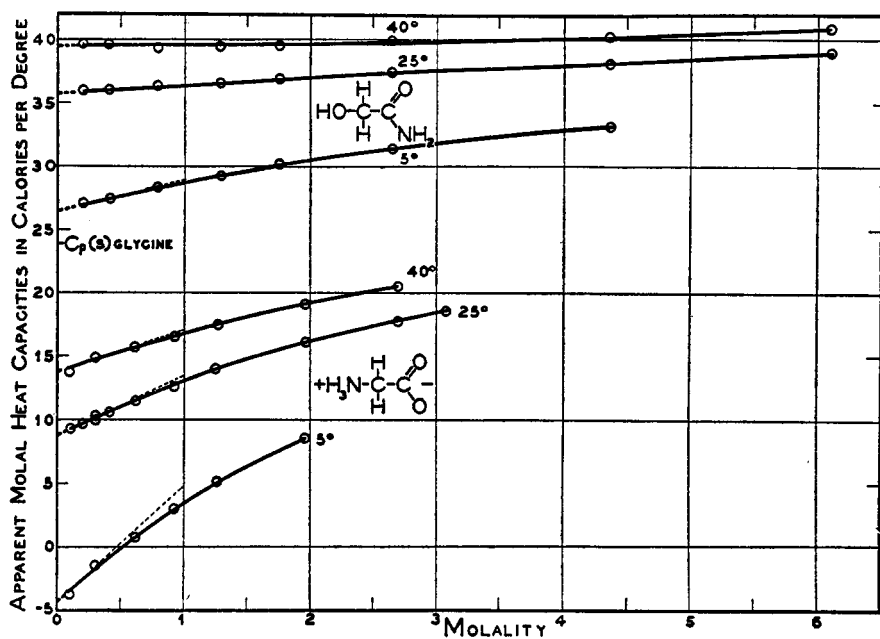


FIG. 1. The apparent molal heat capacities of glycine and glycolamide at 5°, 25°, and 40°C.

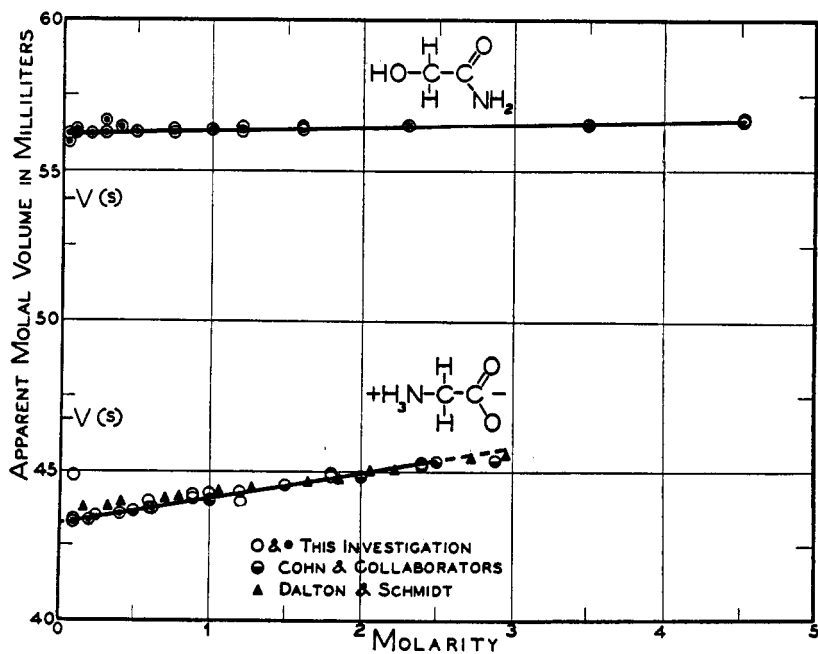


FIG. 2. The apparent molal volumes of glycine and glycolamide at 25°C.

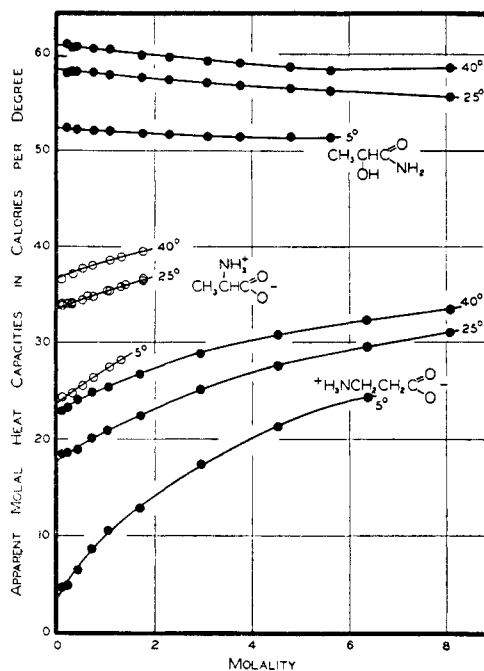


FIG. 3. The apparent molal heat capacities of α -alanine, β -alanine, and lactamide at 5°, 25°, and 40°C.

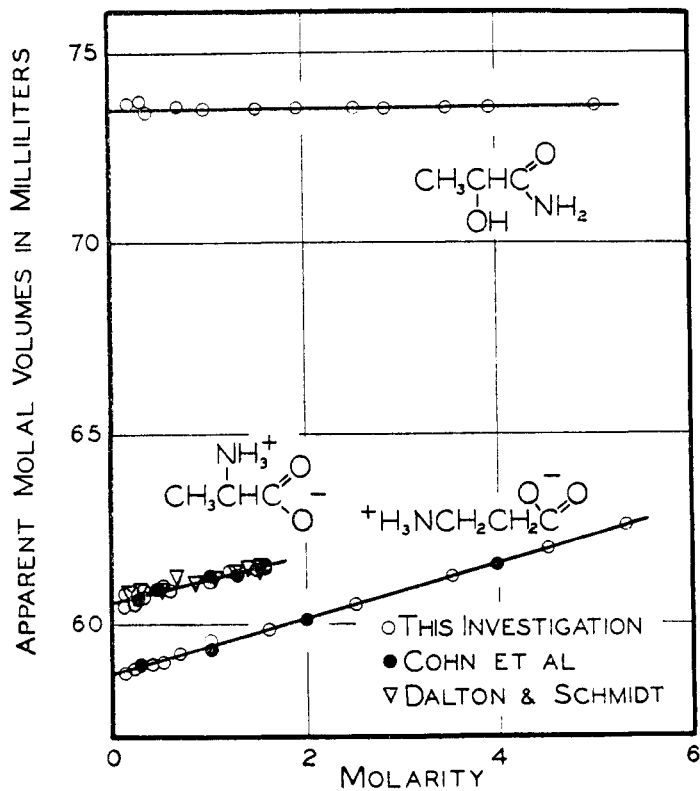


FIG. 4. The apparent molal volumes of α -alanine, β -alanine, and lactamide at 25°C.

II. THEORETICAL INTERPRETATION OF THE RESULTS

An electrostatic treatment of the thermodynamic properties of dipolar solutes may be conveniently divided into two distinct parts. First we shall be interested in the calculation of the limiting slopes of the partial molal heat capacities and volumes, and second, we shall wish to account for the differences between the absolute values of these properties for the amino acids and their corresponding uncharged isomers in the infinitely dilute solution.

As has been pointed out in previous papers (8, 9, 10), we have as yet no theory which will predict quantitatively the behavior of aqueous solutions of dipolar solutes like the amino acids. Fuoss (6) has attempted to describe the thermodynamic properties of such solutions in terms of the mutual interaction of pairs of spherical solute molecules containing central point dipoles. His theory makes use of a parameter:

$$x = \frac{\mu^2}{a^3 D k T}$$

where μ is the dipole moment, a the molecular diameter, D the dielectric constant of the solvent, T the absolute temperature, and k the Boltzmann constant. In the present paper this parameter has been modified as suggested by Kirkwood (12) to take into account the discontinuity of the dielectric constant at the surface of the solute molecule. The new parameter y is

$$y = \left[\frac{3D}{2D + D_i} \right]^2 \frac{\mu^2}{a^3 D k T}$$

where D_i is the dielectric constant within the spherical cavity containing the dipole.

The senior author, in collaboration with Dr. W. L. Ford (5), has employed this new parameter to calculate the contribution of the dipole-dipole interaction to the apparent molal volumes and heat capacities of dipolar solutes in dilute solutions. If we substitute y in the Fuoss equation for the change in partial molal free energy of the solute due to this interaction, we have simply:

$$\bar{F}_2 - \bar{F}_2^0 = \frac{-RTNJ}{V} \quad (1)$$

where R is the gas constant, N is Avogadro's number, and V is the volume (in liters) of solution containing 1 mole of the solute. J is defined by the equation

$$J = 2a^3 y \theta(y) \quad (2)$$

where

$$\theta(y) = \frac{2y}{9} \left(1 + \frac{1}{25} y^2 + \frac{29}{18375} y^4 + \dots \right) \quad (3)$$

Carrying out the necessary differentiations with respect to temperature, we obtain the following equation for the change in partial molal heat capacity due to dipolar interaction:

$$\bar{C}_{p_2} - \bar{C}_{p_2}^0 = \frac{RNT^2}{V} \left[2 \left(\frac{1}{T} - \alpha \right) \left(\frac{J}{T} - J\alpha \right) + \frac{\partial^2 J}{\partial T^2} - \frac{J}{V} \frac{\partial^2 V}{\partial T^2} \right] \quad (4)$$

where α stands for $\frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P$, the coefficient of expansibility of the solvent. It should be pointed out that this equation differs from that of Fuoss in considering the temperature coefficient of the dielectric constant of the medium. Fuoss' treatment apparently considers the dielectric constant of the medium independent of temperature and hence is not applicable to aqueous solutions.

TABLE 1
Limiting slopes for partial molal heat capacities and volumes

	$\frac{\partial \bar{C}_{p_2}}{\partial m}$ (OBSERVED)	$\frac{\partial \bar{C}_{p_2}}{\partial m}$ (CALCULATED)	$\frac{\partial \bar{V}_2}{\partial c}$ (OBSERVED)	$\frac{\partial \bar{V}_2}{\partial c}$ (CALCULATED)
Glycine-glycolamide	7.72	0.55	1.46	0.25
α -Alanine-lactamide	3.92	0.31	1.12	0.16
β -Alanine-lactamide	6.24	0.78	1.40	0.54

Using the values of μ and a from table 2, and the following data, we may evaluate the parameter y for the dipoles under consideration:

$$\begin{aligned} D &= 78.54 \\ D_i &= 1 \text{ (assumed)} \\ k &= 1.37 \times 10^{-16} \text{ ergs per degree per molecule} \\ T &= 298^\circ \text{ A.} \end{aligned}$$

This leads to a solution of equation 4, and the limiting slopes for glycine, α -alanine, and β -alanine, compared with the observed values, are listed in table 1. The observed values are obtained by subtracting the limiting slopes of the corresponding uncharged isomers from those of the amino acids, i.e., glycolamide from glycine, and lactamide from α - and β -alanine. This gives us the closest approximation for the experimental value of the limiting slope for "pure" dipole-dipole interaction. The agreement between theory and experiment (about a factor of 10) is fair, considering the very simple model and the inaccuracies of the calculation which arise from taking the differences between large numbers.

A consideration of the pressure coefficient of the free-energy equation leads to the corresponding equation for the partial molal volume change due to dipolar interaction:

$$\bar{V}_2 - \bar{V}_2^0 = - \frac{RTN}{V} \left[\frac{\partial J}{\partial y} \cdot \frac{\partial y}{\partial P} + J\beta \right] \quad (5)$$

where $\beta = -\frac{1}{\bar{V}} \left(\frac{\partial \bar{V}}{\partial P} \right)_T$, the coefficient of compressibility. Table 1 lists the results of the evaluation of the limiting slopes for the partial molal volumes of glycine, α -alanine, and β -alanine at 25°C. The corresponding observed values, obtained in the same manner given above for the heat capacities, are also to be found in the table. Thus the agreement between theoretical and observed values is somewhat better in the case of the volumes than for the heat capacities.

As a qualitative result of the Fuoss theory, the larger the value of the parameter μ^2/a^3 , the greater should be the value of the limiting slopes $\partial \bar{C}_{p2}/\partial m$ and

TABLE 2
Parameters and limiting slopes for five amino acids and amides

	GLYCINE	β -ALANINE	α -ALANINE	GLYCOLAMIDE	LACTAMIDE
$\mu \times 10^{18}$	15.3	18.9	15.3	2	2
$a \times 10^8$	5.28	5.84	5.82	5.54	6.00
$\frac{\mu^2}{a^3} \times 10^{12}$	1.59	1.79	1.19	0.023	0.018
$\frac{\partial \bar{C}_{p2}}{\partial m}$ (25°C.).....	9.16	5.28	2.96	1.44	-0.96
$\frac{\partial \bar{V}_2}{\partial c}$ (25°C.).....	1.72	1.43	1.15	0.26	0.034

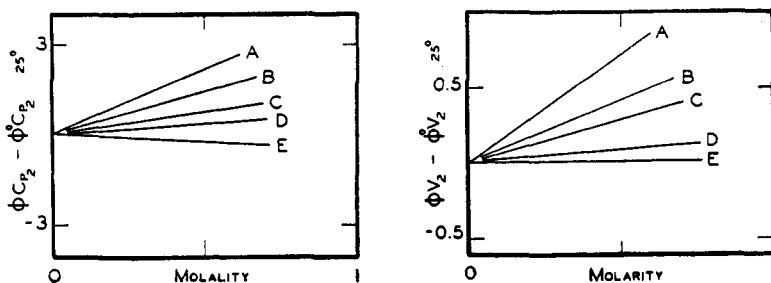


FIG. 5. The limiting slopes of the apparent molal heat capacities and volumes at 25°C. Curve A, glycine; curve B, β -alanine; curve C, α -alanine; curve D, glycolamide; curve E, lactamide.

$\partial \bar{V}_2/\partial c$. It is interesting at this point to compare the values of the parameter and limiting slopes for all five amino acids and amides studied to date in this Laboratory. These values are contained in table 2, and graphical comparison is made in figure 5. In order to make the data in table 2 truly comparable, all values of μ , except those of lactamide and glycolamide, were derived from experimental investigations of the dielectric increment (2), and all values of a from the molal volume of the solid substance. The dipole moments of glycolamide and lactamide were roughly estimated from structural considerations.

Rough agreement with the Fuoss theory is shown in all comparisons except that between glycine and β -alanine. According to the theory, the limiting

slopes of the partial molal volumes and the partial molal heat capacities should be greater for β -alanine than for glycine, but the opposite is observed. • However, this discrepancy may not be significant when one considers the simplicity of the Fuoss model of a point dipole at the center of a sphere, and the sensitivity of the parameter μ^2/a^3 to the choice of values for μ and a . It is obvious that, of the compounds under consideration, the β -alanine molecule would be the least likely to conform to the model of a point dipole at the center of a sphere. A further refinement of the Fuoss model would be to consider the finite distance of separation between the charges of the dipole. Calculations along this line have been started by the senior author, in collaboration with Dr. Hugh B. Pickard, and the results, as yet not complete, indicate a further contribution of about 20 per cent to the thermodynamic properties considered above.

To account for the magnitude of some of the thermodynamic properties of dipolar ions in an infinitely dilute aqueous solution, an electrostatic treatment, employing the Kirkwood (11) formula for the charging energy of an ion, has

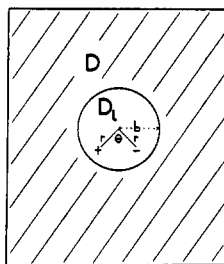


FIG. 6. Model for amino acid molecule

been adopted. We have accepted the model for an amino acid molecule shown in figure 6 and have calculated the apparent molal heat capacity and volume changes in the reaction



For a spherical molecule consisting of an arbitrary charge distribution in a cavity of radius b and dielectric constant D_i , situated in a medium of dielectric constant D and in the absence of electrolyte, the free energy of solvation is given by

$$W_0 = \frac{1}{2} \sum_{n=0}^{\infty} \frac{(n+1)Q_n(D_i - D)}{D_i b^{2n+1} [(n+1)D + nD_i]} \quad (7)$$

where Q_n is

$$Q_n = \sum_{k=1}^m \sum_{l=1}^m \epsilon_k \epsilon_l r_k^n r_l^n P_n(\cos \theta_{kl}) \quad (8)$$

in which " $P_n(\cos \theta)$ " are the ordinary Legendre functions and θ_{kl} is the angle between r_k and r_l , the lines drawn from the center of the sphere b to the charges

ϵ_k and ϵ_j ." In the reaction represented by equation 6 the change in the charging energy will be given by

$$\Delta W_0 = \frac{1}{2} \sum_{n=1}^{\infty} \frac{(n+1)Q_n(D_i - D)}{D_i b^{2n+1}[(n+1)D + nD_i]} - \frac{1}{2} \sum_{n=1}^{\infty} \frac{(n+1)Q'_n(D_i - D)}{D_i b'^{(2n+1)}[(n+1)D + nD_i]} \quad (9)$$

$$\Delta W_0 = \frac{1}{2} \sum_{n=1}^{\infty} \frac{(n+1)}{D_i} \frac{(D_i - D)}{[(n+1)D + nD_i]} \left[\frac{Q_n}{b^{2n+1}} - \frac{Q'_n}{b'^{(2n+1)}} \right] \quad (10)$$

where the primed symbols refer to the amide. If we let N represent Avogadro's number, then

$$\begin{aligned} \frac{\Delta \bar{C}_{p_2}^0}{N} &= -T \left(\frac{\partial^2 \Delta W_0}{\partial T^2} \right)_p \\ &= -\frac{T}{2} \frac{\partial^2}{\partial T^2} \sum_{n=1}^{\infty} \frac{(n+1)}{D_i} \frac{(D_i - D)}{[(n+1)D + nD_i]} \left[\frac{Q_n}{b^{2n+1}} - \frac{Q'_n}{b'^{(2n+1)}} \right] \\ &= -\frac{T}{2} \sum_{n=1}^{\infty} \frac{(n+1)}{D_i} \left[\frac{Q_n}{b^{2n+1}} - \frac{Q'_n}{b'^{(2n+1)}} \right] \frac{\partial^2}{\partial T^2} \left[\frac{(D_i - D)}{(n+1)D + nD_i} \right] \end{aligned} \quad (11)$$

It follows that

$$\begin{aligned} \frac{\partial^2}{\partial T^2} \left[\frac{(D_i - D)}{(n+1)D + nD_i} \right] \\ = \frac{-(2n+1)D_i[(n+1)D + nD_i] \frac{\partial^2 D}{\partial T^2} + 2(2n+1)(n+1)D_i \left(\frac{\partial D}{\partial T} \right)^2}{[(n+1)D + nD_i]^3} \end{aligned} \quad (12)$$

At this point it is convenient to adopt one of the standard equations for the variation of the dielectric constant of water with temperature. We shall consider first the form used both by Åkerlöf and Short (1) and Wyman and Ingalls (18):

$$\ln D = \alpha - \beta T \quad (13)$$

where α and β are constants; but later we shall also consider the effects of two other types of equations. Using equation 13 and assuming that $D_i = 1$, we may simplify equation 12 to:

$$\frac{\partial^2}{\partial T^2} \left[\frac{(D_i - D)}{(n+1)D + nD_i} \right] = \frac{(2n+1)\beta^2 D[(n+1)D - n]}{[(n+1)D + n]^3} \quad (14)$$

Hence it follows that

$$\frac{\Delta \bar{C}_{p_2}^0}{N} = -\frac{T}{2} \sum_{n=1}^{\infty} (n+1) \left[\frac{Q_n}{b^{2n+1}} - \frac{Q'_n}{b'^{(2n+1)}} \right] \frac{(2n+1)\beta^2 D[(n+1)D - n]}{[(n+1)D + n]^3} \quad (15)$$

It is possible to simplify equation 15 by a consideration of the relative magnitudes of some of its terms. Since, for water, D is of the order of 80, $(n+1)D \gg n$, and we may neglect n with respect to $(n+1)D$. Furthermore, since the values of b and b' are roughly equal, whereas $Q_n \gg Q'_n$, we may neglect

$Q'_n/b'^{(2n+1)}$ with respect to $Q_n/b^{(2n+1)}$. In the latter approximation the inclusion of the primed terms would change the value obtained for $\Delta\bar{C}_{p_2}^0$ by less than 2 per cent. Thus we obtain

$$\frac{\Delta\bar{C}_{p_2}^0}{N} = -\frac{T\beta^2}{2D} \sum_{n=1}^{\infty} \frac{(2n+1)}{(n+1)} \frac{Q_n}{b^{2n+1}} \quad (16)$$

According to Cohn (2), Kirkwood has calculated the percentage of the total effect that may be attributed to terms higher than $n = 1$ for the change in the solubility with change in dielectric constant. For glycine the higher multipoles contribute 14 per cent, whereas for α -alanine they are responsible for 33 per cent. Since Kirkwood's calculation is essentially one for the contribution of the higher order multipoles to the charging energy, it is possible to estimate, by a method of comparison of series, the percentage effect in the heat capacities

TABLE 3
 $\Delta\bar{C}_{p_2}^0$ at 25°C. in calories per mole per degree

	DIPOLE TERM	ALL TERMS	EXPERIMENTAL
Glycine-glycolamide.....	-11.3	-13.0	-26.9
α -Alanine-lactamide.....	-8.3	-11.2	-20.1
β -Alanine-lactamide.....	-11.0	*	-35.6

* The effect of higher multipoles is unknown, owing to uncertainty in what to take for the shape factor.

also. Simplifying the equation for the change in solvation energy in the same manner as we have simplified that for the heat-capacity change, we obtain:

$$\Delta W_0 = \frac{1}{2} \sum_{n=1}^{\infty} \frac{Q_n}{b^{2n+1}} \quad (17)$$

If we now consider the ratios of successive terms in the series represented by equations 16 and 17, respectively, we find that the relative contributions of successive terms to the total value of the series is very slightly greater for the heat-capacity series. However, this excess effect is only about 5 per cent of the contribution of the multipoles higher than the dipole, so that the effect on the total heat capacity should be about 15 per cent (14 per cent + 1 per cent) for glycine and about 35 per cent (33 per cent + 2 per cent) for α -alanine.

Table 3 lists the values obtained for $\Delta\bar{C}_{p_2}^0$ by a calculation including only the dipole term of the series and by one including all the terms. These are compared with the experimental values. The total summation is given by the sum of the dipole term plus the per cent of this term (given above for glycine and α -alanine) due to higher multipoles. For the calculation of the theoretical values, the values given in table 4 were adopted for the various constants and parameters.

In the above treatment we have assumed that the variation of the dielectric constant of water with temperature is given by equation 13. A number of other

equations, however, have also been found applicable. Thus Everett and Wynne-Jones (4) have called attention to the fact that an equation of the form

$$\log D = A - B \log T \quad (18)$$

represents very closely the data of Kockel (13) and of Lattey, Gatty, and Davies (15). On the other hand, Wyman and Ingalls (18) use a power series to express their results.

For purposes of comparison we have derived expressions for the heat-capacity change for each of the three types of equation for D , and have evaluated these expressions for the difference between glycine and glycolamide. In these calculations we have considered only the first term of the series for $\Delta\bar{C}_{p_2}^0$ and have

TABLE 4
Constants and parameters used in charging energy calculations

	GLYCINE	α -ALANINE	β -ALANINE
μ in Debye units.	15	15	19
b in Å.	2.64	2.91	2.92

In the Åkerlöf-Short equation, $\beta = 0.00472 \text{ deg.}^{-1}$
At 25°C., $D = 79$.

TABLE 5
Variation in $\Delta\bar{C}_{p_2}^0$ with equation for D ; glycine-glycolamide at 25°C.

EQUATION FOR D	$\Delta\bar{C}_{p_2}^0$
$\ln D = \alpha - \beta T$	-11.3
$\log D = A - B \log T$	-4.0
$D = 78.5\frac{1}{2} [1 - a(t - 25) + \dots]$	-9.3

employed the constants given by the authors for each of the equations. Our calculations, therefore, include not only the effect of the different types of equation but also the discrepancies in the work of the different authors. It should be noted, however, that Wyman and Ingalls (18) fitted their results to an equation of the type of equation 13 and obtained a value of β which does not differ significantly from that of Åkerlöf and Short (1).

From table 5 it is obvious that the value obtained for $\Delta\bar{C}_{p_2}^0$ is very sensitive to the equation used for the variation of the dielectric constant of water with temperature. However, in all cases, the value obtained for $\Delta\bar{C}_{p_2}^0$ is much smaller than the experimental value, -26.9 calories per degree \times mole. It would seem, therefore, either that the model which has been used is too simple to account for the entire heat-capacity change, or, perhaps, that μ^2/b^3 is not truly independent of temperature.

The calculation of the general expression for the change in partial molal

volume at infinite dilution accompanying the reaction represented by equation 6 is quite straightforward. The pressure coefficient of equation 10 would be

$$\frac{\Delta \bar{V}_2^0}{N} = \left(\frac{\partial \Delta W_0}{\partial P} \right)_T = \frac{1}{2} \sum_{n=1}^{\infty} \frac{n+1}{D_i} \left[\frac{Q_n}{b^{2n+1}} - \frac{Q'_n}{b^{(2n+1)'}} \right] \frac{\partial}{\partial P} \left[\frac{D_i - D}{(n+1)D + nD_i} \right] \quad (19)$$

which, if we make the usual approximations, can be reduced to

$$\frac{\Delta \bar{V}_2^0}{N} = -\frac{1}{2D^2} \frac{\partial D}{\partial P} \sum_{n=1}^{\infty} \frac{(2n+1)}{(n+1)} \frac{Q_n}{b^{2n+1}} \quad (20)$$

This equation has the same general form as equation 16, for the change in heat capacity. The consideration of the relative contribution of multipoles higher than the dipole, discussed for the heat capacities, is also applicable to the volume changes. Hence we shall calculate $\Delta \bar{V}_2^0$ from the first term of equation 20.

$$\frac{\Delta \bar{V}_2^0}{N} = -\frac{3}{4} \frac{\mu^2}{b^3 D^2} \frac{\partial D}{\partial P} \quad (21)$$

Gucker (7) and Redlich (16) have considered the available data for the calculation of the pressure coefficient of the dielectric constant of water. The work of Kyropoulos (14) at 20°C. has been most generally accepted. We shall assume that Kyropoulos' data, which can be expressed by the equation

$$D = 80.79(1 + 59.2 \times 10^{-6}P - 3.28 \times 10^{-9}P^2 - 1.61 \times 10^{-12}P^3 + \dots) \quad (22)$$

can be applied at 25°C. Since our calculations are quite crude anyway, any change due to the difference between the pressure coefficient of D at 20° and 25°C. is probably insignificant. Utilizing values for the radii obtained from the molal volumes of the solid substances and the pressure coefficient of D obtained from equation 22, we find the values for $\Delta \bar{V}_2^0$ given in table 6.

The agreement between calculated and observed values of $\Delta \bar{V}_2^0$ is about as good as that for $\Delta \bar{C}_{p_2}^0$. The suggestion of Redlich (17) that $\partial D/\partial P$ be determined from the limiting slopes of the partial molal volumes of electrolytes in aqueous solutions was also considered, but his value would not alter our calculated values significantly. However, there is much uncertainty in the value of $\partial D/\partial P$ and hence in the calculated values of $\Delta \bar{V}_2^0$.

Table 7 lists the calculated values for b obtained from the first terms of the respective series for the apparent molal heat-capacity and apparent molal volume changes at 25°C. The experimental values for $\Delta \bar{C}_{p_2}^0$ and $\Delta \bar{V}_2^0$ were employed.

Table 7 is a convenient way of comparing the results obtained from different types of measurement, although it minimizes the disagreement between the experimental and calculated values, since any error in the heat capacity or volume change enters as a *cube root* in b . It is apparent, then, that the model used for the calculations listed above is perhaps a good first approximation, but does not account for the entire effect observed experimentally.

Recently, Everett and Coulson (3) have made a more detailed model for ions in aqueous solution, in which they attempt to break up the treatment of the

solvent into two different parts. The change in the heat capacity due to the restriction in rotation of the water molecules in the first shell around an ion is calculated by statistical methods, while the contribution of all the other water shells is assumed to be given by the Born charging energy. Such an approach predicts values of the changes in heat capacity upon the ionization of acids which are fairly close to the values experimentally observed.

The above treatment assumes that the ions under consideration are spherically symmetrical, which is not the case for the amino acids. One may attempt, however, to make a very rough application of the method of Everett and Coulson to the amino acids by assuming that the molecule may be represented by a dumbbell, one end containing a sphere of charge $+\epsilon$ and the other a sphere of charge $-\epsilon$. If the radii of these spheres are each about 1 \AA ., and if each sphere

TABLE 6
Values of $\Delta\bar{V}_2^0$ at infinite dilution at 25°C .

	$\Delta\bar{V}_2^0$ (CALCULATED)	$\Delta\bar{V}_2^0$ (EXPERIMENTAL)
	ml.	ml.
Glycine-glycolamide	-4.1	-12.97
α -Alanine-lactamide	-3.1	-12.90
β -Alanine-lactamide	-4.8	-14.79

TABLE 7
Values of b in \AA . from consideration of experimental data at 25°C .

	$\Delta\bar{C}_{p_2}^0$	$\Delta\bar{V}_2^0$	PROM SOLID
Glycine	1.97	1.8	2.64
α -Alanine	2.16	1.8	2.91
β -Alanine	2.10	2.0	2.92

is surrounded by four water molecules in the first shell so that the solvated molecule has a radius of about 4.5 \AA ., then the predicted value of $\Delta\bar{C}_{p_2}^0$ would be about 22 calories per degree per mole. However, a treatment based on this very crude model disregards the asymmetry of the amino acid molecule and neglects the effect of the field of the positive end of the dipole on the water molecules surrounding the negative end, and *vice versa*. For the present, then, one can only say that this new model can be made to account for practically all of the observed change in heat capacity, and that it predicts the correct sign for the temperature coefficient of the heat capacity.

III. SUMMARY

The limiting slopes of the partial molal heat capacities and volumes for glycine, α -alanine, and β -alanine have been calculated from the Fuoss theory of dipolar solute interaction. Observed and calculated slopes agree within a factor of about 10 for the heat capacities and slightly better for the volumes.

The differences in the heat capacities and volumes at infinite dilution between these amino acids and their corresponding uncharged isomers have been estimated from an electrostatic standpoint. The calculated values are approximately one-third of the experimental.

Possible refinements in the theoretical treatment have been indicated.

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