gives the diffusion constant **D** in terms of the axial ratio $\rho = 10/5000$ and $\mathbf{D}_0$, the diffusion constant of the equivalent sphere of radius $a_0 = 5000\ \rho^{2/3}/2 \approx 40$ Å. Assuming Stokes' model, we find

$$D_0 = kT/6\pi\eta a_0 = 0.61 \times 10^{-6} \text{ cm.}^2/\text{sec.} \quad (2)$$

using the familiar Einstein relationship between diffusion coefficient and friction coefficient. Substituting numerical values, $\mathbf{D}/\mathbf{D}_0 = 0.110$ and $\mathbf{D} = 6.7 \times 10^{-8}$. The mobility u in c. g. s. units is then

$$u = Q\mathrm{D}/300kT \quad (3)$$

where Q is 2000 times the electron charge and the factor of 300 converts to practical units from e. s. u. For the rod-like model, we have

$$u = 0.0052 \text{ (cm./sec.)/(volt/cm.)}$$

and on multiplying by the faraday

$$\lambda^+ = 500$$

We would accordingly expect a limiting equivalent conductance of the order of 600, *i. e.*, far above the top of the scale of Fig. 1, for the polybromide. As has already been mentioned, however, we do not expect to find even the beginning of the predicted sharp rise in conductance at any experimentally accessible concentration. On the basis of this calculation, a large Wien effect should appear for polyelectrolytes of this type, but for ordinary low voltage conductance, the $\Lambda - \sqrt{c}$ curves experimentally observed will probably seem to approach the limiting conductance of the gegen ion as their limit.

Acknowledgment.—We are grateful to the Minnesota Mining and Manufacturing Company for a sample of polyacrylic acid, and to E. I. du Pont de Nemours and Company for a sample of Elvanol 71–24.

Summary

1. Conductances and viscosities of poly-4-vinyl-N-*n*-butylpyridonium bromide and of sodium polyacrylate in water at 25° in the moderately concentrated range (up to 0.3 normal) have been measured.

2. In the upper part of this range of concentration, interionic distances, both in the polyelectrolyte and in solutions of one–one electrolytes, become of the same order.

3. The experimental results suggest that n the polyelectrolyte gegen ions behave much like the same ions in simple electrolytes, except that their transference number is nearly unity.

NEW HAVEN, CONNECTICUT RECEIVED OCTOBER 29, 1949

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

The Adiabatic Compressibility of Aqueous Solutions of Some Simple Amino Acids and Their Uncharged Isomers at 25°[1]

BY FRANK T. GUCKER, JR.,*[2] FRANK W. LAMB, GLENN A. MARSH AND ROBERT M. HAAG

For a number of years various thermodynamic properties of solutions of simple amino acids and their uncharged isomers have been studied in this Laboratory in order to determine the influence of the dipole moment of the amino acids. We have found that the apparent molal heat capacities and volumes[3,4] and the heats of dilution[5] of glycine and glycolamide, and the apparent molal heat capacities and volumes of *dl*-α-alanine, β-alanine and lactamide,[6] are linear functions of the molality in dilute solutions, and sometimes over a considerable range of concentration. The interpretation of most of these results was discussed[7] on the basis of the theory developed by R. M. Fuoss[8] for the mutual interaction of pairs of spherical solute molecules each containing a central point dipole, as modified by J. G. Kirkwood[9] to take into account the discontinuity of the dielectric constant between the surface of the solute molecule and the solvent. This theory predicts an increase of all of these apparent molal properties which is linear with the concentration in the infinitely dilute solution, and limiting slopes which are proportional to the fourth power of the dipole moment, divided by the molecular volume. Rough agreement with this theory is shown by most of the solutions. A consideration of the energy of charging the dipolar ion also affords an explanation of the limiting value of the apparent molal volumes and heat capacities. The present paper describes the extension of our experimental work to the determination of the compressibility of some of these solutions, which may be given a similar theoretical treatment since the apparent molal compressibility is simply the negative of the pressure coefficient

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* Harvard University Ph.D. 1925.

[1] This paper was presented at the 115th Meeting of the American Chemical Society, San Francisco, California, March 27–April 1, 1949. This work was supported by grants-in-aid from the Abbott Fund of Northwestern University.

[2] Present address: Indiana University, Bloomington, Indiana.

[3] F. T. Gucker, Jr., W. L. Ford and C. E. Moser, *J. Phys. Chem.*, **43**, 153 (1939).

[4] F. T. Gucker, Jr., and W. L. Ford, *ibid.*, **45**, 309 (1941).

[5] F. T. Gucker, Jr., H. B. Pickard and W. L. Ford, THIS JOURNAL, **62**, 2698 (1940).

[6] F. T. Gucker, Jr., and T. W. Allen, *ibid.*, **64**, 191 (1942).

[7] F. T. Gucker, Jr., I. M. Klotz and T. W. Allen, *Chem. Revs.*, **30**, 191 (1942).

[8] R. M. Fuoss, THIS JOURNAL, **58**, 982 (1936).

[9] J. G. Kirkwood, *Chem. Revs.*, **19**, 275 (1936).

of the apparent molal volume. This relationship has already been discussed in the case of electrolytes.[10]

Few accurate measurements of the compressibility of solutions have been made. The data on strong electrolytes up to 1933 were shown by one of us[11] to indicate a linear change of the apparent molal compressibility with the square root of the concentration, which parallels the other properties of these substances, and can be predicted by the Debye–Hückel theory.[10] Most of the early results were obtained with a piezometer. Recently a more convenient method of determining compressibilities has been developed in the sonic interferometer for precise measurement of the wave length of a standing wave, usually of ultrasonic frequency. From the wave length and frequency of the sound wave, its velocity, v, in the medium is calculated, and this is related to the compressibility, β, and the density, d, by means of the well-known equation derived by I. Newton

$$v = \sqrt{1/\beta d} \qquad (1)$$

As pointed out by P. S. Laplace, the sound wave traverses the medium so rapidly that β measured in this way is the *adiabatic* compressibility of the solution, not the isothermal

$$\beta(\text{adiabatic}) = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_S, \text{ while } \beta(\text{isothermal}) = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$$

A review of ultrasonic interferometers has been given by L. Bergmann.[12] More recently D. R. McMillan, Jr., and R. T. Lagemann[13] and A. Weissler[14] have described improved interferometers. These articles were published subsequent to most of our work.

Apparatus.—Two ultrasonic interferometers were built in this Laboratory for the study of solutions, both operated at approximately 4 megacycles. In the first, built by F. W. L.,[15] the reflector was carried on a Brown and Sharpe metric micrometer depth gage graduated in 0.01 mm. from which the next place could be estimated. In the second, built by G. A. M.,[16] the reflector shaft moved without rotation and carried a fiduciary mark, the position of which could be determined with a reproducibility of ±0.003 mm., using a Gaertner traveling microscope equipped with a built-in illuminator and bifilar crosshairs. This interferometer is shown in the partially-exploded Fig. 1, where the most important parts are indicated by letters identified in the legend. Since the velocity of sound in water changes by 0.17% per degree, the temperature of the cell was held at 25.00 ± 0.05° by circulating water from a 30-liter thermostat at several liters per minute through a coil of copper tubing T wound around the interferometer.

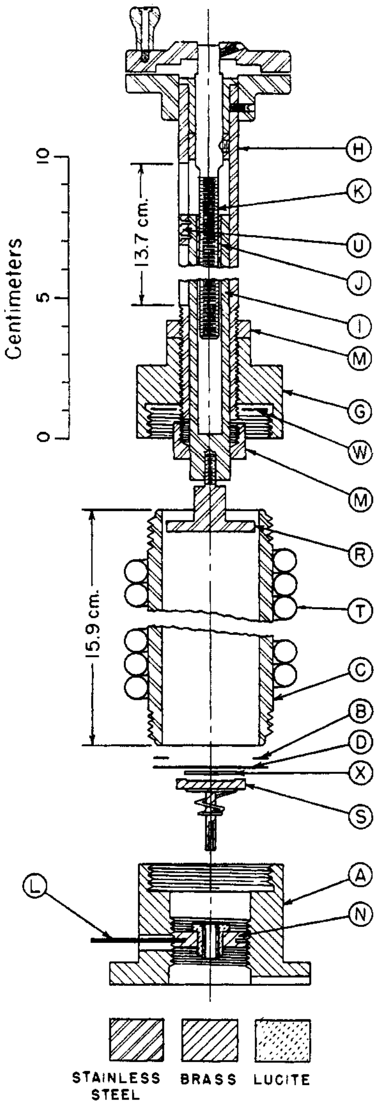

Fig. 1.—The ultrasonic interferometer: A, base; B, tantalum washer; C, cell; D, 0.013-mm, (0.0005 in.) tantalum diaphragm; G, cell cap; H, guide tube; I, reflector shaft; J, threaded bushing; K, metric lead screw; L, lever to adjust tension on crystal; M, lock nut; N, threaded bushing with insulated center bearing; R, reflector; S, crystal support with quarter-wave cavity; T, copper tubing; U, guide block with fiduciary mark; W, tantalum washer; X, crystal.

The final electrical circuits, shown in Fig. 2, are described elsewhere in greater detail.[16,17] The control crystal X_1 is BT-cut to minimize the effect of temperature changes while X_2, adjusted to the same frequency, is X-cut to assure perpendicular vibrations of the interferometer diaphragm. The a. c. signal taken from the 7500-ohm resistor in series with the 0.0002-microfarad condenser and X_2, is rectified by the type 6H6 diode. The motion of the interferometer reflector changes the impedance of X_2, and hence the voltage developed across the plate resistor of the diode. The 6SJ7 and 6C5 are operated as d. c. voltage and current amplifiers, respectively, to give an output

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[10] F. T. Gucker, Jr., *Chem. Revs.*, **13**, 111 (1933).

[11] F. T. Gucker, Jr., THIS JOURNAL, **55**, 2709 (1933).

[12] L. Bergmann, "Ultrasonics and their Scientific Applications," John Wiley and Sons, Inc., New York, N. Y., 1938.

[13] D. R. McMillan, Jr., and R. T. Lagemann, *J. Acoust. Soc. Am.*, **19**, 956 (1947).

[14] A. Weissler, THIS JOURNAL, **70**, 1634 (1948).

[15] Frank W. Lamb, Ph.D. Dissertation, Northwestern University, 1941.

[16] Glenn A. Marsh, M.S. Thesis, Northwestern University, 1946.

[17] Robert M. Haag, M. S. Thesis, Northwestern University, 1948.

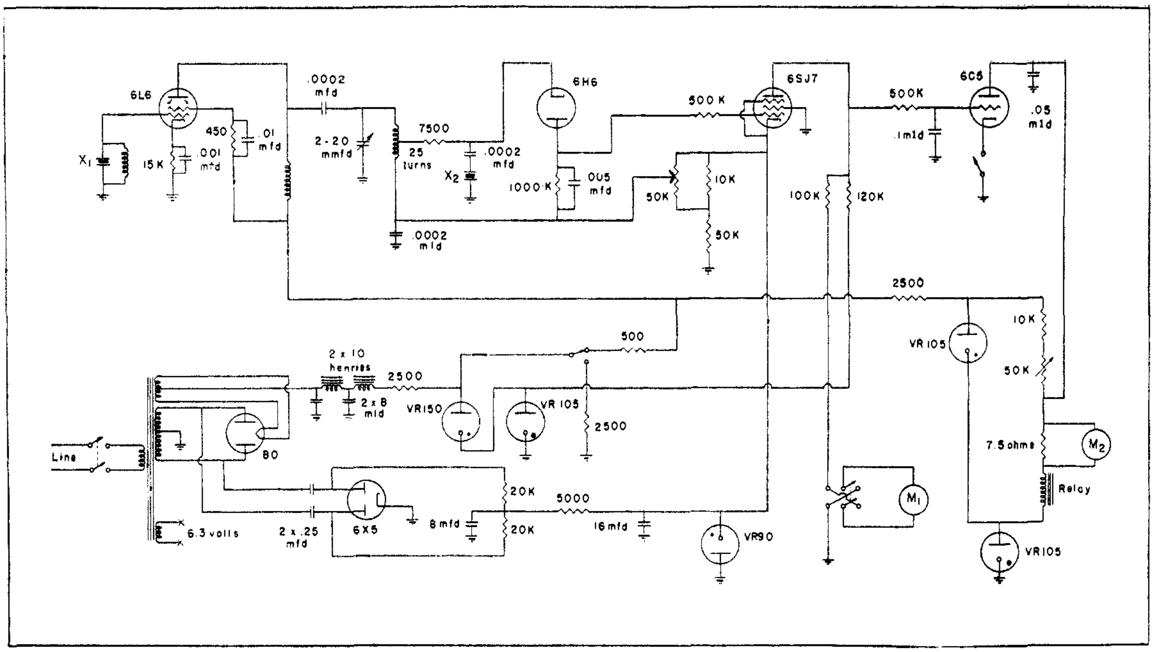

Fig. 2.—Electronic circuits for the interferometer.

which actuates a relay controlling the 6-volt supply to a Cenco Impulse Counter, made by the Central Scientific Company, Chicago, Illinois.

The cathode of the 6SJ7 amplifier is held at −90 v. About 30 v. is developed across the plate resistor of the 6H6 diode, most of which is cancelled out by means of the variable bias introduced by the 50-K potentiometer in the cathode circuit of the 6SJ7 tube.

The change in grid voltage of the 6SJ7 tube over one-half wave length does not exceed 0.2-0.3 v. When the impedance of the driving crystal is greatest, the grid of the 6C5 current amplifier is held at about −5 v., just above cut-off, and the plate current through the 10-K. (kilohm) resistor and 50-K rheostat can be adjusted by turning the latter so that the plate potential exactly balances that of the VR-105 connected between the relay and ground, giving a zero reading on the milliammeter M_2 and no current through the relay. A decrease in the impedance of X_2 reduces the voltage developed across the 6H6-plate resistor, making the grid of the 6SJ7 less negative and increasing the current through the tube. This swings the grid of the 6C5 more negative, decreasing its plate current and plate potential, and sending current through the meter and relay, which give visual evidence of a node and register it on the counter.

Materials and Solutions.—Previous publications from this Laboratory have described the preparation and purification of glycine and glycolamide[3,4,5] and of α- and β-alanine and lactamide.[6] Most of the solutes used in this work were reclaimed from previous experiments by the methods already described,[3,6] supplemented by some freshly-prepared materials. None of the materials gave a test for ammonia with Nessler reagent or for chloride with silver nitrate solution. Electrolytic impurities, determined from the conductance of 1.0 *m* solutions assuming each had an equivalent conductance of 100 mhos, amounted to 0.01-0.04% for all the materials except α-alanine, where they were 0.25%.

All solutions were made up determinate in 100-ml. volumetric flasks, using distilled water with a specific conductance of about 4×10^{-6} mho. The weights were calibrated, and all weighings were reduced to the vacuum basis as in the previous work. A series of dilutions was made from each of the more concentrated solutions. Precautions described in the previous work were taken to avoid contamination with microörganisms, and no solution was allowed to stand for more than one week before use.

Experimental Methods.—In a typical experiment with the improved interferometer, the cell is first assembled and filled with conductivity water. Proper coupling to the crystal is obtained by adjusting the diaphragm tension screw and if necessary applying a new drop of solution of Vaseline in benzene between the crystal and the diaphragm until maximum-minimum swings of the proper magnitude are obtained with the wave length detector. The cell then is clamped in position before the micrometer comparator, connected to the constant-temperature water-circulating system, and allowed to stand for at least forty-five minutes to come to a constant temperature. The bias of the 6SJ7 tube is adjusted to hold the swings of the grid of the 6C5 centered around −6 v., and the balancing current in the plate circuit of the 6C5 is adjusted so that the minimum current through the relay is less than one-half the release current.

The reflector is placed about 1 cm. from the diaphragm, adjusted to give a minimum milliammeter reading, its position determined with the comparator, and the counter reading is recorded. The reflector is moved slowly through ten minima, and the positions and counter readings of the eleventh also is recorded. It is then moved more rapidly through two or three hundred minima, with positions and counter readings determined at intervals of about sixty. A final minimum then is located and its position recorded. As a check on the behavior of the counter, which may fail to record a minimum if the reflector is moved too rapidly, the half-wave length is determined from the first ten half-wave lengths and used to check the other values. Twice the total distance between the first and last minimum, divided by the total number of minima, gives an average wave length. One or two more runs are made and the results are averaged. The average difference obtained is about 0.02%.

The cell is then removed, emptied, rinsed with the solution to be measured, filled, replaced, and allowed to come to constant temperature, after which experiments are made with the solution in the manner described above. The relative velocity of sound in the solution is determined by the ratio of the wave lengths in the solution and in water. Using 1497.20 m./sec.[18,19] as the velocity of

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[18] E. Schreuer, *Akustisch*, **4**, 215 (1939).

[19] N. Seifen, *Z. Physik*, **108**, 681 (1937).

sound in water at 25°, the velocity in the solution is determined.

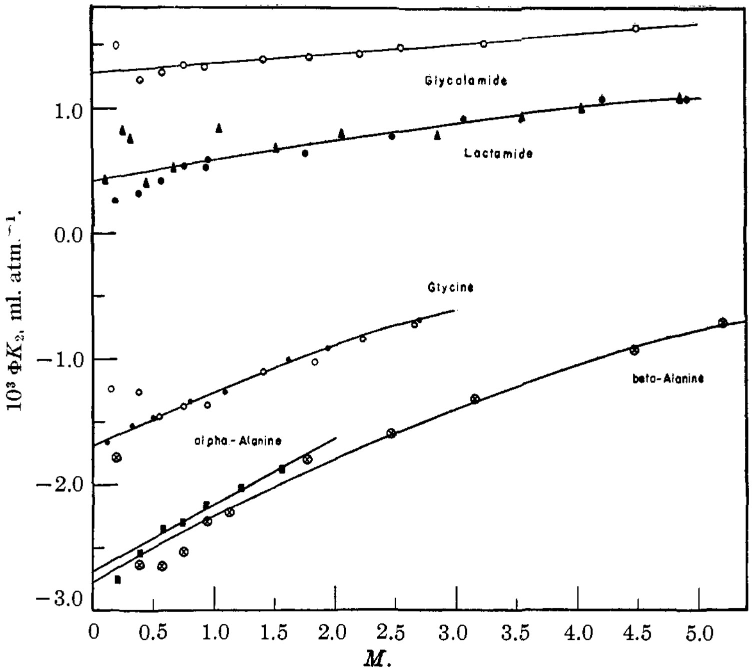

Fig. 3.—Apparent molar compressibilities of glycine and glycolamide (ordinate raised 1 unit), α- and β-alanine and lactamide. Data for lactamide (▲) by G. A. M., those for glycine (●) by R. M. H., all others by F. W. L.

Experimental Results.—From the velocity of sound in the solution and its density which is known as a function of the molarity[3,4,6] the values of the adiabatic compressibility are calculated by means of equation (1), while the corresponding apparent molal adiabatic compressibilities are calculated from the equation

$$\Phi K_2 = \left(\frac{1000}{c}\right)\beta - \left(\frac{1000\,d}{c} - M_2\right)\frac{\beta_1}{d_1} \qquad (2)$$

where c is the molarity (moles solute/l. solution), β, β_1, and d, d_1 are the compressibilities and densities of the solution and water, respectively, and M_2 is the molecular weight of the solute. The apparent molal compressibility is a convenient correlating function for experimental results over a range of concentration. It is proportional to the compressibility of the pure solvent, as we can see by expressing it in terms of the experimentally-determined relative wave length λ_r in the solution referred to the water, and specific gravity or relative density, d_r

$$\Phi K_2 = \left[\frac{1000}{c}\left(\frac{1}{\lambda_r^2 d_r^2} - 1\right) d_r + \frac{M_2}{d_1}\right]\beta_1 \qquad (3)$$

Whenever a more accurate value of β_1 is determined, the value of β for the solutions can be corrected easily through the corresponding change in ΦK_2.

Plots of the apparent molal compressibility against the molarity for all of these solutes give curves which approach straight lines as the concentration approaches zero, as shown in Fig. 3. At higher concentrations they show an appreciable decrease in the slope. All of these results can be expressed satisfactorily by second order equations for the apparent molal compressibility

$$\Phi K_2 = \Phi^\circ K_2 + ac + bc^2 \qquad (4)$$

The coefficients of these equations were determined by method of least squares, weighting each result in a particular series inversely in proportion to the concentration. The lines given in Fig. 3 are the graphs of these equations. The results for glycolamide, α- and β-alanine were obtained by F. W. L. with the first apparatus. One series of results for lactamide was obtained by F. W. L., and a second series by G. A. M. using the improved apparatus with a less satisfactory comparator than that finally chosen. Both of these series apparently were of about the same accuracy and have been weighted equally in drawing the curve. The data for glycine obtained by R. M. H. using the improved apparatus with the Gaertner micrometer microscope previously described are obviously much more self-consistent than the preliminary results of F. W. L., and the equation for this line is based on them alone. These experimental results are given in Table I.

TABLE I[a]

THE VELOCITY OF SOUND IN AQUEOUS GLYCINE SOLUTIONS AT 25°, WITH THE CORRESPONDING VALUES OF THE ADIABATIC COMPRESSIBILITIES AND APPARENT MOLAL COMPRESSIBILITIES

Expt.	c (moles liter^{-1})	Velocity (meters sec.$^{-1}$)	$10^6\beta$ (atm.$^{-1}$)	$10^9\,\Delta\beta$ ($\beta_{\text{obsd.}} - \beta_{\text{calcd.}}$)	$10^3\Phi K_2$ (ml. atm.$^{-1}$)
	0.00000	1497.20	45.336		(−2.719)
4a	.04454	1498.77	45.176	47	−1.624
4	.11128	1503.07	44.823	2	−2.649
1a	.32125	1513.91	43.892	11	−2.525
2	.49578	1522.92	43.140	12	−2.452
1	.80270	1538.67	41.870	5	−2.329
3	1.09532	1554.35	40.675	−49	−2.254
6a	1.61305	1578.36	38.868	32	−1.988
5a	1.93033	1594.82	37.739	−10	−1.902
6	2.68702	1632.77	35.296	− 9	−1.673

[a] The experiments are numbered chronologically. Solutions made by quantitative dilution are labeled (a).

If equation (2) is solved for β, and the values of ΦK_2 and d as functions of c are substituted from equation (4) and previous publications[3,4,6] from this Laboratory, we obtain equations for the adiabatic compressibility of each solution of the form

$$\beta = \beta_1 + Ac + Bc^2 + Cc^3 \qquad (5)$$

TABLE II

COEFFICIENTS OF EQUATIONS (4) AND (5) FOR APPARENT MOLAL COMPRESSIBILITY AND ADIABATIC COMPRESSIBILITY AT 25°

Solute	$10^3\Phi K_2^0$	$10^3 a$	$10^3 b$	$10^6 A$	$10^6 B$	$10^6 C$	$10^8 \Delta\beta$ (av.)
Glycine	−2.719	+0.517	−0.047	−4.678	+0.478	−0.047	1.9
Glycolamide	0.274	+0.081	.....	−2.272	+0.075	.....	2.5
α-Alanine	−2.680	+0.528	.....	−5.426	+0.502	.....	2.2
β-Alanine	−2.769	+0.556	−0.031	−5.429	+0.523	−0.031	7.4
Lactamide	0.432	+0.181	−0.008	−2.900	+0.173	−0.008	6.8

The coefficients of equations (4) and (5) are given in Table II, together with the average deviations between observed and calculated compressibilities. The individual deviations in the second series of experiments on glycine are presented in Table I, while those of all the solutions are presented graphically in Fig. 4.

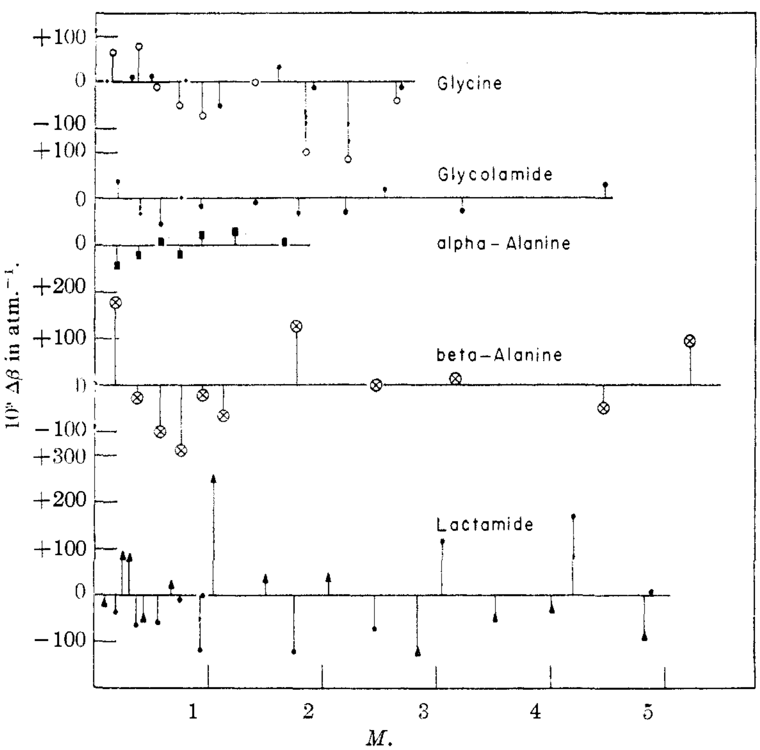

Fig. 4.—Deviations of observed compressibilities from values given by equation (5).

Comparison with Previous Work.—Little work has been published on the compressibility of solutions of the amino acids. In 1935, P. W. Bridgman and R. B. Dow[20] determined $P-V$ data at 25 and 75° for solutions of glycine from 0.5 to 2.5 m over a range of pressure to 5000 atmospheres or more. Although these data could be used to determine the isothermal compressibility of these solutions they would not be directly comparable to our adiabatic values. Recently A. B. Passynskii[21] has used an ultrasonic interferometer to determine the adiabatic compressibility of four solutions each of glycine, at concentrations between 0.14 and 0.63 M, and of β-alanine at concentrations between 0.09 and 0.23 M. For the compressibility of water he uses the value 45.46×10^{-6}, without stating the unit. This is 0.276% more than the value of 45.336 atm.$^{-1}$ which we have used, based on the best available velocity measurements.[18,19] Multiplying his results by the factor 45.336/45.46 to make them comparable with the values of the coefficient of equation (5) in reciprocal atmospheres we find deviations from our equations of $10^9\Delta\beta$ = +40, −10, −90, −390 for glycine and +30, +70, −80, −220 for β-alanine. This agreement is about as satisfactory as our preliminary measurements.

Discussion of the Results

The apparent molal adiabatic compressibilities of these solutions parallel the apparent molal heat capacities and volumes which have been determined previously in this Laboratory[3,4,5,6] and discussed elsewhere.[7] In general, the curves for the dipolar ions are steeper and their limiting values are smaller than those of the uncharged isomers. These facts can be interpreted qualitatively in terms of the theories of Fuoss and Kirkwood to which we have referred before.[8,9] Fuoss showed that the free energy of the solute may be expressed in terms of a parameter which, when we take into account the discontinuity of the dielectric constant at the surface of the solute molecule as pointed out by Kirkwood, becomes

$$y = \left[\frac{3D}{2D + D_i}\right]^2 \frac{\mu^2}{a^3DkT} \tag{6}$$

where D is the dielectric constant of the solvent and D_i is that of the spherical solute molecule having a diameter a and central point dipole moment μ, k is Boltzmann's constant, and T is the absolute temperature. The expression for the contribution of the solute interaction to the partial molal free energy in a very dilute solution then is

$$\bar{F}_2 - \bar{F}_2^0 = -RTNJ/V \tag{7}$$

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[20] P. W. Bridgman and R. B. Dow, *J. Chem. Phys.*, **3**, 35 (1935).

[21] A. B. Passynskii, *Acta Physicochim. U. R. S. S.*, **22**, 137 (1947).

where R is the gas constant, N is Avogadro's number, V is the volume in liters of solution containing 1 mole of solute, and

$$J = \frac{4\pi a^3 y^2}{9}\left[1 + \frac{1}{25}y^2 + \frac{29}{18375}y^4 + \cdots\right] \quad (8)$$

The partial molal volume change due to dipolar interaction has been calculated[7] from the first pressure derivative of (7), while the partial molal isothermal compressibility change depends upon the second pressure derivative, as one of us has shown before.[10] Thus we find

$$\bar{K}_2 - \bar{K}_2^\circ = -\left(\frac{\partial^2(\bar{F}_2 - \bar{F}_2^\circ)}{\partial P^2}\right)_T \quad (9)$$

Carrying out the indicated differentiations gives the equation

$$\bar{K}_2 - \bar{K}_2^\circ = \frac{RTN}{1000} f\,(D,\ V,\ P,\ \mu,\ a)c \quad (10)$$

Thus the partial molal isothermal compressibility should be a linear function of the first power of the concentration in a very dilute solution, and so should the apparent molal isothermal compressibility, which in this case has half the slope of the partial quantity. According to this theory, the slope depends upon f, a function of the dielectric constant, volume, and pressure of the solvent, and the dipole moment and diameter of the solute molecules

$$\begin{aligned} f(D,\ V,\ P,\ \mu,\ a) &= f_1 J + f_2 y(\partial J/\partial y)_T + f_3 y^2(\partial^2 J/\partial y^2)_T \\ &\doteq (f_1 + 2f_2 + 2f_3)J \quad (11) \end{aligned}$$

$$f_1 = \left[\beta^2 + \left(\frac{\partial \beta}{\partial P}\right)_T\right] \quad (12)$$

$$f_2 = \frac{1}{D}\left[\frac{8(D - D_i)}{(2D + D_i)^2}\left(\frac{\partial D}{\partial P}\right)^2 - \left(\frac{2D - D_i}{2D + D_i}\right)\left\{2\beta\left(\frac{\partial D}{\partial P}\right)_T + \left(\frac{\partial^2 D}{\partial P^2}\right)_T\right\}\right] \quad (13)$$

$$f_3 = \left[\frac{1}{D}\left(\frac{2D - D_i}{2D + D_i}\right)\left(\frac{\partial D}{\partial P}\right)_T\right]^2 \quad (14)$$

Using the currently accepted values of the natural constants, we find for the constant term in (10)

$$\frac{RTN}{1000} = 14.932 \times 10^{30}\ \text{ergs} \times \text{molecule} \times l \times \text{cm.}^{-3} \times \text{mole}^{-2} \quad (15)$$

To evaluate the functions f_1, f_2 and f_3 which depend chiefly upon the properties of the solvent, we took the value of Wyman and Ingalls[22] for the dielectric constant of water, $D = 78.54$ at 25°, and assumed that $D_i = 1$ in each case. We used two methods to evaluate the pressure coefficients of the volume and dielectric constant: Method A employed the coefficients previously evaluated,[10] except for $(\partial\alpha/\partial P)_T = -8.51 \times 10^{-9}$ bar^{-2} instead of the slightly higher value there quoted. These values are based upon data at 20°, but presumably would not change appreciably in a five-degree interval. Method B employed the coefficients calculated from the analytical expressions used by B. B. Owen and S. R. Brinkley, Jr.[23] They used the equation of Tait for the volume of water under pressure and a similar equation which they derived[24] for the change in the dielectric constant of water. Using their values of the numerical coefficients, these equations at 25° are

$$\frac{v}{v^1} = 1 - 0.1368 \ln\left(\frac{2996 + P}{2997}\right) \quad (16)$$

$$\frac{D^1}{D} = 1 - 0.1754 \ln\left(\frac{2996 + P}{2997}\right) \quad (17)$$

Here the 1 refers to a pressure of 1 bar. The fact that these equations are of the same form and contain the same numerical constants makes them convenient in calculations of this sort.

TABLE III

COEFFICIENTS OF EQUATION (11) IN CM.^{3} × ATM.$^{-1}$ × ERG.$^{-1}$ × 10^{15} EVALUATED BY TWO DIFFERENT METHODS

	f_1	f_2	f_3
Method A	− 6.63	9.87	3.69
Method B	−11.21	14.11	3.38

As shown in Table III there are rather large differences between the coefficients of equation (11) calculated by these two different methods, which emphasizes the uncertainty in our information about some of the important properties of water.

TABLE IV

MOLECULAR PARAMETERS, THEORETICAL (ISOTHERMAL) LIMITING SLOPES AND OBSERVED (ADIABATIC) DIFFERENCES[a]

	glycine	glycolamide	α-alanine	β-alanine	lactamide
$10^{18}\mu$	15.3	2	15.3	18.9	2
$10^8 a$	5.28	5.54	5.82	5.84	6.00
$10^{12}\mu^2/a^3$	1.59	0.024	1.19	1.79	0.019
y	1.09	.016	0.817	1.23	.013
$10^6 S_0$[a] (A)	90	.019	62	163	.015
(B)	103	.022	72	187	.017
Observed Δ[b]	872		694	750	

[a] S_0 is the limiting slope at infinite dilution. [b] The value of "Observed Δ" is the limiting slope of the amino acid minus that of the corresponding amide calculated from Table II.

In Table IV we have collected the molecular parameters, all values of a being taken from the molal volume of the solid substance, those of μ for the amino acids being derived from experimental studies of the dielectric increment, and those for the amides being roughly estimated from structural considerations.[7] The limiting slopes calculated from the two different sets of coefficients are labeled (A) and (B). These are more consistent than the values of the coefficients, because of the opposite changes in f_1 and f_2. The last line gives the difference between the observed slopes of each of the amino acids and

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(22) J. Wyman, Jr., and E. N. Ingalls, THIS JOURNAL, **60**, 1182 (1938).

(23) B. B. Owen and Stuart R. Brinkley, Jr., *Ann. N. Y. Acad. Sci.*, **51**, 753 (1949).

(24) B. B. Owen and S. R. Brinkley, Jr., *Phys. Rev.*, **64**, 32 (1943).

the corresponding amides, which should correspond to the electrostatic contributions alone. As can be seen, these are from four to eight times as great as the calculated electrostatic contributions. The order of the observed slopes is not the same as that calculated from theory, a discrepancy which probably is greater than the experimental uncertainty. This is not surprising since the model of a point dipole in a spherical molecule is a crude approximation for glycine and alanine.

The isothermal compressibility β_T differs from the adiabatic β_S which we measured, according to the thermodynamic equation

$$\beta_T = \beta_S + \alpha^2 VT/c_p \qquad (18)$$

where $\alpha = (\partial \ln V/\partial T)_P$ and c_p is the heat capacity at constant pressure of the volume V of material. Previously we have calculated the difference between the apparent molal isochoric and isopiestic heat capacities.[25] In the same way, we find that the difference between the apparent molal isothermal and adiabatic compressibilities is

$$\Delta\Phi K_2 = \Phi K_{T_2} - \Phi K_{S_2} = \left[\left(\frac{\alpha^2}{s_p} - \frac{\alpha_1{}^2}{s_{p_1}}\right)\frac{1000}{c} + \frac{\alpha_1{}^2}{s_{p_1}}\Phi V_2\right]T \qquad (19)$$

where s_p and s_{p_1} are the heat capacities *per cc.* of solution and of solute, respectively, and ΦV_2 is the apparent molal volume of the solute. We know the specific heats, but not the expansibilities of these solutions, hence we cannot evaluate the differences and compare experiment exactly with theory. However, we can make the calculation for some 1–1 electrolytes previously considered[25] using an equation for the limiting slope analogous to that developed there

$$\left(\frac{\partial\Delta\Phi K_2}{\partial c^{1/2}}\right)_{c\to 0} = \frac{\alpha_1 T}{s_{p_1}}\left[2\left(\frac{\partial\Phi E_2}{\partial c^{1/2}}\right)_{c\to 0} - \left(\frac{\alpha_1}{s_{p_1}}\right)\left(\frac{\partial\Phi C_{p_2}}{\Phi c^{1/2}}\right)_{c\to 0}\right] \qquad (20)$$

Here ΦE_2 and ΦC_{p_2} are, respectively, the apparent molal expansibility[26] and heat capacity of the solute. For lithium and sodium chlorides in aqueous solution at 25°, we find limiting slopes, respectively, 3.5 and 8% less for the isothermal quantity. If the difference is comparable for the amino acids, it does not account for the difference between experimental values and those calculated from the theory of dipolar interaction.

It is interesting also to consider the differences between the limiting values of the apparent or partial molal compressibilities of the amino acids and the corresponding amides. J. G. Kirkwood[27] has derived an equation for W_0, the free energy of solvation of a spherical molecule of radius b with a dielectric constant D_i containing an arbitrary charge distribution, immersed in the medium of dielectric constant D. We have shown previously[7] how this equation could be used to calculate the difference between the apparent molal heat capacities and volumes of the amino acids and the corresponding uncharged isomers. This can be extended to the treatment of compressibilities since for one molecule

$$\Delta\overline{K}_2^\circ/N = -(\partial^2 W_0/\partial P^2)_T \qquad (21)$$

After carrying out the indicated differentiations, we find

$$\Delta\overline{K}_2^\circ = \tfrac{1}{2}N\sum_{n=0}^{\infty}\frac{(n+1)(2n+1)\,Q_n}{b^{2n+1}[(n+1)D+nD_i]^3}\left[((n+1)D + nD_i)\left(\frac{\partial^2 D}{\partial P^2}\right)_T - 2(n+1)\left(\frac{\partial D}{\partial P}\right)_T^2\right] \qquad (22)$$

For dipolar ions Q_0 vanishes and the most important term corresponds to $n = 1$. In this case $Q_1 = \mu^2$ and the equation becomes

$$\Delta\overline{K}_2^\circ = 6N\left[\frac{(D + \frac{1}{2}D_i)\left(\frac{\partial^2 D}{\partial P^2}\right)_T - 2\left(\frac{\partial D}{\partial P}\right)_T^2}{(D + \frac{1}{2}D_i)^3}\right]\frac{\mu^2}{a^3} \qquad (23)$$

The same values as before were used for D and D_i and the same two methods for the evaluation of the pressure coefficient.

As noted before[7] Kirkwood had estimated the effect of the higher multipole moments upon the charging energy in the case of glycine and α-alanine. The rate of convergence of successive terms in (19) is the same which we found before in the case of $\Delta\overline{C}_{p_2}^\circ$ and $\Delta\overline{V}_2^\circ$. We have added 15% to the calculated dipolar values for glycine, and 35% to those for α-alanine to get the estimated total value marked "all terms." The calculated values of the apparent molal isothermal compressibilities at infinite dilution are given in Table V, along with the differences between the apparent molal adiabatic compressibilities of the amino acids and the corresponding amides.

As before,[25] we find for the difference in these two quantities the expression

$$\Delta\Phi^\circ K_2 = \Phi^\circ K_{T_2} - \Phi^\circ K_{S_2} = \frac{\alpha_1 T}{s_{p_1}}\left[2\Phi^\circ E_2 - \frac{\alpha_1}{s_{p_1}}\Phi^\circ C_{p_2}\right] \qquad (24)$$

In the case of lithium and sodium chlorides for which we have the necessary data, the limiting values are about 2.7 and 4.1% less negative for the apparent molal isothermal compressibilities than for the adiabatic. This does not account for the difference between our experimental results

TABLE V

COMPARISON OF CALCULATED (ISOTHERMAL) AND OBSERVED (ADIABATIC) VALUES OF $-10^3\overline{K}_2^\circ$

	Method A		Method B		
Solute	Dipole	All terms	Dipole	All terms	Expt. $\Delta\overline{K}_2^\circ$
Glycine	1.12	1.29[a]	1.43	1.64[a]	2.993
α-Alanine	0.84	1.13[b]	1.07	1.44[b]	3.112
β-Alanine	1.27	[c]	1.61	[c]	3.221

[a] Preceding value × 1.15. [b] Preceding value × 1.35. [c] Shape factor uncertain and higher multipole moment unknown.

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[25] F. T. Gucker, Jr., and T. R. Rubin, THIS JOURNAL, **57**, 78 (1935).

[26] F. T. Gucker, Jr., *ibid.*, **56**, 1017 (1934).

[27] J. G. Kirkwood, *J. Chem. Phys.*, **2**, 351 (1934).

and the predictions of the dipole interaction theory, if the changes are no larger in the case of these solutes.

Although the agreement is somewhat better than in the case of the slopes, the experimental values are still two or three times as great as the theoretical predictions.

Acknowledgment.—It is a pleasure to acknowledge the assistance of grants-in-aid from the Abbott Fund of Northwestern University which made this work possible, and to Chester T. O'Konski in developing the electronic circuits.

Summary

We have described an ultrasonic interferometer designed for the precise measurement of wave lengths in aqueous solutions at a frequency of about 4 megacycles. With the final design of the apparatus, successive experiments agreed to about 0.02%, and the average deviation of measurements on a series of solutions of different concentrations was 0.05% from a smooth curve.

We have measured a series of aqueous solutions of glycine at 25°, and calculated the adiabatic compressibility and apparent molal compressibilities, which we find to be linear functions of the concentration in the very dilute solution. Preliminary results on glycolamide and on α- and β-alanine and lactamide show that these solutes also behave much like glycine.

The Fuoss–Kirkwood theory of dipolar interaction and the Kirkwood theory of the energy of solvation of a dipolar solute give qualitative although not quantitative agreement with our experimental results.

EVANSTON, ILLINOIS RECEIVED AUGUST 8, 1949

[CONTRIBUTION FROM THE GIBBS CHEMICAL LABORATORY, HARVARD UNIVERSITY]

Inhibition of Urease by Sulfur Compounds

BY JOHN F. AMBROSE,* G. B. KISTIAKOWSKY† AND ANDREW G. KRIDL‡

In a recent investigation Kistiakowsky and Lumry[1] found that the anomalous temperature effects in the hydrolysis of urea by urease in the presence of sulfite ions can be explained by inhibition of the enzyme by these anions. This inhibition, heretofore unreported in the literature, seemed to merit further investigation, all the more so since sulfite has been used as a "preservative" for urease solutions.

The purpose of the investigation was to elucidate the laws of inhibition with respect to the sulfite ions, temperature and *p*H dependence of the equilibrium constant for the inhibition reaction, to determine the type of inhibition caused by the anions, and to see whether organic derivatives of sulfur dioxide and/or sulfur trioxide also possess inhibitory action.

Experimental Details

The activity of the urease samples was determined by the Nesslerization technique of Sumner and Hand[2] with only minor modification. A Lumetron Colorimeter manufactured by the Photovolt Corporation was used for transmission measurements. The reproducibility with this instrument was excellent, the standard deviation being in all instances less than 1%.

Temperature control was provided by water-filled thermostats with liquid cooling coils, electric heating elements and automatic temperature controls such that the temperatures could be maintained to ±0.01° over the short periods of time (about ten minutes) necessary to perform individual experiments. Temperatures were read with Beckmann thermometers calibrated against a Bureau of Standards calibrated mercury thermometer.

An activity determination always consisted of pipetting 20 cc. of an urease–phosphate buffer–sulfite solution into an ordinary test-tube, placing the latter in the thermostat, waiting until temperature equilibrium has been established, and then adding, with a thirty-second stirring, 1 cc. of urea solution containing 315 g. of urea per liter. Upon dilution this gave a 1.5% solution of urea, under which conditions the reaction is of zero order in substrate. Following the mixing the reaction mixture was left in the thermostat for a total of five minutes after which time the reaction was stopped by rapid addition from a hypodermic syringe of 1 cc. of 7 *N* sulfuric acid followed by rapid mixing for about twenty seconds. Two cc. of this reaction mixture was then diluted to 250 cc. with ammonia-free water in a volumetric flask, and 5 cc. of Nessler reagent added. The transmission of the resulting solution was determined after a ten-minute waiting period.

Using 20-cc. volumes of reaction mixture was, to be sure, somewhat wasteful of reagents but assured much higher over-all reproducibility and precision than were obtained using the previous procedure.[1]

The urease solutions used in these experiments were identical with those previously described.[1] However, better preparative and storage procedures resulted in urease stock solutions which were so stable that the activities remained un-

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[1] G. B. Kistiakowsky and Rufus Lumry, THIS JOURNAL, **71**, 2006 (1949).

[2] J. B. Sumner and D. B. Hand, *J. Biol. Chem.*, **76**, 149 (1928).