ammonia molecules are both removed from solution with the formation of a complex when ammonium hydroxide is added to a manganous chloride solution containing ammonium chloride. The evidence of the present work seems to favor the existence of a mangano-complex in these solutions. The specific effect of ammonium chloride in producing a different shaped velocity curve from that obtained in triethanolamine solutions of the same pH, and the fact that changes in ammonium chloride concentration have no effect upon the composition of the final product may both be explained by the assumption of the existence of such a complex. However, since Brezena's work indicates that the amount of complex increases with increasing ammonium chloride concentration, while the present work has shown that the rate of autoxidation decreases with increasing ammonium chloride concentration, it is unlikely that the complex itself is the substance autoxidized. Undoubtedly precipitated manganous hydroxide is autoxidized, and it is probable that the dissolved undissociated manganous hydroxide behaves similarly. Since neutral solutions show no autoxidation, it is evident that manganous ions are not affected.

Summary

1. The rate of autoxidation of manganous hydroxide in ammoniacal solution has been found to decrease with increasing ammonium chloride concentration. An induction period exists when the ammonium chloride concentration is high.

2. Powdered manganese dioxide, stannic oxide, ferric oxide, red lead oxide, ground glass, and diatomaceous earth accelerate the reaction and eliminate the induction period.

3. In the presence of lead dioxide no autoxidation of divalent manganese occurs.

4. Cobalt chloride and copper chloride accelerate the reaction, while glycerol, dextrin, and iodine retard it. A large number of other substances were found to have no effect.

5. The autoxidation of manganous hydroxide does not induce the oxidation of sodium oxalate, sodium formate, sodium arsenite, sodium nitrite, or allyl alcohol.

6. The autoxidation by air is much slower and less complete than that by pure oxygen.

7. The autoxidation of manganous hydroxide precipitated by fixed alkali is very rapid. The product depends upon the temperature and the proportions of manganous ion and alkali. The X-ray diffraction patterns of the products were studied.

8. The autoxidation of manganous hydroxide precipitated by triethanolamine was found to be very slow. It did not display the induction period observed in ammoniacal solution.

9. A mechanism to account for the above results has been proposed.

The Dielectric Investigation of Polypeptides. II. The Dispersion of Simple Amino Acid Polypeptides

BY W. P. CONNER[1] AND C. P. SMYTH

Although important conclusions concerning the nature of polypeptide molecules have been drawn from consideration of their dielectric increments per mole of solute, it is recognized that a more complete picture may be obtained from measurement of the anomalous dispersion of the dielectric constants of their water solutions. The linear increase of increment values of the polypeptides with the number of glycine residues, as suggested by Wyman,[2] lends support to the view that there is almost complete freedom of rotation about the valence bonds which make up the backbone of the peptide chains. Statistical calculations by Kuhn[3] of the polarization of a straight-chain molecule in which there is free rotation about the valence bonds and electrostatic attraction between the oppositely charged ends of the chain show that the polarization as measured by the static dielectric constant would be the same whether the chains underwent orientation polarization or dilation–contraction polarization. Because of the apparent lack of restriction in position of the electrically

(1) Research Assistant on Special Funds from the Rockefeller Foundation.

(2) (a) Wyman, Chem. Rev., 19, 213 (1936); (b) Wyman, J. Phys. Chem., 43, 143 (1939).

(3) Kuhn, Z. physik. Chem., 175A, 1 (1935).

charged end groups of the peptide chains, Wyman suggested[2] that dispersion might not be found for these polypeptide chains inasmuch as they might undergo polarization by stretching rather than orientation. If this were the case, then, size and shape studies from dispersion measurements would be rendered impossible.

Before 1940, no unequivocal data existed in the literature which indicated dispersion in the simpler amino acids and their polypeptides. However, in that year, Bateman and Potapenko[4] reported dispersion measurements at 25.5 cm., for glycine and alanine and their dipeptides. Making use of the energy absorption accompanying dispersion, other investigators[5,6,7] have obtained relaxation times for some amino acid peptides. These data differ widely in the reported relaxation times for the simple peptides.

In this paper, dispersion measurements are reported for the glycine polypeptides and for the simpler di- and tripeptides of alanine, leucine, and glycine in the wave length region of 40 to 80 cm.

Experimental

Method.—For measurement of the static dielectric constant of the aqueous peptide solutions, the Twin-T impedance measuring circuit reported in the first paper of this series[8] was employed. The shortest wave length used was ten meters, which was only just within the region of slight anomalous dispersion for the larger molecules, as indicated by the high frequency measurements. For measurement of the dielectric constants in the dispersion region, approximately 60 cm., the first Drude method was followed. An ultra-high frequency oscillator, similar to that reported by Barrow,[9] was constructed making use of a WE 316-A vacuum tube. Copper was used throughout and catalin rings served for insulation and for mechanical support. To reduce the high frequency loss in the insulation as many holes were drilled in the insulating rings as were possible without lessening the mechanical rigidity. Since the frequency of oscillation is stabilized by the resonant concentric tubes, an attempt was made to increase the Q values of the circuit according to the relations reported by Reukema,[10] in which the influence of the radiative resistance of such transmission lines is fully considered. The tube conductor diameters were: plate, 1.834 and 0.437 inches; filament, 2.00 and 0.187 inches; all three tubes were 20 inches long. The selections were made with the intent to give a maximum Q value to the plate circuit and a maximum impedance to the filament tuned circuit at 50 cm. wave length by the use of copper tubing of standard

(4) Bateman and Potapenko, *Phys. Rev.*, **57**, 1185 (1940).

(5) Fricke and Parts, *J. Phys. Chem.*, **42**, 1171 (1938).

(6) Parts, *Pub. Tech. Univ. Estonia Tallin*, Ser. A No. 8, 3 (1940); *C. A.*, **34**, 4952 (1941).

(7) Linhart, *Z. physik. Chem.*, **B38**, 23 (1937).

(8) Conner, Clark and Smyth, THIS JOURNAL, **64**, 1379 (1942).

(9) Barrow, *Rev. Sci. Instr.*, **9**, 170 (1938).

(10) Reukema, *Elec. Eng.*, **56**, 1002 (1937).

dimensions. The equations followed were: for maximum Q of a shorted quarter wave length concentric line, $b/a = 4.22$ and $b = 0.0634 \lambda^{0.9}$, and for maximum impedance, $b/a = 14.3$ and $b = 0.077 \lambda^{0.9}$, in which a and b are the radii of the inner and outer conductors. A closer approach to the theoretical Q values was attained by the installation of the "standpipe" oscillator on its side, thereby enabling the use of a plunger mechanism for the determination of resonance lengths and thus avoiding slotting the out copper tubes. The theoretical Q value of 3400 at 600 Mc., is considerably less than that reported by Barrow since the equations by which he computed Q values do not consider radiative resistance losses. Since only loose coupling between this oscillator and the detector was desired, a short length of copper wire extending from the coaxial line power output connection into the chamber which contained the vacuum tube was found to be completely adequate. A maximum in the grid current and a minimum in the plate supply indicated oscillation of the instrument. The frequency range of the oscillator was approximately 300–750 Mc.
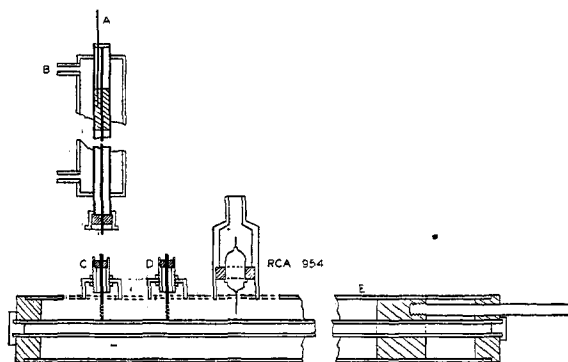

Fig. 1.—Apparatus for the determination of dielectric constants at ultra-high frequencies: A, water resonance chamber; B, water jacket; C, coupling lead to water resonance chamber; D, input lead from oscillator; E, air resonance chamber.

Dielectric measurements required the determination of the wave length of the high frequency oscillation in air and in the water solutions of the polypeptides. For the air measurements (see Fig. 1), standing electric waves were formed in a system of concentric tubes of the same dimensions as those used for the plate tank circuit of the oscillator, the length of which could be varied by means of a shorting plunger. The detector was a simple probe-type voltmeter[11] using an RCA-954 acorn tube capacitatively coupled to the inner tube of the resonance chamber by very short leads. The outer tube of the chamber was slotted so that the voltmeter might be inserted approximately at a voltage antinode. With this arrangement positions of resonance were quite sharp and could be set to ±0.01 cm. · A micrometer was attached to the plunger so that the resonance length might be varied by small steps. With close coupling to the oscillator, a rather large decrease in the oscillator grid current was noted as the resonance chamber passed through a point of resonance. The

(11) Radiotron Division of RCA Manufacturing Co., *Q. S. T.*, **19**, 42 (1935). A one megohm grid leak was added to the grid probe.

coupling was reduced to such an extent that the change in the grid current was less than one-half milliampere, since further loosening of the coupling had been shown to have no effect upon the measured wave length. The wave length was then considered equal to twice the distance between any two positions of the plunger for which the voltmeter indicated a maximum voltage.

The wave length in the water solutions was determined in much the same manner, except that, for this case, the resonance tubes were much smaller, $3/8$ and $1/8$ inches; and were water-jacketed at 25.00 ± 0.02° for most of the experiments. The smaller size was chosen to reduce the volume of material required for measurement and to gain a higher Q value, since the wave length in these media is one-ninth that in air. The water resonance chamber was coupled to the air chamber rather than directly to the oscillator in order to minimize any change in frequency of the oscillator resulting from interaction between the two circuits. The relative positions of the ·connective terminals on the air chamber were varied. However, those indicated in Fig. 1 were the most satisfactory. The connections between the instruments were all of $3/8$ inch coaxial cable with polystyrene bead insulation. Thus, the apparatus was completely shielded so that the position of the observer did not affect the measurements. This was a great improvement over the customary Lecher wire devices.

In making a measurement, the oscillator was first adjusted to one of its positions of most stable oscillation and the wave length determined with the air chamber. Customarily, the wave length was checked when the plunger in the water chamber was first set at a node and then at an antinode. The positions of resonance in the air chamber were different for these two positions in the water chamber but the actual wave length was not modified. With the plunger in the air chamber at a voltage node and with the

Fig. 2.—Resonance minima in aqueous potassium chloride solutions: specific conductance, A, 0.853 × 10⁻²; B, 1.67 × 10⁻³; C, 0.953 × 10⁻³; D, 1.007 × 10⁻⁴ mhos. For each curve, the zero point of the voltmeter reading has been shifted arbitrarily to prevent overlapping.

consequent maximum in voltage indicated by the voltmeter, the plunger in the water chamber was withdrawn slowly. A minimum in the voltmeter now indicated the presence of standing waves in the water resonance chamber, since maximum power had been transferred from the air chamber to the water chamber. The wave length in the solution was considered equal to twice the distance between any two minima. Because of attenuation, the minima became too broad for accurate settings after about four nodes had been detected. Settings were made readily to ±0.015 cm., and greater accuracy could be attained when the voltage was recorded for each millimeter shift in the plunger and the minima read from the plot of these values. Considerable asymmetry was introduced into these plots of voltage against distance in the water chamber depending on the position of the plunger in the air chamber. If the air chamber was set at resonance when the water chamber was completely out of resonance, the curves were symmetrical except for the exponential absorption due to conductance.

In Fig. 2 is recorded such a plot for water solutions of potassium chloride of varied conductivity. The conductance of these solutions at 25° was measured with a one thousand cycle conductance bridge. Since the Debye–Hückel theory of electrolytes predicts an increase in the dielectric constant of aqueous salt solutions above that of pure water, it was of interest to calculate[12] this increase, $\Delta\epsilon_{DH}$, expected for these solutions (see Table I).
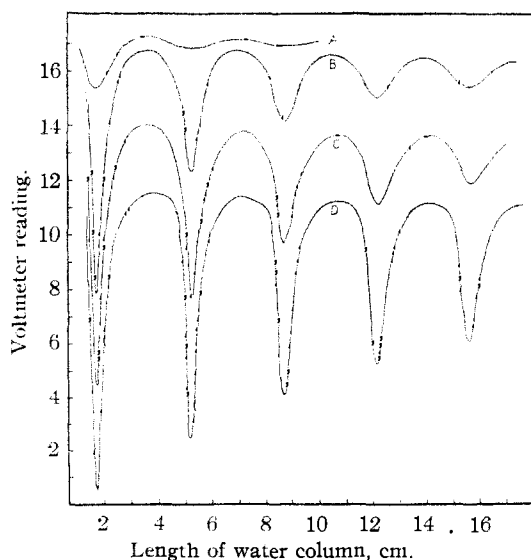
TABLE I

Spec. cond. × 10⁸ ohm⁻¹ cm.⁻¹	$\Delta\epsilon_{DH}$	$\Delta\epsilon_R$	ϵ_{obs}.
0.1077	0.000325	0.0000	78.46 ± 0.13
0.953	.0202	.000	78.57 ± 0.13
1.666	.0529	.006	78.57 ± 0.13
8.53	.548	.157	79.5 ± 0.4

In addition to the increase in the dielectric constant resulting from the polarization of the ionic atmosphere around a central ion, $\Delta\epsilon_{DH}$, there arises an apparent increase, $\Delta\epsilon_R$, in the real dielectric constant resulting from the conduction in the dielectric medium in which the standing electric waves are produced. This effect is comparable with the apparent increase in capacity of a conducting condenser found in low frequency impedance measurements. The dielectric constant increase, $\Delta\epsilon_R$, was calculated according to an approximate treatment of the problem.[13] The dielectric constant values, ϵ_{obs}, observed for these potassium chloride solutions show small increases with increasing concentration, agreeing within the experimental error with the calculated increases.

(12) Falkenhagen, "Electrolytes," The Clarendon Press, Oxford, 1934, pp. 219–221.

(13) Drake, Pierce and Dow, Phys. Rev., 35, 613 (1930).

Since the specific conductivities of all peptide solutions were no greater than 1×10^{-4} ohm^{-1} cm.$^{-1}$, an error due to conduction was considered negligible. A slight initial decrease in the dielectric constant of salt solutions as the salt concentration is increased has been reported,[14] although a complete quantitative treatment has not been given. However, it is likely that this effect lies well within the experimental error of these measurements.

Most of the high frequency measurements were performed at 61.42 cm., the minimum being determined by a plot of the voltage against the length of the resonance chamber. For some measurements, a larger range of wave length, 40 to 80 cm., was used. However, because of the tedium involved in the selection of suitable positions of the three plungers of the oscillator from the many positions at which oscillation gave unstable or distorted frequencies, this procedure was discontinued.

Results

In Table II are recorded the dielectric data for the amino acids investigated, from which the dispersion calculation is made. Some of the high frequency measurements were made at room temperature before the thermostat was installed and have been included as taken without a correction to 25°. To correlate the dispersion data taken over a frequency range with solutions of different concentrations, the critical wave lengths, λ_c, have been calculated according to the dispersion equation[15]

$$\frac{\epsilon - \epsilon_\infty}{\epsilon_0 - \epsilon_\infty} = \frac{1}{1 + (\lambda_0/\lambda)^2} \qquad (1)$$

where ϵ is the dielectric constant of the aqueous solution at wave length λ; ϵ_∞ is taken equal to the dielectric constant of water, 78.54, at 25°; and ϵ_0 is the static dielectric constant of the solution considered equal to that measured with the Twin-T apparatus at approximately 10 meters. The critical wave length is related to the relaxation time by the expression

$$\lambda_c = 2\pi c \tau$$

in which c is the velocity of light in cm./sec., and τ is the relaxation time in seconds.

Viscosity corrections for different concentrations of solute and temperature of solution were

(14) Grubb and Hunt, THIS JOURNAL, **61**, 565 (1939).

(15) Williams and Oncley, *Physics*, **3**, 314 (1932); Williams, *Trans. Faraday Soc.*, **30**, 723 (1934); Elliott and Williams, THIS JOURNAL, **61**, 718 (1939).

applied by multiplying the critical wave length determined by Eq. (1) by the factor $\eta_{H_2O}/\eta_{solution}$. An Ostwald viscometer, with an efflux time for water of 24 sec., was used for the viscosity determinations listed in Table II and the viscosity of water at 25° was taken as 8.94 millipoises. The substances are represented in Tables II and III by abbreviations: A for alanine, L for leucine, G_1 for glycine, G_2 for diglycine, etc. All preparations were racemic mixtures.

Since both measuring cells were constructed of copper, there was a slight formation of the copper complex of the amino acids in solution. Except for those of high glycine content, the solutions were only faintly tinted after the measurements were completed. In view of the excellent agreement with reported data for the measurements at low frequencies, it was considered that, for this case, the formation of the copper complex was negligible. However, inasmuch as the solutions were left in contact with a larger surface of copper for a longer time during the high frequency measurements, the low frequency increments were always determined after the high frequency experiments on the same solutions. Thus the decrease in the dielectric constant of the solution resulting from the formation of the complex was not counted as dispersion of the dielectric constant.

The spread of the calculated results is large for glycine since λ_c in Eq. (1) is very sensitive to slight changes in ϵ when the difference $\epsilon - \epsilon_\infty$ is small, as it is when the measuring wave length is remote from the critical wave length. Thus the apparent trend with increasing concentration of glycine is not held to be significant. Equation (1) is a very much simplified description of the dielectric constants of these aqueous solutions, since it implies the presence of a kinetic unit having only one relaxation time. However, no well-defined trend in the critical frequencies calculated in this manner was noticeable as the viscosity and frequency were varied for any single compound. Since all measurements were made on the low frequency side of the complete dispersion curve, it is unlikely that the effect of a second smaller relaxation time would be greater than the error of the dielectric measurements.

Also the choice of ϵ_∞, the dielectric constant of the solution at a frequency sufficiently great so that dispersion due to the solute molecule has been completed and yet sufficiently small so that dispersion of the solvent has not begun, is some-

what arbitrary. Actually ϵ_∞ should be less than the dielectric constant of water, since, at frequen- cies sufficiently high to eliminate the contribution of the polar solute molecules to the dielectric con-

TABLE II
DISPERSION DATA FOR AMINO ACID PEPTIDES

Substance	t, °C.	Concn., m	ϵ_0	ϵ	λ	η (0.001 c. g. s.)	λ_c
H₂O	25		(78.54)	78.46	61.56	(8.94)	
				78.51	61.42		
				78.55	61.42		
G₁	25	0.6895	93.77	93.67	61.42	9.74	4.6
		0.6950	93.98	93.85	61.42	9.74	5.2
		1.900	118.6	117.4	78.02	11.65	10.5
		2.041	121.3	118.7	60.26	11.84	11.6
		2.264	125.7	122.5	75.88	12.2	15.0
							9.4 ± 3.6
G₂	21	0.1020	87.20	84.94	75.26	10.3	23.5
	25	.3136	100.61	98.06	62.30	9.74	20.7
				98.01	61.04		20.5
				98.20	61.40		19.8
				98.10	62.20		20.5
				97.61	62.22		22.7
	25	.4918	113.20	108.63	62.70	10.18	21.4
				109.01	62.50		20.4
				108.40	62.64		22.1
				108.60	60.72		20.9
							21.0 ± 0.3
G₃	19.6	.0437	85.52	83.02	39.70	10.30	34.6
				84.58	76.24		31.8
				83.02	39.64		34.4
	21.6	.0617	86.84	83.30	38.96	9.92	35.2
				84.93	62.32		34.3
				85.20	71.82		35.7
				85.42	76.40		34.6
							34.3 ± 0.3
G₄	25	.0531	87.77	84.19	61.42	9.17	47.8
			87.55	84.04	62.41		47.8
		.0566	88.40	84.98	57.86	9.20	41.0
				84.18	59.86		50.4
				85.68	75.40		43.1
		.0838	89.66	85.53	62.44	9.30	46.1
		.0938	94.70	88.03	61.50	9.48	48.8
							46.6 ± 0.8
G₅	25	.01890	82.30	80.23	61.42	9.02	66.0
			82.12	80.02	61.42		72.5
							68.6 ± 2.6
A	25	1.4372	109.3	106.3	59.80	12.21	14.7
		1.5782	111.9	109.2	57.32	12.56	9.5
							12.1 ± 2.6
LG	25	.1270	86.89	84.68	62.24	9.81	34.0 ± 3.0
LA	25	.06361	81.88	80.63	61.42	9.10	46.6 ± 0.5
AGG	23.2	.05127	85.21	82.01	38.42	9.65	38.0
				83.15	64.80		43.3
				83.53	68.20		39.4
				83.41	71.24		43.1
				83.96	75.12		35.7
				83.89	75.28		37.1
							39.4 ± 1.1

TABLE II   (*Concluded*)

Substance	t, °C.	Concn., m	ϵ_0	ϵ	λ	$(0.001\overset{\eta}{}$c. g. s.$)$	λ_c
LGG	24	.06095	86.24	81.32	38.20	9.75	50.0
				83.06	62.20		49.8
				82.90	62.20		52.2
				82.36	62.86		61.0
				83.32	72.36		53.8
							53.4 ± 1.5
ALG	25	.08208	88.50	83.89	61.42	9.64	52.9
	21.0	.0787		82.06	38.82	10.43	64.6
				85.27	69.90		55.4
				86.10	72.22		48.2
				86.16	76.06		50.1
				86.92	79.44		43.8
							52.5 ± 2.1

stant of the solution, the solution should behave as if non-polar molecules of the same total volume were dissolved in it. In this case of water acting as the solute, the presence of non-polar molecules would reduce the number of dipolar water molecules per cubic centimeter and thus reduce the dielectric constant of the solution. An estimation of this volume correction for the increment values is recorded in the preceding paper.[8]

In Table III are recorded the average values of the critical wave lengths taken from Table II and the critical wave lengths after the volume correction has been applied. Inasmuch as dispersion has been found for these polypeptides, it is of interest to compare the measured critical wave lengths with those calculated on the assumption that the rotating units are spheres of volumes equal to those of the dissolved molecules and moving according to the laws of hydrodynamics. For this case, the Debye equation

$$\lambda_0 = 2\pi c\tau = 2\pi c\frac{3\eta}{RT}v$$

applies in which η is the viscosity of the solvent and v is the partial molar volume of the solute. In Table III are listed the critical wave lengths, λ_0, thus calculated. The volume v was taken equal to the apparent molar volume plus the electrostriction. For those compounds for which v has not been measured, use was made of the additivity of atomic volumes[16] for their calculation. In addition, there is listed the shape factor a/b, the ratio of major to minor axis of the assumed molecular ellipsoid of revolution, as determined by the quotient of the observed and calculated critical wave lengths in the manner described by Perrin.[17] This calculation assumes, of course, a

(16) Cohn, McMeekin, Edsall and Blanchard, THIS JOURNAL, **56**, 784 (1934).

(17) Perrin. *J. Physique.* **5**, 497 (1934).

rigid particle undergoing orientation polarization. Inasmuch as the mechanism of polarization is not definitely known, these calculations must be regarded as tentative. Also, it must be emphasized that, in view of the error involved in the determinations of λ_c, small differences in a/b are not significant. Correction of the dielectric constant values for the effect of the volume occupied by the solute molecules according to the method previously employed[8] gave slightly smaller values λ_c' for the critical wave lengths and larger values $(a/b)'$ for the axis ratios.

TABLE III

DISPERSION OF AMINO ACIDS

Substance	λ_c (obs.), cm.	λ_0	λ_c/λ_0	a/b	λ_c'	λ_c'/λ_0	$(a/b)'$
G₁	9.4 ± 3.6	11.7	0.803		8.9	0.76	
G₂	21.3 ± 0.3	19.1	1.12	1.40	20.2	1.085	1.27
G₃	34.3 ± 0.3	26.5	1.295	1.68	32.8	1.240	1.58
G₄	46.6 ± 0.8	32.0	1.46	1.92	44.5	1.390	1.83
G₅	68.6 ± 2.6	41.4	1.65	2.15	64.3	1.55	2.06
A	12.1 ± 2.6	14.9	0.812		11.1	0.94	
LG	34.0 ± 1.0	32.4	1.05	1.18	33.6	1.038	1.14
LA	46.5 ± 1.0	35.5	1.31	1.71	40.7	1.146	1.40
AGG	39.4 ± 1.1	29.8	1.32	1.71	37.1	1.243	1.57
LGG	53.4 ± 1.5	39.8	1.34	1.77	49.3	1.238	1.57
ALG	52.5 ± 2.1	43.1	1.22	0.52	48.6	1.126	1.33

Discussion of Results

The agreement of the ratio of the critical wave lengths listed here and those reported elsewhere is satisfactory in the cases of glycine and alanine. Bateman and Potapenko[4] reported ratios of 0.39 and 0.77, whereas Fricke and Parts[5] reported 0.55 and 0.63 as calculated from absorption measurements. For the higher peptides, Bateman and Potapenko listed ratios of 1.38, 1.60 and 1.67 for diglycine, glycylalanine, and alanylglycine, indicating shape factors of 1.8 to 2.2. However, Fricke and Parts reported ratios less than unity for such large molecules as α-aminobutyric acid, γ-aminobutyric acid, and ϵ-aminocaproic acid;

and later Parts[6] reported ratios from 0.7 to 1 for the large molecules of d,l-phenylalanine, diglycine, and ε-aminocaproic acid. On the other hand, Linhart[7] found that the critical wave lengths for glycine, diglycine, and leucylglycylglycine lay between 80 and 100 cm., depending upon the concentration of the solute. It would appear that the results of Bateman and Potapenko are the most trustworthy since they were determined at 25.5 cm., where dispersion is most pronounced. In addition, a relaxation time of 1.29×10^{-10} sec., $\lambda_c = 24.4$ cm., for triglycine has just been reported by Wyman[18] from absorption measurements at 2.61 meters. For the two smallest molecules, glycine and alanine, the observed values for λ_c are less than the values calculated for a spherical model. This discrepancy is customary for investigations of this sort for small molecules of size comparable with those of the solvent, and has led to the suggestion that the inner viscosity is of smaller magnitude than the macroscopic viscosity.

Another approach to the whole process of dielectric relaxation may be obtained by considering it as a rate process involving the rotation of the molecule between two equilibrium positions separated by a potential barrier.[19,20,21] Following

(18) Marcy and Wyman, THIS JOURNAL, **63**, 3388 (1941).

(19) Eyring, *J. Chem. Phys.*, **4**, 283 (1936).

(20) Glasstone, Laidler and Eyring, "The Theory of Rate Processes," McGraw-Hill Book Company, Inc., New York, N. Y., 1941.

(21) Powell, to be published shortly

Eyring's treatment of relaxation times in general, one may calculate the free energy of activation for rotation, $\Delta F^{\ddagger}$, for these polypeptides from the equation

$$\tau = \frac{h}{kT} e^{\Delta F^{\ddagger}/kT}$$

Values of $\Delta F^{\ddagger}$ so determined are listed in Table IV, together with those of the apparent molar volume φ of the solute corrected by adding the electrostriction E. The ratio $\Delta F^{\ddagger}/(\varphi + E)$ is given to show that the increase of free energy of activation with increase of molecular volume becomes less as the molecules increase in size.

These $\Delta F^{\ddagger}$ values may be compared with the free energies of activation for viscous flow by the application of the equation

$$\eta = \frac{Nh}{V} e^{\Delta F^{\ddagger}/RT}$$

where V is the molar volume of the liquid in question. The heat content change $\Delta H^{\ddagger}$ for the same process may be determined from the slope of a log η against $1/T$ plot since

$$\Delta H^{\ddagger} = R \frac{d \ln \eta}{d(1/T)}$$

Unfortunately, this curve is not linear, and hence $\Delta H^{\ddagger}$ varies with the temperature. This temperature variation probably indicates a structural change in the flow process.[22] The results of such a calculation for water are listed below.

VISCOUS FLOW

	$\Delta F^{\ddagger}$	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$
H_2O	2.21	4.058	6.0
Dipole Rotation			
H_2O	2.38		
40% H_2O (in dioxane)	2.57		

Since the temperature dependence of the relaxation time for water has not been determined, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ cannot be calculated explicitly. In all likelihood, the temperature dependence is the same as that for viscosity, as is the case for many small dipole molecules. If this be so, then the entropy change is the same for both processes and requires the breaking of a somewhat organized structure in the formation of a more random system. Undoubtedly, the directed hydrogen bonds are fractured. Thus, the mechanisms of dipole rotation and viscous flow for water are equivalent.

The $\Delta F^{\ddagger}$ for the dipole rotation of the zwitterions increases but very slowly with increasing molecular volume except in the cases of smaller

(22) Ewell and Eyring, *J. Chem. Phys.*, **5**, 726 (1937).

TABLE IV

FREE ENERGY OF ACTIVATION FOR ROTATION OF POLYPEPTIDES

Substance	λ_c	$\tau \times 10^{12}$	$\Delta F^{\ddagger}$ (kcal.)	$\varphi + E$	$\dfrac{\Delta F^{\ddagger}}{(\varphi + E)}$
G_1	9.4	48.7	3.34	57	0.0585
G_2	21.3	114.3	3.96	93.3	.0425
G_3	34.3	181.3	4.23	129.6	.0326
G_4	46.6	247	4.40	166.6	.0265
G_5	68.6	363	4.63	202.6	.0228
A	12.1	64.0	3.58	73.3	.0488
LG	34.0	180.0	4.24	158.5	.0267
LA	46.5	246	4.40	173.7	.0253
AGG	39.4	206	4.32	145.7	.0296
LGG	53.4	282	4.48	194.8	.0230
ALG	52.5	278	4.48	210.9	.0213
Water[a]	1.60	8.52	2.38	18	.1323
40% Water (in dioxane)	2.27	12.04	2.57		

[a] Hackel and Wien, *Physik. Z.*, **38**, 767 (1937); Esau and Bäz [*ibid.*, **38**, 774 (1937)] report λ_c for water equal to 1.85 cm. Slevogt [*Ann. Physik*, **36**, 141 (1939)] reports $\lambda_c = 2.1$ cm. Fricke and Parts [*J. Phys. Chem.*, **42**, 1171 (1939)] report $\lambda_c = 1.85 \pm 10\%$.

molecules. Thus, in contrast to the linear viscous flow of pure liquids, a cavity proportional to the volume of the moving molecule need not be formed for this rotational motion. The temperature coefficient is probably that of water, as it is in the case of the larger protein molecules. Thus, the entropy change in this case is almost zero, perhaps slightly negative. Since the mechanism is basically the same as that of viscous flow in the pure solvent, i. e., movement of one molecule of solvent over the same potential barrier to a second rest position, the entropy change is the sum of an increase due to the breaking of directed valence bonds of the solvent and a decrease which measures the number of molecules which must be organized in the flow process to permit rotary diffusion of the dipole molecule. This decrease in entropy is dependent upon the size and shape of the molecule in solution, and causes the rather large relaxation times found for large protein molecules.

The smallness of the variation of the $\Delta F^{\pm}$ values with change in the size of the molecules results from the fact that the range of relaxation times is extremely short. However, it is noted for both glycine and alanine that the free energy of activation is approaching that for water. From this fact it would appear that the number of solvent molecules which must coöperate in the rotary diffusion of these dipole ions is becoming smaller with the decrease in size of these ions and is approaching unity as it is for the rotary diffusion of water in water.

That the Debye equation for relaxation time fails for these small particles is evident in the fact that λ_c/λ_0 is less than unity. However, the reaction rate hypothesis affords a complete picture of this region of small molecules in which it has been customary to assume a difference between the macroscopic and microscopic viscosities. For large particles the reaction rate calculation and the Debye equation must agree, but the details of the transition have not been worked out.

The mere presence of dispersion in the half meter range of wave length does not completely prove the rigidity of these dipolar molecules. Since the heats of activation have not been determined, the actual mechanism of polarization is still in doubt. The free energies of activation are of such a magnitude that the slow process may be the movement of a water molecule over the potential barrier for viscous flow to create a space to be

occupied by a part of the rotating dipolar molecule, or it may be the crossing of the potential barrier for rotation around the valence bonds within the dipolar molecule in polarization by stretching. Since $\Delta H^{\pm}$ for viscous flow changes with temperature and $\Delta H^{\pm}$ for rotation about a single bond does not, one might differentiate between the two processes from the temperature coefficient of the relaxation times. However, since in the stretching of a valence chain possessing free rotation, the rate of change of stress on its ends with the change in its elongation is inversely proportional to the number of chain links,[23] it becomes increasingly easier to stretch the chain as its length increases. Thus, one would expect that the relaxation time for this process would decrease with increasing chain length since the entropy change decreases. This view may be applied to a chain-stretching mechanism in which a potential barrier must be crossed if the barrier height does not change with chain length. It would appear, then, in view of the experimentally found increase in relaxation times with the chain length of the polypeptides, that stretching of the tangled backbone chain alone is not the slow process. If the slow process is that of the viscous flow of water, then the mechanism is still in doubt for a hole of some sort must be created about the dipolar molecule whether it occupies the new space by expansion and contraction or by orientation in the direction of the field.
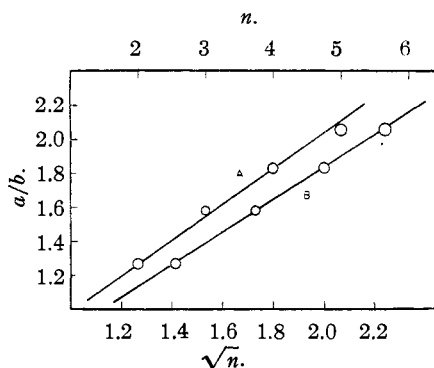

Fig. 3.—Variation of a/b with the number of glycine residues, n: A, variation with n; B, variation with $\sqrt{n}$.

However, it is evident that the orientation hypothesis gives reasonable values for the molecular shapes of the peptides. The shape factors of the glycine peptides appear to increase linearly with the square root of the number of glycine

(23) Mark, "Physical Chemistry of High Polymeric Systems," Vol. II, Interscience Publishers, Inc., New York, N. Y., 1940, p. 75.

residues (see Fig. 3). Although the accuracy of the determinations is not sufficient to exclude the possibility of a linear increase with the first power, the apparent linear dependence upon the square root of the number of glycine residues is what one would expect from a statistical consideration of rigid molecules randomly distributed in all possible configurations resulting from potential minima symmetrically distributed about the valence bonds of the backbone chain. The triglycines appear to have approximately the same shapes, except for alanylleucylglycine which appears somewhat more spherical as would be expected since the large isobutyl group has been attached to the middle of the chain. Leucylglycine is more spherical than would be predicted. Perhaps in this case the Perrin equation fails since the assumed ellipsoid of revolution is a poor approximation for this molecule. The dipolar part of the molecule may undergo motion with very little change in the position of the hydrocarbon chain at one end of the molecule. Undoubtedly a more satisfactory picture would be obtained for these small irregular molecules if it were possible to discard the hydrodynamic view-point and the prolate spheroid model in favor of more accurate knowledge of the nature of the process of rotation.

Other complicating factors which have not been considered are the change in the volume of the rotating unit due to hydration resulting from hydrogen bonding of the dipolar molecule with water, and, second, hydrogen bonding within the peptide chain, which must occur to stabilize the structures of protein molecules. The second factor is probably of little importance since these peptide chains act as denatured proteins.

The writers wish to express their gratitude to Professor Eugene Pacsu for his helpful discussions relating to the polypeptides used in this investigation.

Summary

An apparatus has been constructed for the measurement of the dielectric constants of liquids at wave lengths from 40 to 80 cm. by the first Drude method. The dielectric constants of aqueous solutions of ten amino acid peptides in this region of anomalous dispersion have been measured, as have the viscosities of the solutions. The mechanism of dispersion has been discussed and the results have been combined with previous dielectric constant measurements at 10 meters in this Laboratory to calculate the relaxation times and shape factors for the solute molecules. Although the results are not inexplicable in terms of internal rotation around valence bonds in the molecules, the values and their trend are consistent with the simple picture of rotation of the molecule as a whole.

The Apparent Molal Volumes of Aqueous Solutions of Sulfuric Acid at 25°

BY IRVING M. KLOTZ AND CHARLES F. ECKERT

It has been known for some time that the apparent molal volume of a strong electrolyte may be expressed as a linear function of the square root of its volume concentration. For aqueous solutions of sulfuric acid, however, the apparent molal volumes show an unusual dependence on the concentration. In contrast to most electrolytes, the volumes rise very rapidly in the dilute range but approach a linear function of the square root of the concentration at high molarities. This behavior has been explained qualitatively as being due to the ionization of bisulfate ion.[1] With data on the dissociation constants of bisulfate ion a quantitative explanation of the observed volume changes in terms of the apparent molal volumes of the component ions is also possible. We have determined the densities of solutions of sulfuric acid from 0 to 3 molar, and have calculated, by a method of successive approximations, the apparent molal volumes of $H^+ + HSO_4^-$ ions.

Experimental.—The solutions were placed in Pyrex containers immersed in a thermostat at 25° ($\pm 0.001°$). The density of each solution was measured by means of the sinker method described by Wirth.[2] The method was sensitive to differences of less than one part per million in the density.

(1) Geffcken and Price, Z. physik. Chem., **26B**, 81 (1934).

(2) Wirth, THIS JOURNAL, **59**, 2549 (1937).