2. The reactions have been found to be homogeneous and free from appreciable side reactions, proceeding almost to completion by the process $RI + HI \longrightarrow RH + I_2$.

3. The order of the reactions was found to be complex, the rates being best represented by the kinetic expression

$$\frac{d(I_2)}{dt} = K_1(RI)(HI) + K_2(RI)\frac{(HI)}{(HI) + (I_2)}$$

This is interpreted as being due to two concurrent mechanisms. The rate controlling steps are, respectively, a bimolecular reaction of alkyl iodide and hydrogen iodide, and a unimolecular dissociation of the alkyl iodide into alkyl radical and iodine atom. The constants for the two are, respectively, K_1 and K_2.

4. For methyl, ethyl and *n*-propyl iodides, respectively, the values of K_1 were found to be $5.22 \times 10^{13}T^{1/2}\ e^{-(33,400 - 1/2RT)/RT}$, $1.34 \times 10^{13}\ T^{1/2}e^{-(29,800 - 1/2RT)/KT}$ and $3.43 \times 10^{12}T^{1/2}\ e^{-(29,200 - 1/2RT)/RT}$ (mole/cc.)$^{-1}$ sec.$^{-1}$. The corresponding values of K_2 are 3.93×10^{12}-$e^{-43,000/RT}$, $1.82 \times 10^{13}e^{-43,000/RT}$ and $2.80 \times 10^{13}e^{-43,000/RT}$ sec.$^{-1}$.

5. The unimolecular constant K_2 for methyl and ethyl iodides was found to fall off at low pressures in the manner demanded by collision theories of unimolecular reactions.

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[FROM THE DEPARTMENT OF ZOÖLOGY, HARVARD UNIVERSITY]

Dielectric Constants of Polar Solutions

BY JEFFRIES WYMAN, JR.

There has been a considerable amount of recent work[1] on the dielectric constant of aqueous solutions of amino acids and related compounds, underlying which has been the idea that the abnormally large values of the dielectric constant encountered in the case of nearly all these ampholytes are due to their existence as zwitter ions. For the dielectric constant must reflect the magnitude of the polarization of the solutions, and, taking account of molecular dimensions, it is easy to calculate that the electric moment (polarization) of such zwitter ions should be far greater than that of ordinary un-ionized compounds. On the other hand, increasing evidence from quite other sources of itself places the zwitter ion hypothesis almost beyond doubt.[2] The presentation of the results of these dielectric studies and their correlation with the zwitter ionic properties of the ampholytes in question have been greatly facilitated by the fact that in all the cases investigated the dielectric constant has been found to increase linearly with the concentration of the ampholyte, expressed in moles (or grams) per liter, up to the highest concentrations studied, *i. e.*, about 2.5 moles per liter in the case of the more soluble amino acids. On account of this, the results may all be expressed in terms of the increase of dielectric constant per mole of ampholyte, a quantity to which we will refer hereafter by δ. It has been shown for aqueous solutions that δ is very nearly the same for all amino acids of a given type, *e. g.*, the α-amino aliphatic acids, and that it increases in a very regular way with the separation between the acid and basic groups in the molecule.[3] Since the electric moment, or polarization, of these substances in water must be primarily determined by their properties as zwitter ions, these facts lead to the concept that in general the δ value of a substance in aqueous solution is a measure of its electric moment, or perhaps polarization, and may be used to estimate, at least qualitatively, the magnitude of this on a relative basis.

The situation revealed by the study of aqueous solutions raises a number of questions. For one thing, are the characteristic δ values of these ampholytes the same in other polar solvents where the zwitter ionic form may also be supposed to predominate and where consequently the electric moments, or polarizations, may be supposed to be the same? In general this would not be expected; but the matter can obviously be settled only empirically, for theoretical considerations break down in the case of these

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(1) See Blüh, *Z. physik. Chem.*, **106**, 341 (1923); Devoto, *Gazz. chim. ital.*, **60**, 520 (1930); *ibid.*, **61**, 897 (1932); *ibid.*, **63**, 50 (1933); Fürth, *Ann. Physik*, **70**, 63 (1923); Frankenthal, *Z. physik. Chem.*, **19**, 328 (1932); *ibid.*, **21**, 310 (1933); Hedestrand, *ibid.*, **135**, 36 (1928); Walden and Werner, *ibid.*, **129**, 389 (1927); Wyman and McMeekin, THIS JOURNAL, **55**, 908 (1933); *ibid.*, **55**, 915 (1933).

(2) See Cohn, *Ergebnisse der Physiologie*, **33**, 781 (1931).

(3) Wyman and McMeekin, THIS JOURNAL, **55**, 908 (1933).

polar solutions. As a matter of fact, a certain limited number of observations on glycine dissolved in 20, 40 and 60% alcohol–water mixtures appear to indicate that this possibility is indeed realized.[3] If this should prove to be general it would lead to a number of consequences. For one thing it would make it possible to compare δ values obtained in different polar solvents, a point of great value in the study of such a substance as the protein zein which is insoluble in pure water but dissolves readily in some other polar solvents such as concentrated urea solutions and alcohol–water mixtures. For another thing it would enable us to predict in the absence of measurements the dielectric constant of systems of several components, such as mixtures of amino acids or peptides in water, from a knowledge of the individual cases. This latter possibility would be of considerable importance in the case of numerous systems of biological interest. Another problem raised by the linearity of the dielectric constant–concentration curve and the relation of its slope δ to the polarization of the solute is the possibility of interpreting this empirically in terms of the internal field in the solutions. Evidence concerning the former of these two considerations is presented in the following section of this paper; the second problem, an essentially speculative one, is dealt with in Section III.

II

With the exception of the few measurements on glycine in alcohol–water mixtures already referred to, all the data in the literature concern solutions of a single substance in water. Moreover, the interest in the exactness and range of the linear relationship between dielectric constant and concentration having been secondary, the measurements, except in the case of glycine, have not been pushed to the limit of solubility of the ampholyte. This is in part no doubt due to the difficulties arising from conductivity in the case of the more concentrated solutions. To avoid this it is necessary to work with materials carefully purified by recrystallization from the last traces of impurities in the form of salts, and even then the inherent conductivity of the ampholyte itself may be considerable. This inherent conductivity, governed of course by the dissociation constants, appears to increase with the distance between the carboxyl and amino groups in the ampholyte and makes it impossible, for example, to extend the measurements on the β-amino acids to concentrations greater than about 1 mole per liter.

Before passing on to measurements in other solvents and on systems of more than two components it was decided, therefore, to make a very careful study of one other α-amino acid, namely, α-aminobutyric acid, at concentrations extending up to saturation, in order to ascertain the exactness of this linear relation. The amino acid was several times recrystallized from 50% alcohol and ice cold water until the conductivity had been rendered negligible in its effect on the accuracy of the determinations. These and all other measurements reported in this paper were made with a resonance method described elsewhere[4] at wave lengths in the neighborhood of 3 meters.

TABLE I

α-AMINOBUTYRIC ACID IN WATER AT 25°

Moles per liter	ϵ obs.	ϵ calcd.[a]	Dev., %
0	78.54	78.54	
0.2227	83.61	83.79	−0.21
.2866	85.67	85.29	+ .44
.2874	85.25	85.30	− .06
.4790	89.87	89.82	+ .06
.5815	92.42	92.24	+ .19
.6844	94.46	94.64	− .19
.7371	95.65	95.92	− .18
.7825	97.10	96.97	+ .13
.8727	99.43	99.10	+ .33
1.167	106.08	105.97	+ .10
1.585	115.66	115.84	− .17
1.823	121.03	121.49	− .42
2.042	126.68	126.60	+ .06

[a] From $\epsilon = 78.54 + 23.53\,C$.

The results of this study are given in detail in Table I, from the last column of which it appears that the departures of the observations from linearity are entirely random and have an average value of slightly less than 0.2%. Since the "observed" values are individual determinations, this is probably no more than the experimental error. In Table II are given for comparison data not previously reported in detail on glycine, where the situation is nearly the same.[3] Indeed, in the case of all the results which are reported below without listing individual observations the linear relation was found to hold equally well out to the highest concentrations studied.

We now turn from the question of the linearity of the dielectric constant–concentration curve to that of the constancy of its slope for a given solute

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(4) Wyman, *Phys. Rev.*, **35**, 623 (1930).

TABLE II

GLYCINE IN WATER AT 25°

Moles per liter	ϵ obs.	ϵ calcd.[a]	Dev., %
0.0	78.54	78.54	
.8750	98.03	98.28	−0.26
1.750	117.5	117.99	+ .42
2.000	123.7	123.59	+ .09
2.500	134.5	134.94	− .33

[a] From $\epsilon = 78.54 + 22.58\ C$.

in passing from one polar solvent, mixed or otherwise, to another. In this connection a study was made of glycine and α-aminobutyric acid in alcohol–water mixtures, in aqueous solutions of urea of various concentrations, and in solutions of one another. In addition to this, measurements were made on the hexa- and heptapeptides of glycine in urea solutions.[5] The former of these had been studied previously in water; the latter had proved to be too insoluble in water to allow of measurement. The results of the whole investigation are adequately presented in Table III, which includes also data recorded simultaneously on the density. Several results taken from previous investigations are repeated for comparison, these being marked in each case with an asterisk.[6] Under the column headed ϵ is given the linear expression for the dielectric constant, of which the first term is of course the dielectric constant of the solvent, while the coefficient of the concentration C (moles per liter) in the second term is the slope of the curve, δ. In the third column is indicated the concentration range over which the measurements were extended. In the case of α-aminobutyric acid in 80% alcohol and of the heptapeptide only a single concentration was studied, this being so small owing to the insolubility of the substance that no dilution was attempted. In all other cases measurements were made at three different concentrations, at least, as well as on the pure solvent. In the last column is given the expression for the density, the first term of this being the density of the solvent. Only in the case of glycine was there any observable deviation from linearity in the density–concentration curve, and there the effect was not large.

TABLE III

Solute	Solvent	Concn. range	ϵ	ρ
Glycine	*Water	0–2.5	78.54 + 22.58 C	0.9971 + 0.03276 C − 0.0011 C^2
Glycine	*20% Ethyl alcohol	0–1.27	69.96 + 22.55 C	.9730 + .0302 C
Glycine	*40% Ethyl alcohol	0–0.470	59.69 + 21.7 C	.9464 + .0290 C
Glycine	*60% Ethyl alcohol	0– .133	47.88 + 20.4 C	.9058 + .030 C
Glycine	2.5 Molar urea	0–2.17	84.35 + 22.3 C	1.0358 + .0272 C
Glycine	5.0 Molar urea	0–2.45	90.60 + 22.6 C	1.0740 + .0247 C
Glycine	0.5898 Molar α-aminobutyric acid	0–2.40	92.30 + 21.9 C	1.0132 + .0288 C
Glycine	1.198 Molar α-aminobutyric acid	0–2.30	106.75 + 21.0 C	1.0295 + .0275 C
Glycine	1.826 Molar α-aminobutyric acid	0–2.20	121.5 + 20.6 C	1.0457 + .0263 C
α-Aminobutyric acid	Water	0–2.04	78.54 + 23.53 C	0.9971 + .02685 C
α-Aminobutyric acid	20% Ethyl alcohol	0–0.9776	69.82 + 23.6 C	.9723 + .0313 C^a
α-Aminobutyric acid	40% Ethyl alcohol	0– .5730	59.41 + 22.6 C	.9455 + .0351 C^a
α-Aminobutyric acid	60% Ethyl alcohol	0– .2932	47.20 + 22.1 C	.9046 + .0371 C^a
α-Aminobutyric acid	80% Ethyl alcohol	0– .0644	35.37 + 24.0 C	.8528 + .037 C
α-Aminobutyric acid	2.793 Molar urea	0–1.975	87.37 + 20.9 C	1.0422 + .0207 C
α-Aminobutyric acid	0.961 Molar glycine	0–0.7217	99.8 + 23.1 C	1.0266 + .0242 C
α-Aminobutyric acid	1.993 Molar glycine	0–1.27	124.05 + 19.0 C	1.0590 + .0185 C
α-Aminobutyric acid	2.510 Molar glycine	0–1.29	134.9 + 18.4 C	1.0710 + .0190 C
Glycine hexapeptide	*Water	0–0.0132	78.54 + 234 C	
Glycine hexapeptide	2.582 Molar urea	0– .0179	85.35 + 221 C	1.0363 + .122 C
Glycine heptapeptide	5.14 Molar urea	0– .00313	91.36 + (290 ± 25) C	1.0740 + .18 (±0.03) C

[a] From unpublished measurements by Cohn.

Consideration of these data shows that there is very little variation in δ from solvent to solvent. In the case of α-aminobutyric acid, whereas the dielectric constant of the solvent varies between 35.37 and 134.9, δ varies only between 24 and 18.4. In the case of glycine the variation is even less, although to be sure the range of dielectric constant covered by the solvents is not so great (47.88 to 121.5). There is a similar constancy in the case of the two measurements on the hexapeptide. The heptapeptide was studied only in the 5.14 molar urea solution, but the value obtained for δ (290) is very close to that extrapolated from data on the lower peptides in water (300), for in this homologous series δ appears to vary linearly with the number of glycine units in the peptide. This point has been discussed elsewhere,[3] and is an illustration of the way in which the value of δ appears to be a direct expression of the polarity of the solute molecules.

[5] The material was prepared by McMeekin and was the same studied by Wyman and McMeekin.[3]

[6] These were reported by Wyman and McMeekin.[3]

As a result of this comparative study it appears, therefore, that in polar solvents the dielectric constant is a nearly additive property. This makes it possible to predict with some assurance, in the case at least of the amino acids and peptides, the dielectric constant of mixed solutions, from a knowledge of the individual components. It also makes it possible to compare values of δ obtained in different polar solvents, a point of value in such cases as that of the heptapeptide. We are thus able to answer certain of the questions raised at the outset of this paper.

Before passing on to the next aspect of the problem, it may be worth while to comment incidentally on the density data in Table III. Values of the partial specific volumes calculated from these are given in Table IV. In the case of glycine the value given corresponds to a concentration of 0.5 mole per liter; in all other cases the values are independent of concentration. It is interesting to see from these figures how constant is the partial specific volume of glycine in the different solvents. Moreover, the partial specific volumes are nearly the same (probably the same within the experimental error, large, owing to the diluteness of the solutions) for all the peptides, *i. e.*, the partial molal volumes are proportional to the molecular weights. In the case of α-aminobutyric acid, which is decidedly more soluble in the alcohol–water mixtures than glycine, there is a very definite difference between the partial specific volume in water and in the alcohol solutions.

TABLE IV

Substance	Solvent	Partial sp. vol.
Glycine	Water	0.590 ± 0.002
Glycine	20% Ethyl alcohol	.595 ± .003
Glycine	40% Ethyl alcohol	.611 ± .006
Glycine	60% Ethyl alcohol	.57 ± .06
Glycine	2.5 Molar urea	.615 ± .003
Glycine	5 Molar urea	.620 ± .003
Glycine	0.5898 Molar α-aminobutyric acid	.603 ± .003
Glycine	1.198 Molar α-aminobutyric acid	.618 ± .003
Glycine	1.826 Molar α-aminobutyric acid	.622 ± .003
α-Aminobutyric acid	Water	.740 ± .002
α-Aminobutyric acid	20% Ethyl alcohol	.717 ± .007
α-Aminobutyric acid	40% Ethyl alcohol	.697 ± .007
α-Aminobutyric acid	60% Ethyl alcohol	.711 ± .007
α-Aminobutyric acid	80% Ethyl alcohol	.74 ± .05
α-Aminobutyric acid	2.793 Molar urea	.767 ± .004
α-Aminobutyric acid	0.961 Molar glycine	.741 ± .004
α-Aminobutyric acid	1.993 Molar glycine	.770 ± .004
α-Aminobutyric acid	2.510 Molar glycine	.760 ± .004
Glycine dipeptide	Water	.58 ± .01
Glycine tripeptide	Water	.61 ± .01
Glycine tetrapeptide	Water	.62 ± .01
Glycine pentapeptide	Water	.63 ± .02
Glycine hexapeptide	2.582 Molar urea	.64 ± .03
Glycine heptapeptide	5.14 Molar urea	.52 ± .07

III

We turn now to a possible interpretation of these effects in relation to the theory of dielectric constants. Probably no one would expect the Debye theory,[7] developed for gases and dilute solutions in non-polar liquids, to apply exactly to such cases as those presented above. In the first place, the underlying assumption on the basis of which the internal field F acting on the individual molecules in solution is given by

$$F = E + 4\pi I/3 \qquad (1)$$

where E is the electric intensity and I the electric moment per unit volume, can hardly be expected to hold in such systems. In the second place, the resulting expression for the mass polarization[8] p' of the liquid in terms of the dielectric constant ϵ and the density ρ, namely

$$p' = \frac{\epsilon - 1}{(\epsilon + 2)\rho} \qquad (2)$$

appears to involve an arbitrary limitation on p' not justified by any physical consideration underlying the theory. Thus, even if ϵ becomes infinite, p' can never be greater than $1/\rho$. In the actual case of pure polar liquids the expression may lead to improbably small values of the polarizations. For example, it gives a molar polarization of but 17.35 cc. for liquid water at 25°, as compared with a value of 76.5 cc. for the vapor. Even if the dielectric constant of liquid water were to become infinite the molar polarization would be but 18.1 cc.

It is illuminating nevertheless to consider the theory more specifically in relation to the present results. Modified for a system of n components equation (2) becomes

$$\frac{\epsilon - 1}{\epsilon + 2} = \frac{C_1P_1 + C_2P_2 + \ldots + C_nP_n}{1000} = p \qquad (3)$$

where the P's denote molar polarizations, the C's concentrations in moles per liter and p is the polarization of the system per cc. Since we have seen that the density varies linearly with the molar concentration of the zwitter ion (to which we will refer by subscript 1) the concentrations may all be expressed in terms of C_1, and the right-hand member is then linear in C_1. ϵ cannot therefore be linear in C_1, as it is observed to be, unless there be a variation of the P's with C_1 just such as to compensate the departure from linearity demanded by (3). That this should occur, however, with the required precision in all the cases studied seems highly unlikely, for, owing to the form of (3), ϵ, wherever it is large as in all these

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[7] An account of this is given by Debye, "Polar Molecules," The Chemical Catalog Co., Inc., New York, 1929.

[8] Throughout this paper the following notation is adhered to: p = polarization per cc.; p' = polarization per gram; p'_α = optical polarization per gram; P = polarization per mole.

instances, is extremely sensitive to changes in p (*i. e.*, the P's). Thus in the case of α-aminobutyric acid in water, at $C_1 = 2.5$, a 0.1% change in p from 0.9785, the value calculated from (3), to 0.9795 would involve a 5% change in ϵ from 137.44 to 144.34, quite sufficient to destroy entirely the observed linearity; and a 1% change in p would actually lead to a 90% increase in ϵ. If we assume the polarization of the water to be independent of C_1, the 0.1% change in p would imply a 0.5% change in P_1.

But even if we grant the required variation of the polarization with composition in any given solvent, we are left, on the basis of the classical theory, with the problem of accounting for the constancy of δ from solvent to solvent. This demands, at every concentration, a variation of p (*i. e.*, the P's) from solvent to solvent, quite independent of the variation with concentration in any given solvent and even more delicately adjusted, for δ is of course considerably more sensitive to p than ϵ itself. Thus the 0.1% change in p in the case of α-aminobutyric acid in water at $C_1 = 2.5$ would involve an approximately 11% change in δ; and the same change in 2.51 molar glycine as solvent would involve a 24% change in δ. That both these sets of coincidences required by the classical theory should be realized with such uniformity and precision is almost beyond the bounds of credibility.

But this is not the only difficulty, for the actual magnitude of the polarizations of the zwitter ions implied by the theory are almost certainly far too small. Thus the value of the molar polarization of α-aminobutyric acid in water at $C_1 = 2.5$ calculated by equation (3), assuming the polarization of the solvent to be unaffected by the solute, is 79.9 cc. This is less than two-thirds that obtained in benzene (128.8 cc.), where there can be no ionization and where, therefore, we should expect the polarization to be many times smaller. Other values of the polarizations of the zwitter ions calculated from the data of Table III on the same basis, are of much the same magnitude.

It seems likely that the failure of the classical theory to deal with the results on these polar solutions may arise from the underlying assumption with regard to the internal field resulting in equation (1). If we assume, what appears not unreasonable in view of the linear relation between density and concentration, that the polarization of the solution per cc. is also (approximately) linear in the concentration of the ampholyte, then it may easily be shown from elementary considerations that the linear relation observed between dielectric constant and concentration demands that the effective field be the same as the electric intensity E.

The starting point of the standard theory is the two expressions

$$D = \epsilon E$$

and

$$D = E + 4\pi I$$

in which D is the electric induction, and I, the electric moment per cc., is equal to $3pF/4\pi$, p being the polarization per cc. and F the actual field acting on a molecule. In order to carry out the required eliminations to obtain the relation between the dielectric constant and the polarization p it is necessary to express F in terms of the other quantities. F is classically resolved into three components as follows: F_1, arising from the charges on the surface of the conductors; F_2, arising from the polarized dielectric with the exception of a small sphere surrounding the molecule in question; and F_3, due to the polarized dielectric within this sphere. Of these, $F_1 = E$, and $F_2 = 4\pi I/3$. But it is impossible to calculate F_3 for the general case and in the derivation of the standard theory it is neglected. If now we retain F_3 as an unknown in order to see what condition it must satisfy to provide for the linear relation between ϵ and p, we obtain as the result of elimination

$$\epsilon = 1 + \frac{3p}{1 - p\left(1 + \frac{3}{4\pi}\frac{F_3}{I}\right)}$$

From this it appears that the condition of linearity is that $F_3 = -4\pi I/3$, that is, that it be equal and opposite to F_2, whence $F = F_1 = E$.

Consequently

$$(\epsilon - 1)/3 = p \tag{4}$$

This last expression, to be contrasted with the corresponding classical equation (2), is identical with the approximate form assumed by equation (2) for the case of a gas at low pressure, where ϵ is nearly equal to 1. Equation (4) has a number of consequences other than the linearity which it was derived to provide for. In the first place, whenever ϵ is high, it leads to very much larger values of the polarizations than the classical equation (2), as we shall see below. In the second place, it renders the dielectric constant enormously less sensitive to changes in the polarization p, the two being very nearly proportional to one another in the case of polar liquids. And finally, owing to this proportionality, it would explain why a substance of a given mass (molar) polarization should cause roughly the same increase of dielectric constant independent of the solvent, such as has been observed.

In reality, the simplest form in which to use equation (4) is to express p in terms of the mass polarizations $p'_1, p'_2 \ldots, p'_n$ and weight fractions $w_1, w_2 \ldots, w_n$ of the components. Then, if ρ denotes density

$$\frac{\epsilon - 1}{3\rho} = w_1p'_1 + w_2p'_2 + \ldots + w_np'_n \qquad (4')$$

If we take such a set of data as that on α-aminobutyric acid and in the case of each solvent plot $(\epsilon - 1)/3\rho$ against w_1, the weight fraction of the acid, we should expect to get a family of straight lines intersecting at the point ($w_1 = 1$ $(\epsilon - 1)/3\rho = p'_1$), provided of course that the p's did not vary with w_1 nor p'_1 from solvent to solvent.[9] In each case the ordinate corresponding to $w_1 = 0$ would be the mass polarization of the solvent. That the lines are straight we already know, the expression having been derived to provide for this. The extent to which the values of p'_1 for α-aminobutyric acid are the same from solvent to solvent (condition for intersection) is shown by the following values of the molar polarization P_1 (p'_1 times the molecular weight) calculated by equation (4) from the data in Table III: in 80% alcohol, $P_1 = 8900$; in 60% alcohol, $P_1 = 8500$; in 40% alcohol, $P_1 = 9300$; in 20% alcohol $P_1 = 9400$; in water, $P_1 = 9820$; in 2.793 molar urea, $P_1 = 9400$; in 0.961 molar glycine, $P_1 = 10{,}200$; in 1.993 molar glycine, $P_1 = 9600$; in 2.582 molar glycine, $P_1 = 9800$.

As to constancy, these figures vary less from solvent to solvent than the corresponding values of δ. It might appear, however, that they were unreasonably large. Thus making use of the figure 35 cc. (from Wyman and McMeekin[10]) for the optical polarization, the polarization calculated for α-aminobutyric acid in water leads to a value of 21.7×10^{-18} e. s. u. for the electric moment, on the basis of Debye's relation between polarization and electric moment. It must be realized, however, that the moment of even an α-amino acid in the zwitter ionic form may be very large. Thus on the basis of solubility data of E. J. Cohn, Kerkwood and Scatchard have estimated the distance separating the amino and carboxyl groups in glycine in aqueous solution to be about 3 Ångströms.[11] X-ray data indicate a distance at least as great as this. This would of itself imply a moment of $3 \times 10^{-8} \times 4.77 \times 10^{-10} = 14.3 \times 10^{-18}$ e. s. u., and it is possible that this might be augmented by whatever remains after ionization of the moment belonging to the undissociated molecule, which is 2.1×10^{-18} e. s. u.; so the figure arrived at above is by no means impossible. The same would of course be true for the moments calculated for all other ampholytes from equation (4). Probably the least acceptable implication of the suggestion embodied in equation (4) is the large moments implied for water and other polar liquids. For example, the moment calculated for water would be about 4.7×10^{-18} at 25° (4.81 at 0 and 4.5 at 100°). This is to be contrasted with the value 1.87×10^{-18} for the vapor. The effects of association, however, must not be forgotten.

One point which ought to be considered is the possibility of the internal field arising from the molecules of the polarized dielectric (*i. e.*, $F_2 + F_3$) not exactly vanishing. If there is a small residual field due to these we may define this by a quantity l and write

$$F = E + (4\pi l I/3)$$

Equation (4) then becomes

$$\frac{\epsilon - 1}{3}\,\frac{1}{1 + l(\epsilon - 1)/3} = p \qquad (5)$$

The graph of $(\epsilon - 1)/3$ against p is a rectangular hyperbola with asymptotes $(\epsilon - 1)/3 = -1/l$ and $p = 1/l$. For $l = 1$ this of course reduces to the classical theory and for $l = 0$ to the hypothesis developed above. It may be seen that the product $l(\epsilon - 1)/3$ determines the curvature of the graph between any two points, corresponding, say, to the solvent, for which $\epsilon = \epsilon_0$, and to the most concentrated solution, for which $\epsilon = \epsilon_1$. This is shown in Fig. 1, in which $\frac{\epsilon - 1}{3}\Big/\frac{\epsilon_0 - 1}{3}$ is plotted against $p(\epsilon_0 - 1)/3$ for various values of $l(\epsilon_0 - 1)/3$, the scale of abscissas being in each case so chosen to facilitate comparison that all the curves intersect at the ordinates 1 and 2. None of the data reported above extend beyond the range (an approximately two-fold change of dielectric constant) covered by this figure. It is evident from the figure that for values of $l(\epsilon_0 - 1)/3$ up to about 0.1 the curves depart hardly perceptibly from linearity.

On the other hand, the value of the polarization is sensitive to small changes of $l(\epsilon_0 - 1)/3$ or l. This is illustrated by the following values of P_1,

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(9) If, as is to be expected, the amino acid is predominantly in the zwitter ionic form in all the solvents considered the values of p' should be the same in all, or perhaps should show a slight increase with the dielectric constant of the solvent corresponding to the greater completeness of zwitter ionization.

(10) See Wyman and McMeekin, THIS JOURNAL, **55**, 915 (1933).

(11) An unpublished result communicated by Kerkwood and Scatchard.

the molar polarization of α-aminobutyric acid in water calculated for different values of l:

$l(\epsilon - 1)/3$	l	P_l
0	0	9820
0.013	0.0005	9600
.026	.001	9300
.129	.005	7700
1.29	.05	2200
25.85	1.0	79.9

Thus by assuming a small value of l, not inconsistent with the observed linearity of the curves, it would be possible to reduce the calculated values of the polarization somewhat.

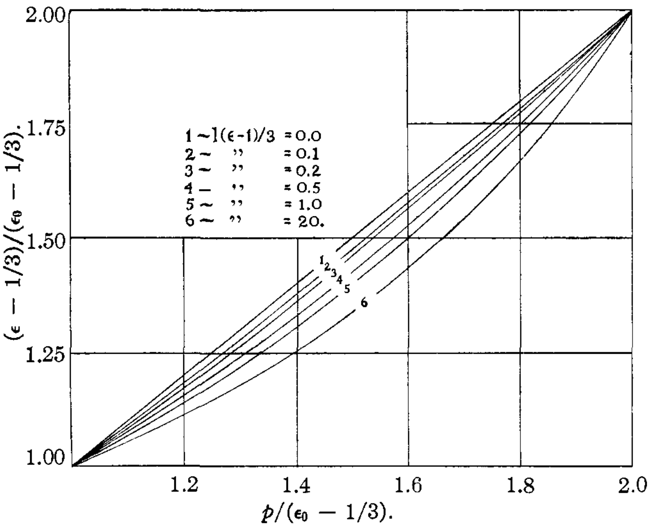

Fig. 1.

There is a considerable amount of material at hand by Danforth[12] on the variation with pressure of the dielectric constant of pure liquids, which is of interest in this connection. Danforth used the technique of Bridgman to obtain pressures up to 12,000 atmospheres and studied a variety of liquids of dielectric constant ranging from 1.82 (pentane) up to 60 (glycerin). Danforth points out that although in the case of the more polar liquids studied (all except ether, carbon disulfide and pentane), there is no constancy in the Clausius–Mossotti function, $(\epsilon-1)/(\epsilon + 2)\rho$; nevertheless, the reciprocal of this function is linear against density, the slopes of all the lines being the same (and, he might have added, equal to 1). Now it may be shown that just this is a necessary consequence of the hypothesis suggested above in regard to the internal field in polar solutions, provided of course the polarizations do not vary with pressure. We have seen above, however, that the Clausius–Mossotti function is very insensitive to changes of dielectric constant in the case of liquids of high dielectric constant and this observation is therefore not so significant as might be supposed. A much better, more direct and more critical way to consider the results in relation to the hypothesis is to examine the variation of ϵ with the density. For in equation (4) the right-hand member p, *i. e.*, the polarization per cc., may be expressed as the product of the density times the mass polarization p'; and accordingly the dielectric constant–density curves should all be straight lines intersecting at $\rho = 0$, $\epsilon = 1$ and having a slope $3p'$. Actually when a plot is made it is found that the curves are not quite straight but are all somewhat concave upward, more in the case of the less polar, less in the case of the more polar, liquids. This discrepancy might be accounted for by resorting to the quantity l discussed above; that is, the curves may all be fitted (with the exception of ether at 30° above 4000 atmospheres and ethyl alcohol at 0°) to within the accuracy of the observations, by equation (5), again setting $p = \rho p'$, with a proper choice of l and p'. This is shown in Fig. 2, in which the full curves correspond to the values of l and p' given in Table V and the points are the experimental data. Table V shows that in general the values of l decrease, as might be expected, from the less to the more polar liquids. It is interesting, moreover, to see that in the case of carbon disulfide, a non-polar compound, the value of p' (or P) is independent, or nearly independent, of temperature.

Of course, it must be realized that the practice of dissecting the internal field arising from the surrounding molecules into F_2 and F_3 is simply a mathematical device to aid in the calculations. The result embodied in equation (5) does not by any means imply physically that the force exerted by the molecules within the small sphere surrounding the molecule in question just counterbalances that due to the remaining molecules of the dielectric; rather, equation (4) simply states that the total force arising from both these arbitrary classes of molecules vanishes. It has been suggested in conversation by Dr. Kerkwood that possibly the force exerted on any molecule by the surrounding molecules may fluctuate so

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(12) Danforth, *Phys. Rev.*, **38**, 1224 (1931).

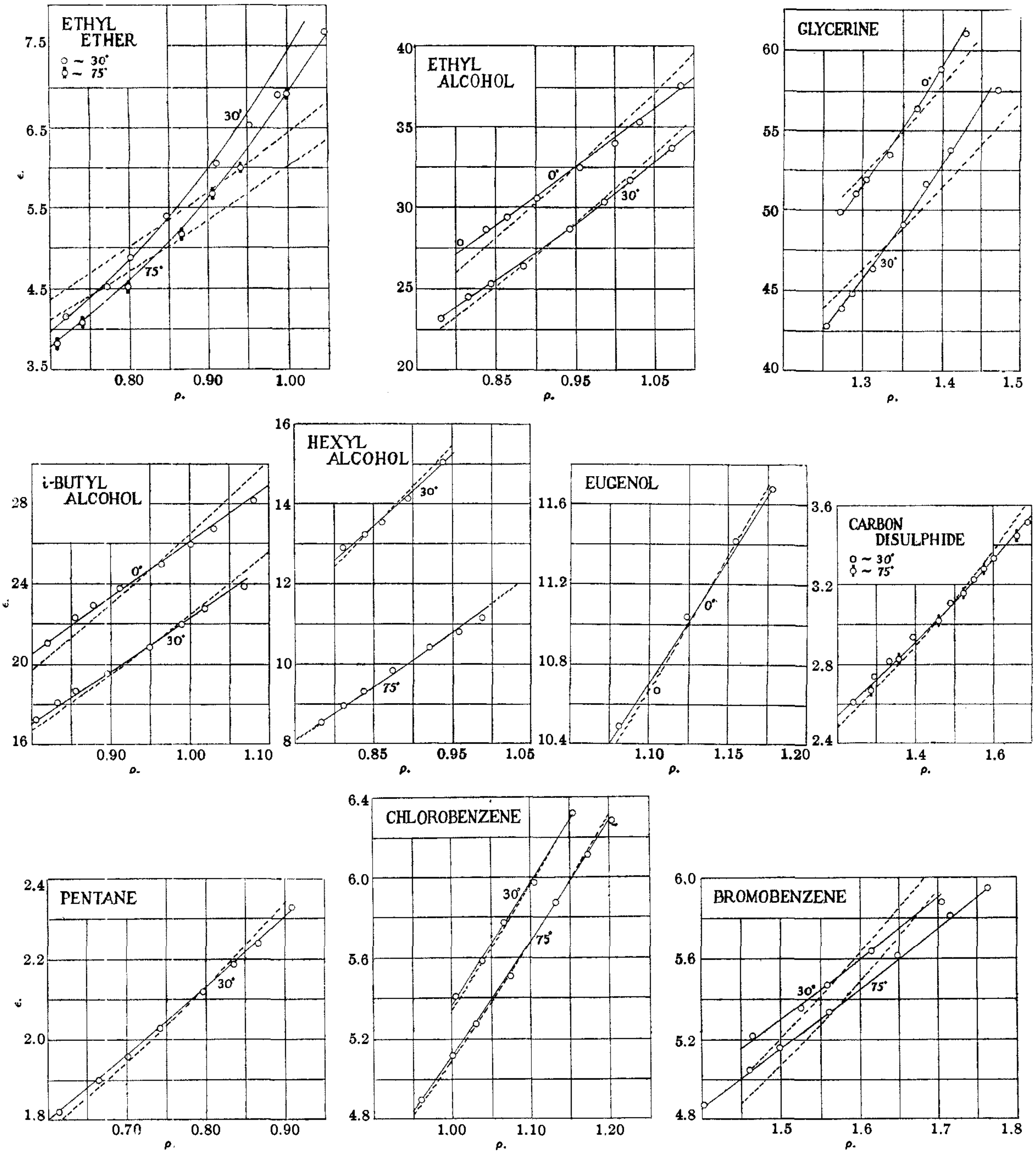

Fig. 2.

rapidly owing to thermal agitations as to be ineffective except in relation to the optical polarization. The underlying idea here is that the net effect on the molecule is to be thought of as the average of the individual effects arising from the fields of the surrounding molecules taken separately, and not as the effect of a field equal to the time average of these individual fields. If this were so, the quantity l introduced above would denote the ratio of the optical to the total polarization, which should increase with the temperature, just as the corresponding values of p' should decrease. It may be seen from Table V that this condition is in fact realized qualitatively; nevertheless, when the product lp' is compared with the optical polarization per gram, p'_{α}, obtained from the literature (both these are given in Table V) there is found to be a considerable discrepancy, although, except for bromobenzene, the results are of the right magnitude. Another way of considering this suggestion is to make use of the known values of p'_α in fitting equation (5) to Danforth's data. We are then left with only one undetermined constant, p'^*. In general it is not possible to fit the results satisfactorily in this way, as is seen from the dotted curves in Fig. 2, which correspond to the values of p'_α and p'^* given in Table V. It is worth pointing out that the product of $p'-p'_\alpha$, or $p'^*-p'_\alpha$ (it makes small difference which) times the absolute temperature is fairly constant, as may be verified.

TABLE V

Substance	t, °C.	ϵ	l	p'	lp'	p'	p'^*
Carbon disulfide	30	2.61[a]	0.683	0.317	0.216	0.281	0.272
Carbon disulfide	75	2.69[b]	.683	.317	.216	.281	.272
Pentane	30	1.82[a]	.633	.381	.242	.347	.342
Ethyl ether	30	4.15[a]	.831	.774	.644	.303	1.268
Ethyl ether	75	3.82[c]	.823	.753	.620	.303	1.171
Chlorobenzene	30	5.41[a]	.228	1.095	.250	.277	1.047
Chlorobenzene	75	4.90[a]	.25	1.02	.255	.277	0.987
Bromobenzene	30	5.22[a]	.019	0.930	.018	.216	.631
Bromobenzene	75	4.87[a]	.060	.850	.051	.216	.613
Eugenol	0	10.49[a]	.118	2.13	.252	.295	1.98
Hexyl alcohol	30	12.90[a]	.0455	4.10	.187	.306	.60
Hexyl alcohol	75	8.55[a]	.1145	2.50	.286	.306	2.44
i-Butyl alcohol	0	21.1[a]	.0153	7.40	.113	.300	5.94
i-Butyl alcohol	30	17.3[a]	.0313	5.80	.182	.300	5.00
Ethyl alcohol	0	27.8[a]	.0100	10.00	.10	.280	8.10
Ethyl alcohol	30	23.2[a]	.0243	8.03	.195	.280	7.22
Glycerin	0	49.9[a]	.0596	7.05	.420	.223	9.32
Glycerin	30	42.8[a]	.0621	5.95	.370	.223	8.25

[a] At 1 atmosphere. [b] At 1000 atmospheres. [c] At 500 atmospheres.

In conclusion, we must of course admit that the physical meaning of equations (4) and (5) remains uncertain. Such a suggestion as Kerkwood's could be in any case only a very rough approximation to the facts. Indeed, where the molecules were all the same we should expect rather a kind of anomalous dispersion in regard to their interaction, and where the system contained several types of molecules, as in the case of the data described in Part II of this paper, the situation would be more complicated still. Nevertheless, the main point of view developed in this section of the paper appears to be the only reasonable way of explaining what would otherwise remain a rather extraordinary set of numerical coincidences.

Summary

An account is given of measurements of the dielectric constant of solutions of several ampholytes, forming zwitter ions, in a variety of solvents. The results indicate in a rather surprising way that in all these cases the dielectric constant is a nearly additive property of the solutions. A discussion is given of a possible interpretation of this in terms of the internal field, which, if valid, would allow of approximate estimates of polarizations and electric moments in the case of polar solutions.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

A Thermodynamic Study of Dilute Thallous Chloride Solutions by Electromotive Force Measurements of the Cell Tl-Hg/TlCl(m)/AgCl(s), Ag(s)[1]

BY I. A. COWPERTHWAITE, V. K. LA MER AND J. BARKSDALE

Introduction

Precise measurements of the activity coefficient of thallous chloride in the region of highly dilute solution are of particular interest in view of the interpretations which have been placed upon the existing data as regards the completeness of its dissociation and its obedience to the Debye–Hückel[2] limiting law. Onsager[3] concluded, from an analysis of Kohlrausch's[4] conductivity data in the light of his theoretical equation for conductance, that this salt was incompletely dissociated ($K = 0.31$). Davies[5] reports that the extensive solubility data require, in addition to this dissociation constant, a Debye–Hückel limiting slope of 0.38 instead of the theoretical value, 0.506.[6] Davies finds support for his interpretation in the earlier freezing point measurements of Randall

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[1] This paper is from a dissertation submitted in May, 1933, by Jelks Barksdale to the Faculty of Pure Science of Columbia University in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Debye and Hückel, *Physik. Z.*, **24**, 185 (1923); **25**, 97 (1924).

[3] Onsager, *ibid.*, **28**, 277 (1927).

[4] Kohlrausch, *Z. Elektrochem.*, **8**, 628 (1902).

[5] Blayden and Davies, *J. Chem. Soc.*, 949 (1930); Davies, *ibid.*, 2410 (1930); *Trans. Faraday Soc.*, **23**, 351 (1927).

[6] A similar conclusion in the case of hydrochloric acid has recently been modified [Davies, THIS JOURNAL, **54**, 1698 (1932)].