TALLINNA TEHNIKAÜLIKOOLI TOIMETUSED
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The measurements of dielectric absorption of solutions of six amino acids in water were presented in a previous publication (15). Dielectric absorption measurements for seven amino acid solutions are reported here for the first time. For four amino acids the absorption measurements were also conducted in mixtures of water-ethanol. The experimental results are discussed on the basis of the Onsager theory.

Experimental Procedure.

For dielectric absorption the resonance method for relative measurements was used. The frequencies were 65,6, 32,8 and 16,4 megacycles. A push-pull valve generator was loosely coupled to the resonance circuit. The plate current of the valve voltmeter was compensated in the usual way and a micro-ammeter used as indicator for its change. The measuring cell (Fig. 2 (15)) is placed into the resonance circuit and the resonance with the generator is established by a parallel variable condenser. The reading of the micro-ammeter is then recorded within an accuracy of 0,1 μA. The measuring cell is thereafter substituted for a comparison cell filled with the same solvent to which sufficient KCl solution is added so that it shows the same absorption in the resonance circuit compared with the measuring cell. Actually the solution in the comparison cell is adjusted twice with different concentrations of KCl and in such a way that the comparison cell shows little more and little less absorption in the resonance circuit than the measuring cell with amino acid solution. With each concentration of KCl solution the substitution of the measuring cell for the comparison cell in the resonance circuit is carried out at least six times, each time the μA reading being registered. The low frequency conductivity of KCl in the comparison cell and of amino acid solution in the measuring cell are recorded. At the frequency used for this — usually 4 kilocycles — the polarisation resistances of the cells are negligible.

Supposing that the low frequency conductivity of KCl and amino acid solutions are independent of frequency, the difference of both represents the relative dielectric absorption of amino acid solution as compared with that of pure solvent. The KCl solution to be used for this calculation is one that would show the same absorption as amino acid solution. As the concentration of KCl solution is very small, the dielectric absorption of KCl solution may be taken to be equal to that of pure solvent. The total dielectric absorption of amino acid solution is then equal to the sum of the measured difference and the dielectric absorption of pure solvent.

As an illustration the actual measurements on 0,503 molar d-leycylglycine solution are recorded. They show also the reproducibility of the results. Cell 17 contained the solution, cell 17A served as comparison cell. The cell constant k ($k = \frac{\varkappa_0}{\varkappa}$, $\varkappa_0$ — specific conductivity of solution and $\varkappa$ — the measured conductivity of solution in cell) for cell 17 was 0,702.

Table 1.

Readings in μA when in resonance circuit

cell 17		cell 17A	
16,0	Average 15,98	15,4	Average 15,30
16,0		15,3	
16,0		15,4	
15,9		15,2	
15,9		15,3	
16,1		15,2	
low frequency cond. $115{,}8.10^{-6}$		$354{,}7.10^{-6}$	
solution in 17A changed			
14,9	Average 14,82	15,9	Average 15,90
14,8		15,9	
14,8		15,9	
14,9		16,0	
14,8		15,9	
14,7		15,8	
low frequency cond. $115{,}8.10^{-6}$		$334{,}1.10^{-6}$	

The low frequency conductivity of KCl solution in cell 17A that would show the dielectric absorption equal to that of amino acid solution is

$$\left(334{,}1 + \frac{20{,}6}{1{,}76}\,1{,}08\right).10^{-6} = 346{,}7.10^{-6}$$

and the relative dielectric absorption of amino acid solution

$$346{,}7.10^{-6} - 115{,}8.10^{-6} = 230{,}9.10^{-6}.$$

The relative specific dielectric absorption of 0,503 molar d-leycyl-glycine solution is

$$230{,}9.10^{-6} \cdot 0{,}702 = 162.10^{-6}\ \text{ohm}^{-1}\ \text{cm}^{-1}.$$

The same amino acid solution when measured in cell 47 and compared with 47A yielded for the specific dielectric absorption $160.10^{-6}\ \text{ohm}^{-1}\ \text{cm}^{-1}$. The cell constant of 47 was 2,94.

The following objection might arise in connection with the experimental procedure. The dielectric constants of amino acid solutions are larger than the dielectric constant of KCl solutions — which may be identified with the dielectric constant of pure solvent. If measuring and comparison cells have practically equal cell constants, then the capacity of the measuring cell is larger than that of the comparison cell. The cells placed into resonance circuit require different settings of the parallel variable condenser. The question is: does this change in the position of the variable condenser introduce additional absorption and how to account for it? The experiments show that two cells with approximately the same cell constants are practically equivalent to one another with regard to the dielectric absorption at all frequencies in the sense that both must contain KCl solutions of the same low-frequency conductivity. The attachment of an auxiliary condenser to one of the cells does not disturb their equivalence, even if one now has to change the position of the parallel variable condenser much more than in the actual experiment to obtain resonance.

Another possibility for actual measurements is the use of two cells with different cell constants so that one of them filled with amino acid solution and other with KCl solution would show the same capacity. There is no change then in the position of the parallel variable condenser if one cell is replaced by the other in the resonance circuit. The specific relative dielectric absorption for certain amino acids are now smaller than in the previous case. When both cells are compared containing KCl solution and showing the same low frequency conductivity, they are no longer equivalent to one another in the high frequency resonance circuit, the cell with the larger cell constant having smaller dielectric absorption.

The difference between two cells increases with increasing frequency. It is logical to explain this difference by the dielectric absorption of the solvent. The dielectric absorption caused by the solvent is more pronounced in the cell with the smaller cell constant. The correction for the difference in dielectric absorption of cells when applied to amino acid solution yields then in this case the same value for the relative specific absorption as found from two cells with the same cell constants.

The dispersion of the dielectric constant of solution with frequency is a second order effect when compared with the dielectric absorption of the same solution. No attempt was made in the present case to determine the dispersion of dielectric constant. The dielectric constant was measured on a high frequency bridge using a frequency high enough to be free from polarization capacities of the electrodes. Five hundred kilocycles was used. The measuring cell with amino acid solution was balanced in one arm of the bridge. The cell was exchanged for a comparison cell with KCl solution of nearly the same conductivity and capacity balance established by a parallel precision condenser. For balancing the resistance the electrode distance of a parallel electrolytic resistance cell with a movable electrode was adjusted. If the conductivity of liquid in this cell is properly selected, only a displacement of the order of 0,001 cm of the micrometer screw of the movable electrode is sufficient. If the amino acid solution in measuring cell is now replaced by KCl solution and balance established, then the difference of the precision condenser settings is equal to the change of capacities connected with the replacement of amino acid solution (small correction applied to the difference in distance of the electrolytic resistance). The dielectric constant change of amino acid solution is thus easily found.

The calculation of the influence of stray capacities presented in the previous publication (15) on page 1176 needs a correction, which I take the opportunity to make here. The correct expression for C_y should read

$$C_y = \frac{\frac{1+a^2\omega^2}{a^2\omega^2} C_i C_m}{\frac{1+a^2\omega^2}{a^2\omega^2} C_i + C_m}$$

that is the bracket in the denominator is superfluous, as well as the factor 10^{-12}. In the expression for σ', in the second bracket of the nominator a should be replaced by ω. It is worth mentioning that the expressions for σ' and C' may be simplified to the form:

$$\sigma' = \frac{\sigma_i \omega^2 C_m^2}{\sigma_i^2 + \omega^2 (C_i + C_m)^2}$$

$$C' = \frac{C_m [\sigma_i^2 + C_i \omega^2 (C_m + C_i)]}{\sigma_i^2 + \omega^2 (C_i + C_m)^2}.$$

Experimental Results and Their Preliminary Discussion.

All the amino acids used were recrystallized several times from mixtures of water-ethanol or from pure water. The low frequency conductivity of solutions diminishes by recrystallization as illustrated by the following data. dl-α-aminovaleric acid—a product of Eastman Kodak Co—had in 0,6 molar solution the specific conductivity 378.10^{-6} ohm^{-1} cm^{-1}. After three recrystallizations the solution of the same concentration had specific conductivity of $14{,}6.10^{-6}$ ohm^{-1} cm^{-1}. The low frequency conductivity of amino acid solutions is surely an indicator of their purity. It is important to note that the molar conductivities of glycine, dl-alanine, dl-α-aminobutyric acid, dl-α-aminovaleric acid, dl-α-aminocaproic acid, dl-methionine and dl-phenylalanine were as following: 0,020; 0,085; 0,014; 0,024; 0,080; 0,056; 0,082 ohm^{-1} cm^2 mol^{-1}. The conductivities recorded in literature for some of the mentioned amino acids are larger (2, 3, 4, 12, 13, 18, 19, 22, 23, 26). The molar conductivities of γ-aminobutyrie acid, ε-aminocaproic acid, hydroxyproline, glycylglycine, d-leycylglycine and glycyl-dl-leycine were correspondingly 0,186; 0,190; 0,374; 0,254; 0,159; 0,125 ohm^{-1} cm^2 mol^{-1}. Even if the conductivities in this group were larger than in the former, they were considerably smaller than found in literature (20, 26). How far the conductivities could be lowered by further purification could not

be investigated, because of the limited amount of the substances.

Table 2.

Substance	Concentration	$\frac{\Delta\varepsilon}{\Delta C}$	$\frac{\varkappa_{orel}}{C} \times 10^6$ ohm^{-1} cm^{-1} at			$\frac{\eta}{\eta_0}$
			65,6 MC	32,8 MC	16,4 MC	
dl-α-aminovaleric acid	0,602	23,4	53,0	12,3	3,3	1,301
dl-methionine	0,226	20,9	43,8	11,0	2,7	1,082
dl-phenylalanine	0,085	21,3	54,1	13,5	3,4	1,05
hydroxyproline	1,006	29,0	54,2	13,6	3,4	1,332
glycylglycine	0,500	62,2	130	33,0	8,1	1,143
d-leycylglycine	0,503	62,6	321	84,3	20,3	1,408
glycyl-dl-leycine	0,503	73,6	338	83,5	20,9	1,407

In table 2 are represented the results for seven amino acids. The dielectric constant and dielectric absorption were measured at least in two cells, differing in cell constants and cell form, and averaged. The individual values do not differ more than 1%. By $\frac{\Delta\varepsilon}{\Delta C}$ is meant the increase of dielectric constant of 1 molar amino acid solution compared with that of pure solvent. The value is calculated assuming proportionality between molarity and increase of dielectric constant. The dielectric constants for dl-methionine, hydroxyproline and d-leycylglycine solutions have not been recorded previously. The dielectric constant of dl-α-aminovalerie acid solution has been measured by Wyman (26) with substantially the same results. For dl-phenylalanine Frankenthal (14) found $\frac{\Delta\varepsilon}{\Delta C} = 27$ starting from 0,048 m. solution. For glycylglycine solutions the determinations of Devoto (10), Frankenthal (14) Halbedel (16), Hausser (17) and Wyman (26) yield for $\frac{\Delta\varepsilon}{\Delta C}$ values between 70 and 80. For glycyl-dl-leycine Frankenthal (14) found 75 for $\frac{\Delta\varepsilon}{\Delta C}$ but Devoto (11) (for the d-compund) reports 54. The values found in 4th, 5th and 6th coulumns for the relative dielectric absorption of 1-molar solution of corresponding amino acid are calculated on the same assumption as that of $\frac{\Delta\varepsilon}{\Delta C}$. The dielectric absorption increases nearly as the square of frequency. There are no data in literature for dielectric

absorption measurements except that of Fricke and Parts (15). The viscosities η of solutions (also in table 3) are measured relative to η_0 — the viscosity of pure solvent — in an Ostwald viscosimeter at 21,0° C. This is also the temperature of all the measurements. The densities for solutions were calculated from molal volumes of amino acids in solution, using the data of Cohn, McMeekin, Edsall, Blanchard (5).

In the following table 3 are to be found the change of dielectric constants and dielectric absorption for four amino-acids in 26,22 weight % ethanol in water as solvent. The $\frac{\Delta\varepsilon}{\Delta C}$ and dielectric absorptions are given with respect to pure solvent.

Table 3.

Substance	Concentration	$\frac{\Delta\varepsilon}{\Delta C}$	$\frac{\varkappa_{orel}}{C} \times 10^6$ ohm^{-1} cm^{-1} at			$\frac{\eta}{\eta_0}$
			65,6 MC	32,8 MC	16,4 MC	
Glycine	0,751	24,0	39,3	10,0	2,6	1,092
dl-α-aminobutyric acid	0,747	24,1	89,4	23,4	5,6	1,249
γ-aminobutyric acid	0,365	49,3	160	43,3	11,0	1,13
ε-aminocaproic acid	0,218	82,5	490	130	32	1,117

For the discussion of dielectric absorption it is not rational to use the well known Debye equations (6, 7) which in the case of pure solvent yield

$$\varepsilon''\omega = 3{,}6.10^{+12}\,\pi\varkappa_{abs} = \frac{(\varepsilon_0 - \varepsilon_\infty)\dfrac{\varepsilon_0 + 2}{\varepsilon_\infty + 2}\,\omega^2\tau}{1 + \left(\dfrac{\varepsilon_0 + 2}{\varepsilon_\infty + 2}\right)^2 \omega^2\tau^2}. \qquad \text{(I)}$$

ε'' is the imaginary part of complex dielectric constant, $\omega = 2\pi\nu$, ν being the frequency of electromagnetic field, τ relaxation time, ε_0 the static dielectric constant caused from the orientation of permanent dipoles and polarizability of molecules and ε_∞ the dielectric constant at so high frequencies that the orientation of permanent dipoles does not contribute to the dielectric constant. Relaxation time is defined by the equation

$$\tau = \frac{3\eta v}{RT}, \qquad \text{(II)}$$

η denoting the viscosity of medium, v molal volume of substance, T absolute temperature and R gas constant. The

Debye equation has been arrived at on the assumption that the electric field intensity that acts upon individual molecules is given by the familiar Lorentz expression

$$\mathfrak{F} = \mathfrak{E} + \frac{4\pi}{3}\mathfrak{P}. \qquad \text{(III)}$$

At the same time it is supposed that the molecules with permanent dipoles during their orientation in the electric field are hindered only by viscous forces.

The calculated static dielectric constant of dipole liquid, using for dipole moment the value measured from the gaseous state and the equation (III) for the internal field is not in agreement with the measured one. Similarly, dispersion of dielectric constant or dielectric absorption yields values of molal volumes that cannot be real. To explain the discrepancies two possible explanations are put forward. Debye (8, 9) presents the idea, that the dipole molecule is bound to a certain position because of the configuration of the neighbouring molecules and posesses, therefore, a certain amount of potential energy, if not in this position. On the other hand, Onsager (21) and van Vleck (24) arrived at the conclusion that the expression (III) for the inner field is inadequate.

The original Debye theory yields for the static dielectric constant of the pure substance

$$\frac{\varepsilon_0 - 1}{\varepsilon_0 + 2} = \frac{n^2 - 1}{n^2 + 2} + \frac{4\pi}{3} N \frac{\mu^2}{3kT} \qquad \text{(IV)}$$

where $n^2 = \varepsilon_\infty$, μ — the permanent dipole moment of molecule, k Boltzmann's constant, N-number of molecules in a unit volume. According to Onsager (IV) should be replaced by

$$\varepsilon_0 = n^2 + \frac{(n^2+2)^2}{2}\frac{4\pi}{3} N \frac{\mu^2}{3kT} \qquad \text{(V)}$$

and for a binary mixture

$$\varepsilon_{0m} = \vartheta_1 n_1^2 + \vartheta_2 n_2^2 + \frac{(n_1+2)^2}{2}\frac{4\pi}{3} N_1 \frac{\mu_1^2}{3kT} + \frac{(n_2+2)^2}{2}\frac{4\pi}{3} N_2 \frac{\mu_2^2}{3kT} \qquad \text{(VI)}$$

Indices 1 and 2 refer to the respective kind of molecules. ϑ designates the part of the total volume filled with molecules.

Dielectric absorption and dispersion of dielectric constant assuming for static electric field the equations (V) or (VI) is to be found on the basis of original Debye dispersion and ab-

sorption theory multiplying the members containing dipole moments with factor $\frac{1}{1+i\omega\tau}$. So we arrive at a complex dielectric constant

$$\varepsilon = \varepsilon' - i\varepsilon'' \qquad \text{(VII)}$$

where ε' represents the frequency dependent part of dielectric constant and $\varepsilon''\omega$ corresponds to dielectric absorption. For a binary mixture

$$\varepsilon_m = \varepsilon'_m - i\varepsilon''_m = \vartheta_1 n_1^2 + \vartheta_2 n_2^2 + \frac{(n_1+2)^2}{2}\frac{4\pi}{3} N_1 \frac{\mu_1^2}{3kT}\cdot\frac{1}{1+i\omega\tau_1} +$$

$$+ \frac{(n_2+2)^2}{2}\frac{4\pi}{3} N_2 \frac{\mu_2^2}{3kT}\cdot\frac{1}{1+i\omega\tau_2}. \qquad \text{(VIII)}$$

Designating

$$\vartheta_1 n_1^2 + \vartheta_2 n_2^2 = A; \quad \frac{(n_1+2)^2}{2}\frac{4\pi}{3} N_1 \frac{\mu_1^2}{3kT} = B_1$$

$$\frac{(n_2+2)^2}{2}\frac{4\pi}{3} N_2 \frac{\mu_2^2}{3kT} = B_2, \qquad \text{(IX)}$$

then

$$\varepsilon_m = \varepsilon'_m - i\varepsilon''_m = A + \frac{B_1}{1+\omega^2\tau_1^2} +$$

$$+ \frac{B_2}{1+\omega^2\tau_2^2} - i\left(\frac{B_1\omega\tau_1}{1+\omega^2\tau_1^2} + \frac{B_2\omega\tau_2}{1+\omega^2\tau_2^2}\right). \qquad \text{(X)}$$

If $\omega\tau_1 \ll 1$ and $\omega\tau_2 \ll 1$, that is if the frequency is sufficiently low so that $\varepsilon'_m = \varepsilon_{0m}$ or no dispersion of dielectric constant exists, then

$$\varepsilon_m = \varepsilon'_m - i\varepsilon''_m = A + B_1 + B_2 - i(B_1\omega\tau_1 + B_2\omega\tau_2);$$

$$\varepsilon'_m = A + B_1 + B_2; \quad \varepsilon''_m\,\omega = B_1\omega^2\tau_1 + B_2\omega^2\tau_2. \qquad \text{(XI)}$$

In the case of a pure solvent $N_2 = 0$ and

$$\varepsilon''_0\,\omega = B_{10}\omega^2\tau_{10} \qquad \text{(XII)}$$

with

$$B_{10} = \frac{(n_1+2)^2}{2}\frac{4\pi}{3} N_{10}\frac{\mu_1^2}{3kT} \qquad \text{(XIII)}$$

and τ_{10} is the relaxation time for solvent molecules in a pure solvent, which may be different from τ_1 — the relaxation time of the same molecule in solution. By comparison of (IX) and (XIII) follows:

$$B_1 = \frac{N_1}{N_{10}} B_{10} = \vartheta_1 B_{10} = (1 - \vartheta_2) B_{10}. \qquad \text{(XIV)}$$

If the relaxation times τ_{10} and τ_1 are solely determined by viscosities of respective solutions and molal volumes of solvent molecules in solvent and solution are the same, then

$$\tau_1 = \tau_{10} \frac{\eta_1}{\eta_{10}} \qquad \text{(XV)}$$

where η_{10} stands for the viscosity of the pure solvent. From (XI) one has

$$B_2 = \varepsilon_{0m} - A_1 - B_1 = \varepsilon_{0m} - \vartheta_1 n_1^2 - \vartheta_2 n_2^2 - \vartheta_1 B_{10} \qquad \text{(XVI)}$$

and from (V) for the pure solvent

$$\varepsilon_0 = n_1^2 + B_{10} \qquad \text{(XVII)}$$

so that

$$B_2 = \varepsilon_{0m} - \vartheta_1 \varepsilon_0 - \vartheta_2 n_2^2 \qquad \text{(XVIII)}$$

and for

$$\omega^2 \tau_2 = \frac{\varepsilon_m'' \omega - \vartheta_1 \varepsilon_0'' \omega \frac{\eta_1}{\eta_0}}{\varepsilon_{0m} - \vartheta_1 \varepsilon_0 - \vartheta_2 n_2^2}. \qquad \text{(XIX)}$$

The relaxation time for a molecule of solute in solution is thus easily calculated supposing the dielectric losses of solution and pure solvent as well as dielectric constants are measured, if the relative viscosity of solution is given and volume fractions of substances are known.

In table 4 are presented the molal volumes for amino acids in solution calculated thus from the measurements presented here and in (15).

Amino acids might be divided into two groups. The first group is formed by α-acids. Their molal volumes are between 58 and 69% of the actual molal volumes given by (5). The remaining amino acids where the amino- and carboxy-groups are separated by 3 or 5 carbon atoms belong to the second group. In this group the molal volumes as calculated from dielectric absorption are between 82 and 103% of the molal volumes as found in (5). The molal volumes as given by Cohn, McMeekin, Edsall, Blanchard (5) and reported in table 4 are calculated as sums of individual group volumes (CH_2, NH_2, COOH etc.) in molecules. Computing for instance the apparent molal

Table 4.

Substance	Concentration	Molal volume from (5)	$\frac{\varepsilon'' \omega}{3{,}6.10^6 \pi}$	Calculated molal volume from dielectric absorption
Glycine	1,000	57,0	32,8	33,0
dl-α-alanine	0,255	73,3	19,7	47,5
dl-α-aminobutyric acid .	0,332	89,6	25,1	57,6
hydroxyproline	1,006	87,7	66,5	59,8
dl-α-aminovaleric acid .	0,602	105,9	43,9	65,3
dl-methionine	0,226	121,1	21,9	69,5
dl-α-aminocaproic acid .	0,077	122,2	16,6	84,4
dl-phenylalanine	0,085	130,8	16,6	84,4
γ-aminobutyric acid . .	0,202	89,6	29,2	73,7
glycylglycine	0,500	93,3	77,0	88,9
ε-aminocaproic acid . .	0,196	122,2	57,8	118
d-leycylglycine	0,503	158,5	182,0	151
glycyl-dl-leucine	0,503	158,5	173,6	164

volume of glycine from the density of solutions in water there results 43,5 instead of 57,0 as given in table. The difference is explained by "electrostriction" which is caused by zwitterions of glycine, the aminogroup having positive and carboxygroup negative charge. The "electrostriction" for all α-amino acids so far investigated is about 13 cm^3, for amino acids where the groups are more separated it is larger, e. g. for ε-amino acids 17 cm^3. Using (XIX) for the calculation of relaxation time with molal volumes determined from density measurements the calculated molal volume increases by several per cent. The general picture of two groups of amino acids remains unaltered.

The validity of (XIX) assumes that the molecules of solute in solution do not influence the molecules of solvent more than in ordinary mechanical mixture. It may also be objected that (XV) does not represent the actual conditions. But it was shown (15) that the molal volume, as calculated from dielectric absorption, is practically independent of the concentration of the respective amino acid solution. The viscosity of the solution changed thereby more than 40%. It is reasonable to suppose, that the more exactly (XIX) is fulfilled, the less is the mutual influence between molecules of solute and solvent. This mutual influence should diminish if the

dipol moment of solvent molecules is diminished. Experiments are required to test this.

From dielectric absorption measurements in ethanol-water

Table 5.

Substance	Concentration	Molal volume from (5)	$\frac{\varepsilon'' \omega}{3{,}6.10^6 \pi}$	Calculated molal volume from dielectric absorption
Glycine	0,751	57,0	52,5	28,0
dl-α-aminobutyric acid .	0,747	89,6	89,8	49,8
γ-aminobutyric acid . .	0,365	89,6	84,8	58,8
ε-aminocaproic acid . .	0,218	122,2	129,8	107

mixtures the molal volumes, of amino acids as presented in table 5 were calculated. The concentration of the amino acid solution was selected so as to give for the dielectric constant the value of pure water. Ethanol-water mixture was selected so as to give nearly the maximum viscosity known for these mixtures. The molal volumes thus found are slightly smaller than for pure water as solvent. The relative decrease is largest for γ-amino butyric acid. It is hard to decide whether this decrease is real or caused by experimental errors. But it is certain, that the change in the viscosity of the solvent 2,41 times has no profound influence on the molal volume of solute, as calculated from dielectric absorption data.

From Onsager relations (V and VI) it follows that the change in the dielectric constant of amino acid solution with the same volume concertration of acid should depend on the dielectric constant of pure solvent. Denoting by ε_0 und ε_0' the dielectric constants of pure solvents and by $\Delta\varepsilon_0$ and $\Delta\varepsilon_0'$ the corresponding changes of dielectric constants upon solution of amino acids in these solvents the Onsager relation requires

$$\Delta\varepsilon_0' - \Delta\varepsilon_0 = (\varepsilon_0 - \varepsilon_0')\,\vartheta_2 \qquad \text{(XX)}$$

where ϑ_2 is the volume fraction of amino acid in solution. The increase of dielectric constant of solution due to presence of amino acid should be the larger the smaller the dielectric constant of pure solvent. According to table III presented in the work of Wyman (27) for solutions of glycine in α-aminobutyric acid solutions of various concentrations as well as from

solutions of α-aminobutyric acid in glycine solutions the predicted trend in the change of dielectric constant of solution is qualitatively fulfilled. That is $\Delta\varepsilon_0' - \Delta\varepsilon_0 < 0$ for these solutions. For water-ethanol mixtures as solvent $\Delta\varepsilon_0' - \Delta\varepsilon$ should be > 0 but Wyman's data referred to yield for glycine solutions $\Delta\varepsilon_0' - \Delta\varepsilon_0 < 0$ and for α-aminobutyric acid solutions irregular values. But the data of Wyman do not pretend to be very accurate for they do not yield the generally accepted values for dielectric constants of water-ethanol mixtures (1,25).

For 26,22 weight% ethanol solution in water the dielectric absorption was compared with that of pure water. Table 6 represents the measurements at different frequencies.

Table 6.

Specific relative dielectric absorption $\varkappa_{orel}$ $10^6 ohm^{-1} cm^{-1}$ of 26,22 weight % ethanol in water at frequencies

	65,6 MC	32,8 MC	16,4 MC
Cell 17	11,2	2,78	0,74
Cell 15	10,2	2,55	0,74

For molal volume of ethanol using (XIX) results in this case 7,8 cm^3, which value cannot represent the true volume of alcohol in solution. Dielectric absorption of pure water yields for molal volume of water 8,5 cm^3, again a value that is too small.

In conclusion it seems, that a systematic study of the dielectric losses of amino acids in solvents of low dielectric constant is highly desirable, as well as a similar study of dielectric absorption of binary mixtures of dipole liquids.

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