

THE ANALYSIS OF DIELECTRIC ABSORPTION DISPERSION OF GLYCINE WATER SOLUTION

S.T. AZIZOV, O.A. ALIYEV

Institute of Physics of Azerbaijan NAS, AZ 1143, H.Javid ave.,131, Baku, Azerbaijan
 Institute of Physics of Azerbaijan NAS, AZ 1143, H.Javid ave.,131, Baku, Azerbaijan
 e – mail: samir_azizov@mail.ru

The analysis of glycine water solution measured by dielectric constant at temperature from 20 до 50 ° C on 5 frequencies in centimetric range is carried out.

The dielectric spectra are studied taking under consideration other frequencies given in scientific literature.

Keywords: dielectric spectroscopy, molecular spectroscopy, glycine, glycine dielectric properties, glycine water solution.

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INTRODUCTION

The analysis of obtained results of observable dielectric absorption dispersion of glycine water solution in [1] with calculated results, presented earlier in [2], reveals the divergences exceeding the measurement errors. That’s why the necessity of conclusion review [2] based on model [3] in which the presence of two dielectrically active types of kinetic units in amino-acid water solutions are postulated, takes place.

THE RESULTS AND DISCUSSION

The presented analysis is related to results of measurements of dielectric constants ϵ' and absorption indexes ϵ'' at temperatures from 20 up to 50° C and wave length $\lambda = 66,7; 50,0; 39,5; 33,3$ [2]; 8,28 [4]; 5,83; 4,02; 3,23 [1]; 3,17 [4]; 2,10; 1,40 [1]; 0,85 cm [4]. The measurement errors don’t exceed 1 and 4% [2]; 3 and 6% [1]; 2 and 5% [4] for ϵ' and ϵ'' . The error of equilibrium dielectric constant ϵ_0 is less than 0,5% [2,5].

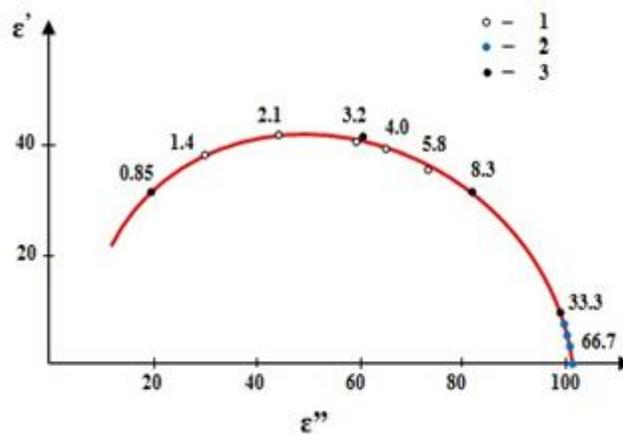


Fig.1. Arc diagram of glycine water solution at 20°C.

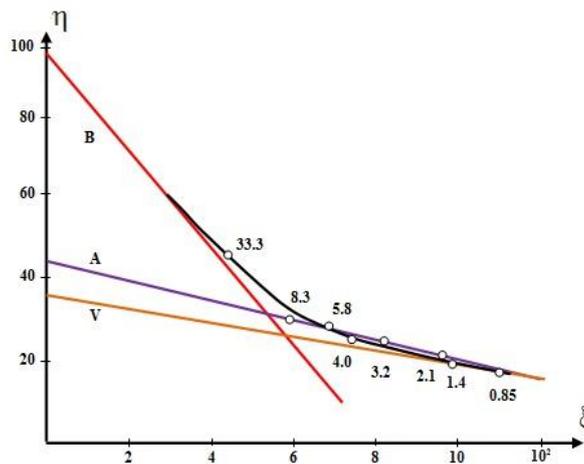


Fig.2. Line diagram of glycine water solution at 20°C.

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The measurement results at 20° C character for whole studied temperature interval in arc representation are shown in fig.1. At it is seen that spectrum is characterized by strongly expressed asymmetry. Let's suppose that observable relaxation of oriented part of solution polarization can be described by linear superposition of arbitrary number of i Debye processes

$$\varepsilon' - j\varepsilon'' = \varepsilon_{\infty} + \sum(\varepsilon_{0i} - \varepsilon_{\infty i}) (1 + j\omega\tau_i)^{-1}, \quad (1)$$

where $\tau_i > \tau_{i+1}$; $\varepsilon_{\infty i} = \varepsilon_{0(i+1)}$; the rest designations have the usual meaning. For $i = 2$ this equation transforms into the following form:

$$[(\tau_1\tau_2)\tau_0^{-2}]\xi + \eta\eta = (\tau_1 + \tau_2)\tau_0^{-1}, \quad (2)$$

$$\xi = \omega\tau_0 (\varepsilon' - \varepsilon_{\infty}) (\varepsilon'')^{-1}, \quad (2a)$$

$$\eta = (\varepsilon_0 - \varepsilon')(\omega\tau_0\varepsilon'')^{-1}, \quad (2b)$$

where homogenization constant is $\tau_0 = 10^{-12}$ c. According to (2) the dielectric spectrum satisfying to equation (1) with $i = 2$ is presented in $\eta = f(\xi)$ graph by the line with inclination equal to $(\tau_1\tau_2)\tau_0^{-2}$ and point of intersection with ordinate axis equal to $(\tau_1+\tau_2)\tau_0^{-1}$. The partial amplitudes $\Delta_i = \varepsilon_{0i} - \varepsilon_{\infty i}$ including in (1) are calculated with the help of experimental values ε' , ε'' , ε_0 and estimated τ_1 , τ_2 , ε_{∞} by the following formulae

$$\Delta_1 = (1 + \omega^2\tau_1^2)[(\varepsilon' - \varepsilon_{\infty})\tau_2 - \varepsilon''\omega^{-1}](\tau_2 - \tau_1)^{-1} \quad (3)$$

$$\Delta_2 = (1 + \omega^2\tau_2^2)[(\varepsilon' - \varepsilon_{\infty})\tau_1 - \varepsilon''\omega^{-1}](\tau_1 - \tau_2)^{-1} \quad (4)$$

which may be obtained from (1). The preliminary value can be found from equation from following equation

$$\varepsilon' = \varepsilon'' (\omega\tau)^{-1} + \varepsilon_{\infty}, \quad (5)$$

obtained from (1) at $i = 1$.

Δ_1 and Δ_3 values are calculated by (3)-(4) correspondingly. The characteristics of intermediate regions are obtained from the following expression:

$$\varepsilon_2' - j\varepsilon_2'' = \varepsilon' - j\varepsilon'' - [(\varepsilon_{\infty} + \Delta_1(1 + j\omega\tau_1)^{-1} + \Delta_3(1 + j\omega\tau_3)^{-1})] \quad (6)$$

Note that such approach gives the only rough values of relaxation parameters and that's why the further fitting is required. The criteria of analysis satisfaction are: 1) approximate constancy of Δ_i partial amplitudes at different λ calculated by (3-4) [6,7]; 2) carrying out of condition [8]

$$S \leq S_m \quad (7)$$

where $S_m = 2n$ (n is number of used λ). The sum S of standard deviation of measured ε' , ε'' on estimated ε'_{cal} , ε''_{cal} is calculated by the formula:

$$S = \sum(S_1 + S_2) = \sum \left\{ [(\varepsilon' - \varepsilon'_{cal})(\varepsilon'v')^{-1}]^2 + \frac{\varepsilon'' - \varepsilon''_{cal}}{\varepsilon''v'' - 12} \right\} \quad (8)$$

where v', v'' are relative errors of ε' , ε'' measurements at given λ .

Table 1

The comparison of experimental and calculative spectra of glycine water solution at 20°C ($\varepsilon_0 = 102,5$; $\varepsilon_{\infty} = 5,0$; $\tau_1 \cdot 10^{12}$ s)

λ cm	ε'	ε''	A		[2]		B + V	
			$\tau_1=39,0$ $\Delta_1=22,2$	$\tau_2=8,3$ $\Delta_2=59,3$	$\tau_1=72,0$ $\Delta_1=22,2$	$\tau_2=9,0$ $\Delta_2=75,3$	$\tau_1=72,0$ $\tau_3=8,1$ $\Delta_2=28,5$	$\tau_2=25,0$ $\Delta_1=16,0$ $\Delta_3=53,0$
			S_1	S_2	S_1	S_2	S_1	S_2
66,7	101,0	6,34	1,02	9,77	0,28	0,10	0,48	0,16
50,0	101,4	8,51	0,05	11,64	0,16	0,84	0,09	0,35
39,5	100,5	10,5	0,39	9,43	0,09	1,09	0,04	0,23
33,3	99,4	12,3	1,47	8,93	0,01	1,69	0,04	0,37
8,28	84,3	29,7	0,06	0,00	0,16	11,34	0,69	0,29
5,83	74,7	32,5	0,09	0,21	1,79	0,86	0,02	0,02
4,02	65,2	37,4	0,00	0,34	8,98	2,49	0,09	0,39
3,23	59,2	37,1	0,00	0,01	11,41	0,24	0,26	0,02
3,17	61,4	38,2	4,84	0,16	7,23	1,01	8,56	0,16
2,10	44,5	37,1	1,52	0,36	25,34	2,01	0,05	0,24
1,40	31,2	35,5	2,12	0,18	24,47	3,31	0,28	0,02
0,85	19,1	28,9	0,03	0,04	4,39	3,75	1,10	0,08
S	$S_m = 24,0$		52,7		113,0		14,0	

According to line diagram at $\lambda \leq 8,3$ cm the superposition of two Debye processes takes place.

The set of parameters (see 4,5 rows, table 1) corresponding to **A** line indeed allows us to reproduce this region of observable spectrum ($S=10,0$; $S_m=16,0$). However, $S = 40,3$ at $S_m = 16,0$ outside its limits ($\lambda \geq 33,3$ cm). All these facts prove the nonrandom nature of inclinations from linearity in fig.2 at $\lambda > 8,3$ cm. Unfortunately, the use of decimeter points for the definition of long-wave edge true shape of $\eta(\xi)$ graph is difficult because of the fact that the difference $\varepsilon_0 - \varepsilon'$ including in expression (2b) is comparable with measurement error. Thus, $\varepsilon_0 - \varepsilon' = 1,5$ at $\lambda = 66,7$ cm whereas $\varepsilon_0 = 102,5 \pm 1,0$; $\varepsilon' = 101,0 \pm 1,0$. The point at $\lambda = 33,3$ cm where $\varepsilon_0 - \varepsilon' = 3,1$ is the unique relatively reliable point. In this case $\eta(\xi)$ graph has the form of curve the one of the possible variants of which is shown in fig.2.

The approximation of low- and high-frequency regions of $\eta(\xi)$ curve by **B** and **V** segments allows us to find the previous values of equation parameters (1) with $i = 3$ with the help of above mentioned technique. As it is seen the interval of possible relaxation times is between 84 and 7ps. According to values $\tau_1' = 16,5$ ps and $\tau_3' = 27,7$ ps intermediate frequency process has $\tau_2 \sim 20$ ps. These estimates coincide with $\tau_1 = 39$ ps value corresponding to **A**

line which can be considered as relaxation time of sum process formed by contributions with $\tau \sim 80$ and ~ 20 ps.

The final results of spectrum treatment with $i = 3$ are given in 8,9 rows of table 1. The strong loss ($S=8,56$) of the point at $\lambda=3,17$ cm is caused by ε' value that is proved by independent data at $\lambda=3,20$ cm [9].

As the spectrum division in three regions leads to $S < S_m$ the further fitting of calculation to the experiment becomes the unfounded. Note that closeness of τ_3 value to τ_{water} pure water which is by data of different authors is from 8,9 up to 9,5ps (20°C). The high-frequency region at given τ_3 and τ_{water} is divided in two contributions [11, 12]. The best agreement is achieved at choice $\tau_{\text{water}} = 8,6$ ps.

CONCLUSION

According to [13, 14] the solvent polarity doesn't influence on orientational dynamics of glycine water solution. At the same time the partial contribution in spectrum of glycine water solution system at all studied concentrations and temperatures is characterized by values of relaxation times [8,15]. The intermediate-frequency process (2) in spectrum of water-glycine system reflects the existence of regions with undisturbed submolecular organization correspondingly.

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