INVESTIGATION OF DIELECTRIC PROPERTIES OF STRONGLY-ABSORBING LIQUIDS AND THEIR SOLUTIONS

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The investigation results of dielectric properties of solutions of some amides and nitromethane in dioane in SHF range are given in the work and the existence of two dispersion relaxation regions of Debye type in these polar liquids and solutions, from which the low-frequency one is defined by decay processes of molecular processes of dipole molecules, is established. The non-reflecting absorption effect of electromagnetic radiation is observed in these solutions.

Introduction.

The investigations of dielectric solution properties of polar liquids in the region of their wave dispersion allow obtaining the information about their molecular structure. Besides, as it is shown in works [1,2], these investigations give possibility to study the demonstration of non-reflecting absorption effect of electromagnetic radiation which reveals in dilute solutions of polar molecules.

The study of microwave radiation reflection in acetone-benzol and water-dioane solutions shows the case of effect on definite width and concentration of these solutions of non-reflecting absorption [1, 2, 3]. The existence of similar effect forms the application perspective of dielectric materials as the basis for absorption thin layer of microwave radiation. All this makes the investigation of absorption reflection effect of microwave radiation in two-layered system reasonable, because polar solutions have the high dielectric constant and short time of dipole relaxation in nonpolar solvent. The individual polar liquids (acetone, water alcohols, acetonitrile, amides and others) and their solutions in nonpolar solvents (dioane, benzol) are used in the capacity of investigation objects. In the given article the investigations of dielectric properties and molecular structures of amides and nitromethane and their solutions in nonpolar dioane are given.

Investigation method.

The polar amides suppose the presence of amine group having the big value of equilibrium dielectric constant ε_0 ; for example: for formamide it is equal to 110 units and has enough short relaxation time lying in the limits $1,5\cdot10^{-11}$sec.

It has been established by us that the amide dielectric properties in the range of centi- and millimeter radio waves and their solutions in nonpolar dioane are well described in terms of two relaxation processes. These processes are defined by decay processes of hydrogen-connected associates of amide molecules and relaxation of free dipole molecules [4, 5]. Besides, the existence the polar component of non-reflecting absorption effect of incident electromagnetic radiation in polar amides has been revealed by investigations of microwave reflection characteristics from regulated layer width of diluted solutions of polar amides in nonpolar dioane [4, 5].

The properties of these solutions aren't investigated in microwave region. That's why parallel study of dielectric properties and reflection characteristics of these solutions has the definite theoretical and practical interest.

The investigations are carried out at temperature 20°C and λ=1,5cm and λ=8,15mm wave lengths with the use of panoramic measurer of standing wave on voltage R2-66, RR-67 and indicator device Y2R-67 with which the measuring wave-guide cells, short-circuited on the end, are connected. The last ones are thermostated and have the devices for regulation of solution reflecting layer width. The nitromethane, formamide, dymetilformamide, *N*-methylformamide, *NN*-dymethylacetamide and dioane by HCA trend are used in the capacity of components of investigated solutions. The method based on measurements of coefficients of standing wave η and width *1* of substance reflecting layer at which amplitudes of reflected wave achieve their minimal values is used for definition of dielectric constant ε' and dielectric loss ε'' of individual polar liquids and their solutions in dioane. The results of these measurements are presented in table 1.

Result discussion.

The estimation of intermolecular short-range forces with the use of correlation parameter $q = \mu_l^2 / \mu_g^2$ where μ_l and μ_g are values of molecule dipole moments defined in liquid and gas phases is carried out for preliminary discussion about molecular nature of nitrogen-containing polar liquids and their solutions in nonpolar solvent correspondingly. The values of dipole moments of investigated substances, obtained on data of works [6,7] in gas phase are used in the capacity of μ_g. The reference data of low-frequency measurements of equilibrium dielectric constant ε_0 [8] are used for finding μ_l. The calculation of μ_l is carried out on Onzonger-Kirkwood-Frelih equation obtained from polarization static theory [9]

$$\mu_l = \left[(\varepsilon_0 - \varepsilon_\infty)(2\varepsilon_0 + \varepsilon_\infty)\right] / \left[\varepsilon_0(\varepsilon_\infty + 2)^2\right] \cdot \left[9KT / 4\Pi N_A\right] \quad (1)$$

where T is absolute temperature, N_A is Avogadro constant, k is Boltzman constant.

The value of high-frequency limit of dielectric constant ε_∞ including in (1) is defined from Klauzius-Mosotti equation

$$[(\varepsilon_\infty - 1)/(\varepsilon_\infty + 1)] = 1{,}05[(n^2 - 1)/(n^2 + 2)] \qquad (2)$$

where n is optical substance refraction index, coefficient 1,05 takes into consideration the contribution of atom polarization in ε_∞ [9].

The character of dispersion and absorption dependences of formamide, dymethylformamide, *N*-methylformamide and NN-dymethylacetamide in microwave regions essentially differs from analogous dependences for nitromethane. The ε' and ε'' changes with frequency show that relaxation processes in them can't be described in limits of unique time of dipole relaxation, and also symmetric or asymmetric distribution of relaxation times on example of nitromethane-dioane solutions at temperature 20°C (see fig.1).

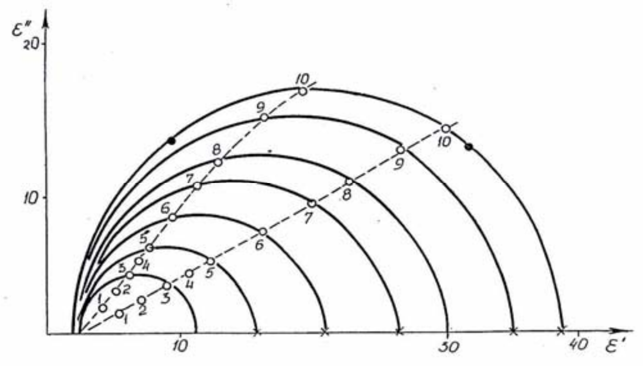

Fig.1. Debye – Kouel diagrams of nitromethane-dioane solutions at temperature 20°C and volume concentrations of nitromethane 10(1); 20(2); 30(3); 40(4); 50(5); 60(6); 70(7); 80(8); 90(9); 100(10) % on data of work [5].

Table 1.

Dielectric constant ε' and dielectric loss ε'' of nitromethane, *N*-methylformamide and *NN*-dymethylacetamide solutions in dioane at temperature 20°C and λ=1,5cm and λ=8,15mm wave lengths. Volume concentrations φ of polar component are in %.

φ % volume	Nitromethane-dioane				*NN*-dymethylacetamide-dioane				*N*-methylformamide-dioane	
	λ=1,5cm		λ=8,15mm		λ=1,5cm		λ=8,15mm		λ=1,5 cm	
	ε'	ε''	ε'	ε''	ε'	ε''	ε'	ε''	ε'	ε''
100	30,2	15,1	19.2	18,1	14,1	14,9	5,8	8,01	29,7	52,9
80	26,9	13,6	16,3	16,1	12,2	11,5	5,21	5,61	16,7	29,5
60	22,7	11,3	12,8	12,8	9,92	8,24	4,53	3,85	10,2	14,0
50	19,8	9,7	11,2	11,2	8,7	6,55	4,24	3,19	8,33	9,86
40	16,3	7,5	9,41	8,59	7,45	5,1	3,92	2,49	6,9	6,84
30	12,5	5,35	7,7	6,27	6,29	3,65	3,54	1,82	5,81	4,63
20	8,92	3,45	6,04	4,25	4,98	2,4	3,2	1,19	4,68	2,37
10	5,5	1,7	4,25	1,92	3,44	1,1	2,8	0,75	3,26	0,87
0	2,28		2,28		2,28		2,28		2,28	

φ%	Formamide-dioane				Dymethylformamide-dioane			
	λ=1,5cm		λ=8,15mm		λ=1,5cm		λ=8,15mm	
	ε'	ε''	ε'	ε''	ε'	ε''	ε'	ε''
0	2,28	-	2,28	-	2,28	-	2,28	-
1	2,42	0,18	2,36	0,10	2,36	0,07	2,33	0,05
2	2,56	0,34	2,41	0,16	2,45	0,17	2,37	0,12
3	2,70	0,50	2,48	0,28	2,55	0,36	2,42	0,17
5	2,98	0,86	2,58	0,40	2,74	0,46	2,52	0,30
8	3,42	1,40	2,74	0,64	3,07	0,78	2,66	0,47
10	3,73	1,80	2,85	0,75	3,30	0,98	2,75	0,60
15	4,50	2,56	3,10	1,08	4,00	1,50	2,95	0,92
20	5,22	3,35	3,37	1,48	4,62	2,00	3,21	1,30
25	5,92	4,05	3,64	1,80	5,15	2,60	3,43	1,66
30	6,60	4,82	3,92	2,20	5,76	3,22	3,70	2,20
40	7,90	6,35	4,53	3,14	6,70	4,20	4,15	3,02
50	9,35	7,68	5,10	3,95	7,65	5,28	4,60	4,00
60	10,8	8,95	5,65	5,05	8,60	6,60	5,10	5,11
80	13,2	11,20	6,20	6,61	10,4	9,75	6,23	7,12
100	15,8	13,20	6,25	8,16	12,2	13,75	8,12	9,73

The analysis of experimental data shows that dielectric properties of formamide, dymethylformamide, N-methylformamide and NN-dymethylacetamide are well described in terms of two independent relaxation processes. In these cases the real frequency dependences ε' and ε'' of substance are expressed by equations of the following form:

$$\left[(\varepsilon' - \varepsilon_\infty)/(\varepsilon_0 - \varepsilon_\infty)\right] = \left[C_1/\left(1\omega\tau_1^2\right) + C/\left(1\omega\tau_2^2\right)\right]$$
$$\left[\varepsilon''/(\varepsilon_0 - \varepsilon_\infty)\right] = \left[\omega\tau_1 C_1/\left(1+\omega\tau_1^2\right) + \omega\tau_2 C/\left(1+\omega\tau_2^2\right)\right] \quad (4)$$

where τ_1, τ_2, C_1 and C_2 are relaxation times and relative depositions of two dispersions correspondingly [4]. In general case the calculation τ_1, τ_2, C_1 and C_2 on equations (4) requires the application of calculation special methods. The parameter calculation results of two dispersion regions with application of calculation technique described in [5].

In accordance with data of low-frequency measurements ε_o one can consider that low-frequency dispersion region of amides is defined by decay processes of hydrogen-connected chains. Moreover, the value which is inverse one to relaxation time of this dispersion characterizes the probability of hydrogen bond breakdown. The relaxation of monomeric molecules on chain ends defines the existence of second high-frequency dispersion region on microwaves.

Table 2.

φ% volume	Nitrometane-dioane		*N*-methylformamide-dioane			*NN*-dymethylacetamide-dioane			
	$\tau \cdot 10^{-12}$	α	τ_1 10^{-12}	C	$\varepsilon_{\infty 2}$	τ_1 10^{-12}	τ_2 10^{-12}	C_1	$\varepsilon_{\infty 2}$
100	4,40	0,01	24,2	0,96	12,3	13,1	9,98	0,86	5,50
80	4,63	0,03	24,2	0,96	7,0	12,2	7,83	0,84	5,06
60	4,80	0,04	23,2	0,94	5,3	11,5	6,26	0,81	4,50
40	4,69	0,03	20,7	0,90	4,3	10,4	5,91	0,74	3,80
20	4,48	0,02	17,9	0,86	3,4	9,80	4,50	0,64	3,10

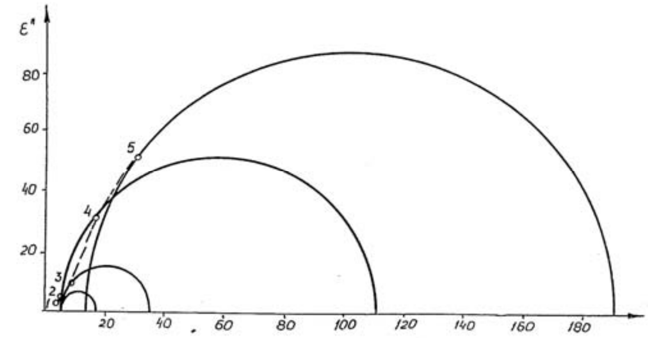

Fig.2. Debye – Kouel diagrams of N-methylformamide-dioane solutions at temperature 20°C and volume concentrations of *N*-methylformamide 20(1); 30(2); 50(3); 80(4); 100(5) % on data of work [5].

The decrease of τ value of main dispersion region of *NN*-dymethylacetamide in the comparison with *N*-methylformamide is defined by locking actions of methyl groups decreasing the possibility of formation of molecular associates formed because of hydrogen bonds. It is character that relaxation times and relative depositions of second dispersions are close between each other in spite of differences in behavior of main dispersion regions of amides.

Dielectric behavior of *N*-methylformamide and *NN*-dymethylacetamide solutions in dioane in studied concentration interval is so close to behavior of pure polar components (fig.2) as in the case of pure polar amides, the obtained results aren't in limits of symmetric or asymmetric distribution of relaxation times. The mechanism of two relaxation processes which probably keeps its significance at amide dilution by nonpolar solvent, gives the best approximation. In N-methylformamide solutions the relaxation time τ_1 defining the low-frequency dispersion region in formamide and its solutions decreases on value with increase of dioane content (table 2).

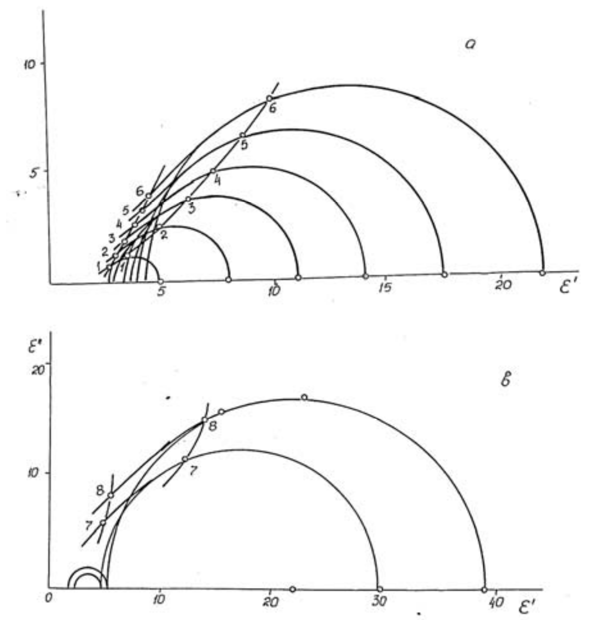

Fig.3. Debye – Kouel diagrams of *N*-dymethylacetamide-dioane solutions at temperature 20°C and volume concentrations of *NN*-dymethylacetamide 20(2); 30(3); 40(4); 50(5); 60(6); 80(7); 100(8) % on data of work [5].

This result shows that the decay of chain complexes of formamide molecules formed with help of hydrogen bonds takes place at *N*-methylformamide dissolution, this leads to decrease of asociate life time and also to life time of average size of such associates of *N*-methylformamide molecules and molecules on chain ends. This is experimentally confirmed by the fact that the relative deposition C_1 of low-frequency region decreases with dilution of *N*-methylacetamide by dioane. The similar result is observed in *NN*-dymethylacetamide-dioane solutions, the decrease of relaxation time value τ_1 of solutions with increase of nonpolar dioane in them is accompanied by increase of part of second dispersion regions; Moreover τ_2 value stays practically independent on dioane concentration (see table 2, fig.3).

Conclusion.

The obtained experimental data ε′ and ε″ solutions of different concentrations are used for finding of resonance concentrations of solution polar components at which it is expected the revealing of predictable effect of non-reflecting absorption of electromagnetic radiation of given wave length and at known sizes of wave-guide directing system by graph-analytic method.

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YÜKSƏKUDUŞLU MAYELƏRİN VƏ ONLARIN MƏHLULLARININ DİELEKTRİK XASSƏLƏRİNİN TƏDQİQİ

Bəzi amidlərin və nitrometanın dioksanda olan məhlullarında ƏYT diapozonunda dielektrik xassələrinin tədqiqatının nəticələri göstərilib və bu polyar mayelərdə və onların məhlullarında iki dispersiyalı Debay tipli relaksasiya sahələri müəyyən olunmuşdur ki, bunlardan da aşağıtezliklisi dipol molekul komplekslərinin molekullarının dağılma prosesi ilə təyin edilmişdir. Bu məhlullarda elektromaqnit şüaların əksolunmadan udulması effekti müşahidə edilmişdir.

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ИССЛЕДОВАНИЕ ДИЭЛЕКТРИЧЕСКИХ СВОЙСТВ СИЛЬНОПОГЛОЩАЮЩИХ ЖИДКОСТЕЙ И ИХ РАСТВОРОВ

В статье приведены исследования диэлектрических свойств растворов некоторых амидов и нитрометана в диоксане в диапазоне СВЧ и установлено существование в этих полярных жидкостях и растворах двух дисперсионных областей релаксации дебаевского типа, из которых низкочастотная определена процессами распада молекулярных комплексов дипольных молекул. В этих растворах наблюдался эффект безотражательного поглощения электромагнитного излучения.

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