DIELECTRIC PROPERTIES AND MOLECULAR STRUCTURE OF SOLUTIONS FORMAMID - DIOXAN AND DIMETHYLFORMAMID - DIOXAN

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Dielectric properties of solutions formamid- dioxan and dimethylformamid-dioxan were investigated in microwave region, and of two dispersion region of Debay's type relaxation were observed. Existence of law frequency region was explained by process of dissociate of molecular complexes, of polar molecule. In these solutions the effect of reflectionless absorption of electromagnetic radiation was observed.

Study of the reflection of microwave radiation in solutions aceton-benzol and water-dioxan show occurrence at the certain thickness and concentration of these solutions of effect of selective reflectionless absorption [1,2]. Existence of similar effect creates prospect of application of dielectric materials as a basis for the thin layer absorbers of a microwave radiation. All this makes expedient researches of the effect of reflectless absorption of microwave radiation in binary mixes and solutions having high dielectric permittivity and small time of dipole relaxsation.

Objects

As objects of study the binary solutions of polar formamid-unpolar dioxan and polar dimethylformamid-unpolar dioxan were chosen. Polar amids, due to presence at them aceton and amin groups, have the large equilibrum permittivity ε_0, reaching, for example, for formamid 110 units, and rather small time of relaxation, laying within $1{,}5\text{-}5\cdot10^{-11}$ s [3]. Increase of concentration unpolar components of these solutions changes geometry of the arc diagrams determining functional connection between dielectric losses ε'' and dielectric permittivity ε' in region of dispercy, and makes possible overlapping in a wide range of frequencies of real and «resonant» dependences ε'' from ε'.

Properties of these solutions are not investigated in a microwave region. Therefore parallel study of dielectric properties and characteristics of reflection of these solutions has the certain theoretical and practical interest.

Methods of the investigation

Study of the dielectric properties and reflection coefficient were carried out at temperature 20°C and waveslengths λ=1,5 cm and λ=8,15 mm by the panoramic reflectometers P2-66, P2-67 and monitor Я2Р-67 and connected with them waveguide cell with short-circueted output. The cell is thermostated and has inlet for operative introduction in it a studied solutions.

As the studied solutions has the rather large absorbtion coefficient in a microwave region, for definition of dielectric coefficients the methods based on measurement of thickness of a substance (and the voltage standing -wave ratio VSWR) at which the reflection of a wave is minimal were used [4,5].

The results of measurement of dielectric permittivity ε' and of dielectric losses $\varepsilon''$of solutions are given in Table 1

Table 1.

Dielectric permittivity ε' and dielectric losses ε'' of solutions of formamid-dioxan and dimethylformamid-dioxan at temperature 20°C and wavelengths λ=1,5 cm и 8.15 mm. Volumetric concentration of φ amids in %.

φ %	Formamid- Dioxan [5]				Dimethylformamid - Dioxan			
	λ=1,5 cm		λ=8,15 mm		λ=1,5 cm		λ=8,15 mm	
	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	11,2	6,20	6,61	10,4	9,75	6,23	7,12
100	15,8	13,2	6,25	8,16	12,2	13,75	8,12	9,73

Discussion of results

For preliminary estimation of a molecular structure of amids and their solutions was estimated the intermolecular forces of pure liquids with use of the parameter of correlation $g = \mu_x^2 / \mu_r^2$, where μ_1 and μ_g - dipole moments of molecules determined in liquid and gas phases, accordingly. As μ_g the dipole moments of the amids, in a gas phase were used [6]. For calculation of μ_1 data of low-frequency measurements of equilibrum dielectric permittivity ε_0 were used. [3]. Calculations of μ_1 was carried out by the equation of Onsager-Kirkwud-Frölich [7]:

$$\mu_1^2 = \frac{(\varepsilon_0 - \varepsilon_\infty)(2\varepsilon_0 + \varepsilon_\infty)}{\varepsilon_0(\varepsilon_\infty + 2)^2} \cdot \frac{9kT}{4\pi N_A}, \quad (1)$$

where T - absolute temperature; N_A - Avogadro's number; k - of Boltzmann constant, ε_∞ - determined from the equation Klausius - Mossoty:

$$\frac{\varepsilon_\infty - 1}{\varepsilon_\infty + 2} = 1,05 \cdot \frac{n^2 - 1}{n^2 + 2} \quad . \quad (2)$$

where n- index of refraction; factor 1,05 takes into account the contribution in ε_∞ nuclear polarization [7].

Calculated ($T = 20°$) g were equal to 2.02 and 1.31 for formamid and dimethylformamid, accordingly and tended to be increased with decreasing of temperature.

The larger than unit g testified about large correlation of molecules of amid, caused by exist hydrogen binding. The existence of hydrogen bonds results to formation of chained associats of dipol molecules with a parallel disposited dipoles. It is obvious, that the degree of association depends on temperature and rise with its falling.

As the association of these molecules are formed by hydrogen binding between atoms of hydrogen and nitrogen of the near by molecules, it is possible to believe, that actions of these hydrogen bonds partially is blocked in dimethylformamid due to presence in aminogroups of two methyl radicals. It can explain decrease of parameter of correlation g of dimethylformamid in comparison with formamid.

The character of dispersion and absorbtion dependences of formamid in the microwave region point out that relaxation processes having a place in formamid, cannot be described within the framework of idea about one time of dipole relaxation, and symmetric or asymmetric distribution of times of relaxations [5].The carried out analysis of experimental data has shown, that dielectric property of formamid are best described in the terms of two independent relaxation processes. The results of calculation of parameters of dispersion regions are shown on Fig.1. There the times of relaxation τ_1, τ_2 of both processes, and also C_1 - the relative contributions of second dispersions are given. According to works [7,8], and in the consent with the data of low-frequency measurements of ε_0, it is possible to consider, that the low-frequency dispersion region of formamid is determined by processes of dissociation of hidrogen-bonded chains. Thus the parameter, inversely depending of relaxation time of this dispersion characterizes probability of break out the hydrogen bonds. Relaxation of monomer molecules on the ends of chains, explain existence on microwaves, second high-frequency dispersion region.

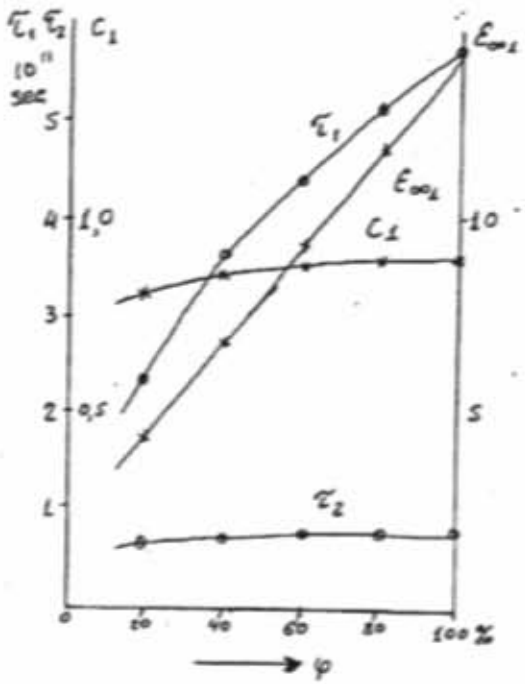

Fig.1 Concentracion dependences of time relaxation τ_1, relative contribution - C_1, high-frequency limit $\varepsilon_{\infty 1}$ of low-frequency dispersion region and time relaxation τ_2 of high-frequency dispersion region of solutions of formamid-dioxan at temperature 20°C.

Two dispersion region were discovered and in dimethylformamid (fig.2,3). The reduction in comparison with formamid of τ of its basic dispersion region it is possible to explainis by blocking actions of methyl groups on formation of hydrogen-bonded molecular associats. It is interesting, that despite of distinctions in behaviour of basic dispersion regions of amids, relaxation times and the relative contributions of their second dispersions are very close among themselves.

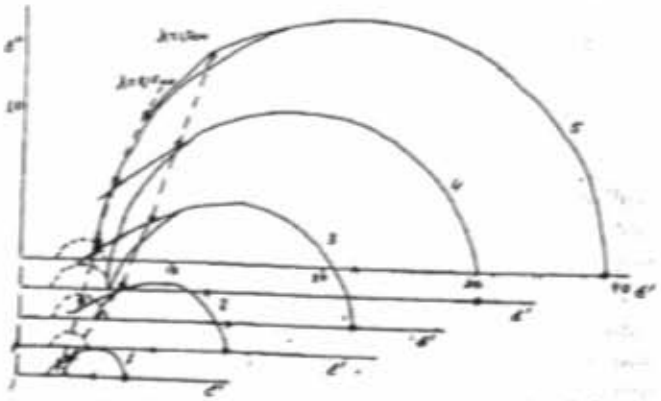

Fig.2 The diagrams of Debay-Coolls of solutions dimethyl formamid - dioxan at temperature 20°C and at volumetric concentration of dimethylformamid 20 (1); 40 (2); 60 (3); 80 (4); 100 (5) %.

The dielectric behaviours of solutions of formamid-dioxan and dimethylformamid-dioxan in the interval of studied concentration is close to behaviours a pure polar components; as well as in case of pure polar amids the obtained results are not settled in idea about existence in solutions symmetric or asymmetric distribution of relaxation's times. The best approach gives the mechanism of two relaxation processes, which keeps the importance and after rising the concentration of the unpolar dioxan.

In solutions of formamid,relaxation's time τ_2,defining low frequency dispersion region, decrease with increasing of the contents of dioxan (fig.1). This result specifies that at dissolution of formamid observed a destruction of hydrogen bonds in complexes of formamid molecules; it results to reduction of lifetime of associats, and to decrease of average sizes of such associats. With growth of dioxan's concentration an increase of a number of the free monomers of formamid molecules and molecules on the ends of chains in a solution take place. Experimentally it proves to be true by the fact that dilution of formamid by dioxan the relative contribution C_2 of high-frequency dispersion region is increased. C_2 in pure formamid is wholly connected with the relaxation of these types of kinetic units. At the average concentration of dioxan observed some stabilization of parameters of second high-frequency dispersion region τ_2 and C_2. The similar result is marked and in solutions of dimethylformamid-dioxan: the reduction of time of relaxation τ_2 with increase of concentracion of dioxan is accompanied by increase of a share of second dispersion regions; thus the τ_2 is kept practically independent from concentration of dioxan (Fig.3).

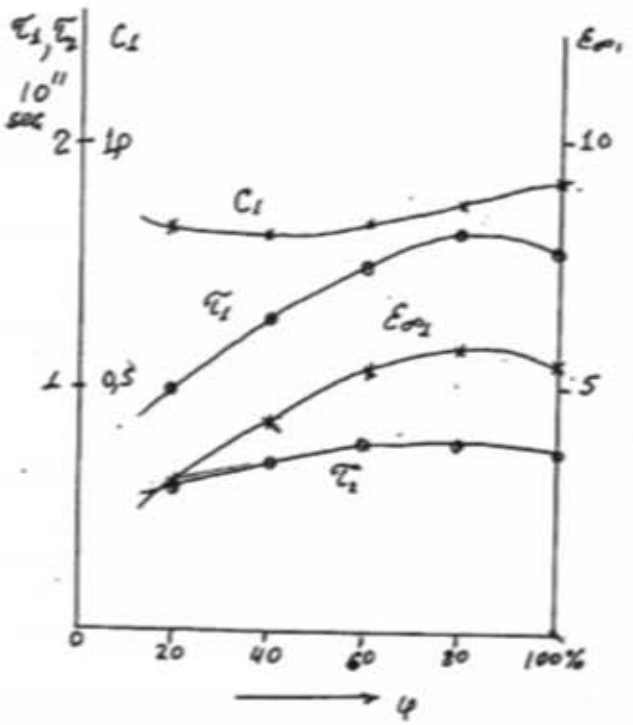

Fig.3 Concentration dependences of time of relaxation τ_1, relative contribution C_1, high-frequency limit $\varepsilon_{\infty 1}$ low-frequency dispersion region and time of relaxation τ_2 high-frequency dispersion region of solutiondimethyl formamid- dioxan at temperature 20°C.

The obtained experimental ε^I and ε^{II} for solutions of various concentration were used for prediction concentrations of solutions, at which should be observed effect of reflectionless absorption of microwave radiation. The experiments for determination of such concentration were carried out. For this purpose the concentration dependences of reflection coefficient ρ consistently for each next number N of a minimum of function ρ (l) were plotted. The results of these experiments are represented on Fig.4. The *resonant* concentrations of solutions, obtained from this dependences, were close to their calculated meanings and are given in Table 2. It additionally confirm assumption [1] of general character of the effect of the reflectionless absorption: this effect can be observed practically in any polar solutions at any temperature T and wavelength λ but under condition of existence dispersion of waves in studied solution.

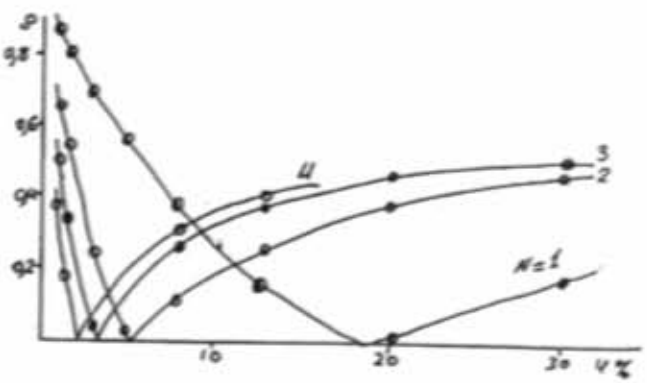

Fig.4. Experimental dependences of the module of reflection coefficient ρ from volumetric concentration φ of polar component of solution dimethylformamid-dioxan at wavelength 1,5 cm and temperature 20°C.

Table 2.

Experimental *resonant* meanings of volumetric concentrations φ of the polar components of solutions Formamid-Dioxan (1) and Dimethyl -Dioxan (2) at temperature 20°C.

Wavelength λ, cm	Critical wavelength wave in waveguide, cm.	Number of Zero Minimum ρ	1 φ, %	2 φ, %
1,5	2,3	1	9,6	19,2
		2	3,2	5,7
		3	1,9	3,4
		4	1,3	2,5
		5	1,0	1,9
0,815	1,44	1	28,4	26,8
		2	7,6	6,3
		3	1,5	3,0
		4	0,8	1,8

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DİOKSAN MƏHLULUNDA FORMAMİD VƏ DİMETİLFORMAMİDİN DİELEKTRİK XASSƏLƏRİ VƏ MOLEKULYAR STRUKTURU

İnfra yüksək tezliklər diapozonunda formamid və dimetilformamid dioksan və dioksazan məhlulunda SVÇ dispersiya spektri tədqiq olunmuş və bu polyar maye məhlullarda Debay tipli relaksasiyanın iki dispersiya oblastının olması müşahidə edilmişdir, onlardan ancaq tezliklisi hidrogen əlaqəsinin tə'siri ilə əmələ gələn polyar molekulların parçalanmasının prosesləri ilə tə'yin olunur. Bu məhlullarda elektromaqnit dalğalarının əksetdirilmədən udulmaq şərtləri tapılmışdır.

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ДИЭЛЕКТРИЧЕСКИЕ СВОЙСТВА И МОЛЕКУЛЯРНАЯ СТРУКТУРА РАСТВОРОВ ФОРМАМИДА И ДИМЕТИЛФОРМАМИДА В ДИОКСАНЕ

Исследованы диэлектрические свойства растворов формамида и диметилформамида 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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