THE DIELECTRIC PERMEABILITY OF TWO-LIQUID SYSTEMS CONSISTING OF POLAR COMPONENTS

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The applicability of measurements of dielectric permeability of liquid systems for determining interactions between components has been established by a number of studies [1-7]. The majority of the studies were devoted to an examination of benzene solutions of these systems. The use of physical chemical methods of studying liquid systems in solution, along with some positive advantages, does have some substantial disadvantages [8]. Because of this, a study of the polar properties of liquid systems must be carried out both in solution and without solvents. This makes it possible to show a number of new regularities and to investigate the behavior of systems consisting of components with very similar or strongly differing dipole moments.

We have studied the dielectric permeability of a number of two-liquid systems. In the case of some systems the dielectric permeability was measured at various temperatures.

The dielectric permeability was determined by the pulse method which we described previously [9]. The components of the systems studied were subjected to careful purification by the usual methods. The purified substances and the solvents were kept in sealed ampoules. Concentration is always expressed in molar portions. During the measurements every precaution was taken against the penetration of moisture.

All the systems studied by us may be divided into three groups. In the first group are systems whose components have dipole moments that are closely similar (Table 1) and whose isotherms of dielectric permeability are linear. In the second group are systems formed from components whose dipole moments differ from one another (Table 2). For these systems the deviations of the experimental values of dielectric permeability from additivity have a negative sign. In the third group are systems with positive deviations of dielectric permeability from the additive value (Table 3). In the latter case the equality and difference of the values of the dipole moments do not, apparently, play a significant role. The results of studies of the dielectric permeability of systems belonging to the first group are shown in Figs. 1-5.

As can be seen from the data presented, the isotherms of dielectric permeability for all eight systems are straight lines throughout the entire concentration interval.

A change in the temperature does not interfere with the linear character of the isotherms of dielectric permeability, and the maximum deviation of the latter from additivity (Table 1) does not exceed 0.9% at any temperature.

The isotherms of two-liquid systems whose components are normal non-dipole liquids are linear throughout the concentration interval. Similar systems behave normally [10, 11]. On comparing the isotherms of dielectric permeability of the systems we studied with the permeability isotherms of systems formed from normal non-dipole components (Table 1) one may conclude that systems composed of polar components that do not react chemically and which have closely similar dipole moments, should be close to normal in their behavior. This is confirmed by the results of studies of other physical chemical properties of analogous systems [12-14].

The behavior of these systems may apparently be explained in the following way. If the first approach toward association is viewed as an orientation of the molecules of the polar liquid in the internal field, the relation between the number of disoriented (dissociated) molecules and the total number of molecules may be expressed by the following equation [15]:

$$N = N\left[1 - L^2\left(\frac{\mu E}{kT}\right)\right], \qquad (1)$$

TABLE 1. Systems of the First Group

System	Dipole moment of 1st component (in D)	Dipole moment of 2nd component (in D)	Maximum deviation from additivity (in %)
Acetone – methylethylketone	2.76	2.79	0.5
n-Propyl alcohol – n-butyl alcohol	1.66	1.66	0.4
Dimethylaniline – diethylaniline	1.59	1.65	0.4
Isoamyl acetate – methyl ester of caproic acid	1.82	1.76*	0.2
Methylethylketone – benzaldehyde	2.79	2.75	0.1
Diethylaniline – methyl ester of caproic acid	1.65	1.76*	0.3
Pyridine – quinoline	2.25	2.18	0.9
Dimethylaniline – chlorobenzene	1.59	1.55	0.5

* The dipole moment of the methyl ester of caproic acid was determined by us in benzene at 25°.

TABLE 2. Systems of the Second Group

System	Dipole moment of 1st component (in D)	Dipole moment of 2nd component (in D)	Maximum deviation from additivity (in %)
Isobutyl alcohol – nitrobenzene	1.79	3.96	–13.2
Isobutyl alcohol – acetone	1.79	2.76	–15.9
Isobutyl alcohol – cyclohexanone	1.79	3.01	–24.3
Isobutyl alcohol – aniline	1.79	1.48	–23.0
n-Propyl alcohol – diethyl ether	1.66	1.10	–30.0
Methyl acetate – piperidine	1.75	1.17	– 3.3

TABLE 3. Systems of the Third Group

System	Dipole moment of 1st component (in D)	Dipole moment of 2nd component (in D)	Maximum deviation from additivity (in %)
Quinoline – chloroform	2.18	1.10	+23.6
Quinoline – aniline	2.18	1.48	+13.6
Pyridine – aniline	2.25	1.48	+10.6
Chloroform – diethyl ether	1.10	1.22	+33.2
Chloroform – methyl acetate	1.10	1.75	+18.8
Chloroform – dibutyl ether	1.10	1.18	+17.0
Aniline – diethyl ether	1.48	1.22	+14.4
Chloroform – benzyl acetate	1.10	1.80	+11.3
Titanium tetrachloride – ethyl ester of trichloroacetic acid	0	2.55	+36.3

where N' is the number of disoriented molecules, $L^2\left(\frac{\mu E}{kT}\right)$ is the Langevin function, μ is the dipole moment, E is the internal field, k is the Boltzmann constant, T is the absolute temperature.

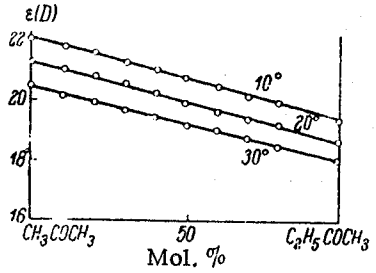

Fig. 1. Dielectric permeability of mixtures: $CH_3COCH_3 - C_2H_5COCH_3$.

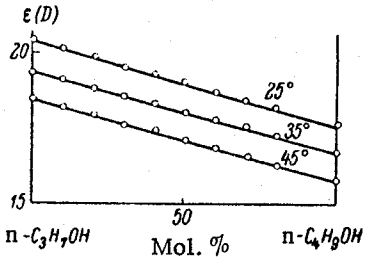

Fig. 2. Dielectric permeability of mixtures: $n\text{-}C_3H_7OH - n\text{-}C_4H_9OH$.

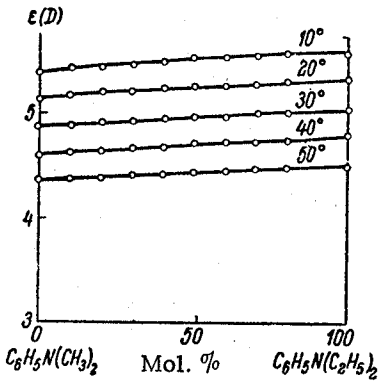

Fig. 3. Dielectric permeability of mixtures: $C_6H_5N(CH_3)_2 - C_6H_5N(C_2H_5)_2$.

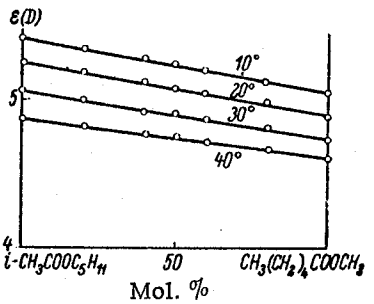

Fig. 4. Dielectric permeability of mixtures: $iso\text{-}CH_3COOC_5H_{11} - CH_3(CH_2)_4COOCH_3$.

From equation (1) it is evident that the degree of disorientation of the molecules of a polar liquid in the internal field is dependent on the magnitude of the dipole. On mixing two polar liquids with closely similar values of the internal fields and dipole moments, the degree of disorientation of the molecules of each of the components remains, within a first approximation, the same as that of the pure liquid. Of course this only occurs when the components do not react chemically with one another. As a matter of fact, in the case of the reaction of two similar polar molecules with a dipole moment μ, the potential energy of orientation will be equal to [16]

$$U_0 = -\frac{2}{3} \cdot \frac{\mu^4}{kTr^6}, \qquad (2)$$

where r is the distance between interacting dipoles.

If, however, two unlike molecules with dipole moments μ_1 and μ_2 interact with each other, the potential energy of orientation U'_0 in this case will be equal to

$$U'_0 = -\frac{2}{3} \cdot \frac{\mu_1^2 \cdot \mu_2^2}{kTr^6}. \qquad (3)$$

From the latter equation it is apparent that when the dipole moments are equal ($\mu_1 = \mu_2$), the potential energies of orientation of similar and unlike molecules become identical; consequently the molecular state of the components should not change on mixing. It is true that in equations (2) and (3) the induction effect was not taken into consideration; however taking it into consideration does not result in any substantial changes since the interacting molecules have identical dipole moments.

The results of studies of the dielectric permeability of systems belonging to the second group are shown in Figs. 6-8. In the last column of Table 2 are shown the relative deviations of the experimental values of the dielectric

permeability from additivity. From the data given it is clearly evident that the isotherms of dielectric permeability of all the systems studied, with the exception of the system methyl acetate-piperidine, have significant negative deviations from the additive value. This fact may be explained by the elimination of the chain association of the alcohol molecules at the expense of the hydrogen bond.

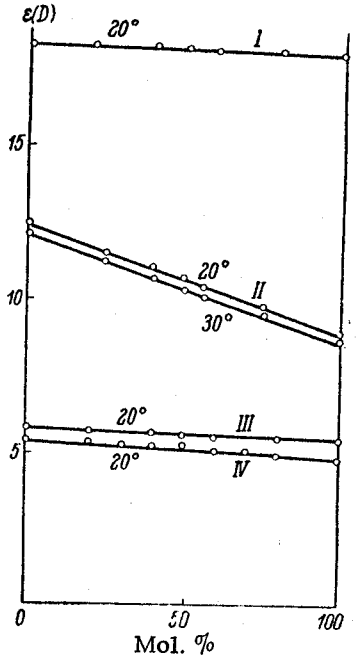

Fig. 5. Dielectric permeability of mixtures: I) $C_2H_5COCH_3 - C_6H_5CHO$; II) $C_5H_5N - C_9H_7N$; III) $C_6H_5Cl - C_6H_5N(CH_3)_2$; IV) $C_6H_5N(C_2H_5)_2 - CH_3(CH_2)_4 \cdot COOCH_3$.

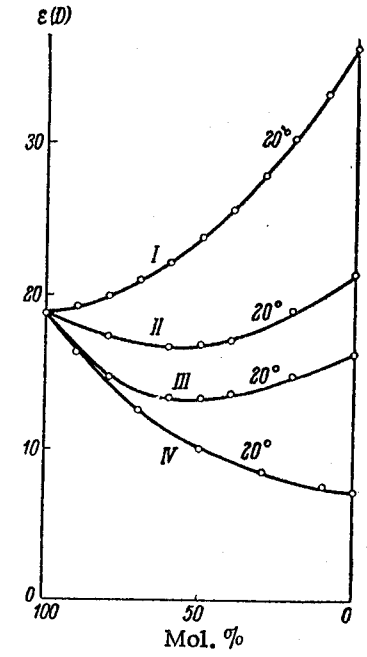

Fig. 6. Dielectric permeability of mixtures: I) iso-$C_4H_9OH - C_6H_5NO_2$; II) iso-$C_4H_9OH - CH_3COCH_3$; III) iso-$C_4H_9OH - C_6H_{10}O$; IV) iso-C_4H_9OH – $- C_6H_5NH_2$.

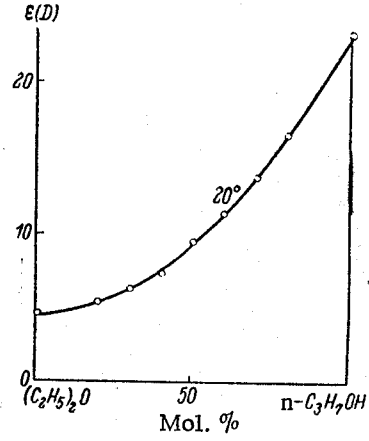

Fig. 7. Dielectric permeability of mixtures: $(C_2H_5)_2O - n\text{-}C_3H_7OH$.

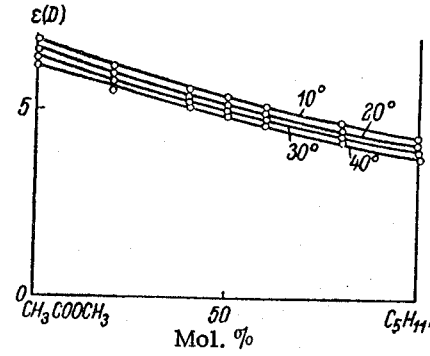

Fig. 8. Dielectric permeability of mixtures: $CH_3COOCH_3 - C_5H_{11}N$.

In analyzing the experimental data of Table 2, attention should be drawn to the following interesting fact. There is no definite connection between the relative deviations of the dielectric permeability of systems from additivity and the difference between the dipole moments. This phenomenon may apparently be explained as follows. In the first place, the ability of a given molecule dipole to interact with dipoles of adjacent molecules depends to a considerable degree on the location of the given dipole [17]. The data of Table 2 show that the difference between

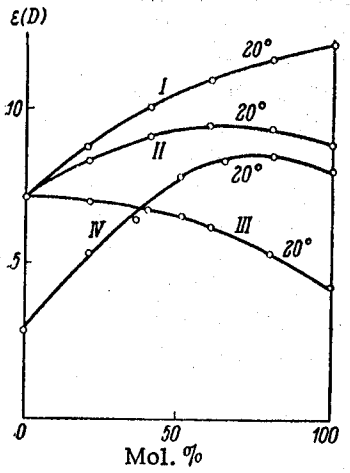

Fig. 9. Dielectric permeability of mixtures: I) $C_6H_5NH_2 - C_5H_5N$; II) $C_6H_5NH_2 - C_9H_7N$; III) $C_6H_5NH_2 - (C_2H_5)_2O$; IV) $TiCl_4 - CCl_3COOC_2H_5$.

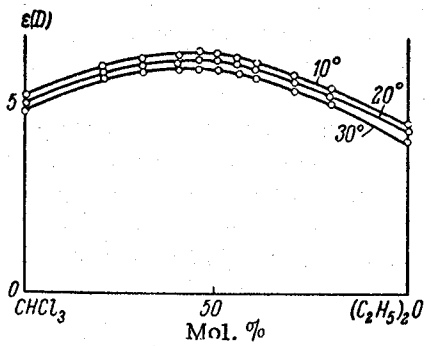

Fig. 10. Dielectric permeability of mixtures: $CHCl_3 - (C_2H_5)_2O$.

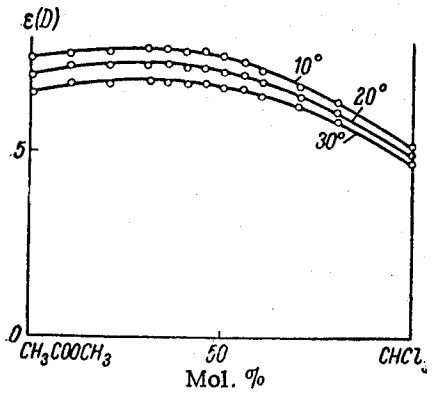

Fig. 11. Dielectric permeability of mixtures: $CH_3COOCH_3 - CHCl_3$.

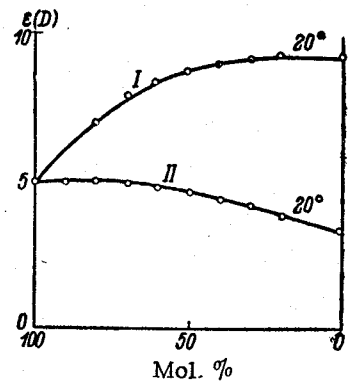

Fig. 12. Dielectric permeability of mixtures: I) $CHCl_3 - C_9H_7N$; II) $CHCl_3 - (C_4H_9)_2O$.

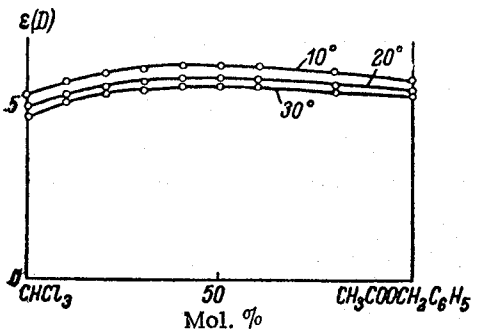

Fig. 13. Dielectric permeability of mixtures: $CH_3COOCH_2C_6H_5 - CHCl_3$.

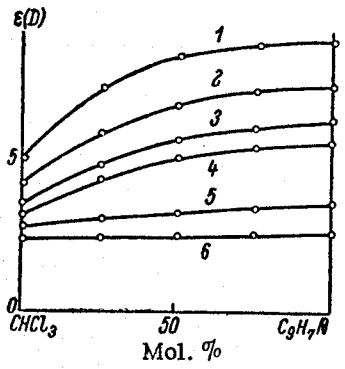

Fig. 14. Dielectric permeability of mixtures in benzene: content of benzene in mol. %: 1) 0.0; 2) 20.0; 3) 40.0; 4) 50.0; 5) 60.0; 6) 80.0.

the dipole moments of nitrobenzene and isobutyl alcohol is considerably greater than the difference between the moments of the same alcohol and acetone, aniline and cyclohexanone. However the relative deviation of the dielectric permeability from additivity in the isobutyl alcohol – nitrobenzene system is considerably less than in the other systems. The fact is that the dipole of nitrobenzene is located far from the surface of the molecule, and since the strength of the field created by this dipole decreases proportionally to distance by the third power, the influence of the nitrobenzene dipole on the association of alcohol is of course considerably weakened. In the second place, the degree of interaction of the components with each other may be dissimilar. In other words, the negative deviations of the isotherms ε does not mean that only a breaking up of the associated molecules of the components occurs in the system, and not an interaction between the latter. In this case the negative deviations of the dielectric permeability from additivity give evidence of the fact that the polarity, in the case of chain association of the components, is considerably higher than the polarity in the case of complex formation. This is confirmed by studies of the electrical and optical properties of solutions of alcohols and phenols in such oxygen-containing solvents as nitrobenzene, ethers and others [18, 19]. Spectrographic studies also show that the nitro group is a weaker acceptor than the oxygen of ether and carbonyl.

In the methyl acetate -piperidine system whose dielectric permeability we studied at 10, 20, 30 and 40°, the negative deviations from additivity at all temperatures did not exceed 3%, which, apparently, is due to the considerable interaction between the carbonyl oxygen of the ester and the mobile hydrogen at the nitrogen of the piperidine.

The results of measurements of the dielectric permeability of the third group of systems are shown in Figs. 9-13 and in Table 3.

The data presented show that in all systems the isotherms of dielectric permeability have a positive deviation from the additive values, and in the following systems – chloroform-diethyl ether, quinoline-aniline, chloroform-methyl acetate, chloroform-benzyl acetate and chloroform-dibutyl ether, they pass through a maximum. The greatest deviations occur at concentrations corresponding to an equimolecular ratio of components. This becomes understandable if we take into consideration the fact that the reason for the increase in dielectric permeability is the chemical reaction between components with the formation of molecular aggregates and, consequently, the magnitude of the deviation must be proportional to the concentration of the aggregate formed. In a number of physical chemical studies it was shown that in some of the above-mentioned systems the components interact with one another with the formation of equimolecular aggregates [20, 21].

All this indicates that the classification of the isotherms of two-liquid systems and their interpretation from the point of view of the presence or absence of interaction between the components cannot be rational without calculating the properties of the micro particles of the components, in particular the polarity and character of their changes.

In conclusion we present the results of measurements of the dielectric permeability of the quinoline-chloroform system in benzene solution.

As can be seen from Fig. 14, as dilution with benzene increases, the magnitude of the deviation of the experimental isotherms of dielectric permeability from the additive values, and consequently, the degree of interaction between quinoline and chloroform decrease, and by the time 80 mol. % of benzene is reached, the isotherm becomes practically a straight line. We have presented this example in order to show that even at not very great dilutions, in the presence of a third component, it is sometimes impossible to detect interaction between the components of a binary system by the usual calculation of deviation from additivity.

SUMMARY

1. By means of measurements of the dielectric permeability of 23 two-liquid systems consisting of polar components it was shown that they may be divided into three groups on the basis of the shape of the isotherms.

2. Systems formed from components that do not react chemically and which have closely similar dipole moments have linear isotherms of dielectric permeability and this linearity is hardly affected by temperature changes.

3. Influence on the shape of the isotherms of dielectric permeability of two-liquid systems must result not only from reaction between components and dissociation of their molecules, but also from changes in polarity which may either increase or decrease during these processes. Therefore the sign of the deviation of the isotherms of dielectric permeability from additivity for systems consisting of polar components cannot serve as the sole criterion of the relation of the components to each other.

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