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AN ION-DIPOLE MODEL OF CHARGE CLUSTERS IN LOW-CONDUCTIVITY LIQUIDS

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An ion-dipole model of charge-cluster formation in low-conductivity liquids is suggested and the numbers of molecules in its dense and loose parts are estimated.

Experimental studies of the synergestic features of low-conductivity liquids in an electric field [1, 2] have revealed the presence of molecular-ordered microregions in these media, which consist of hydrogen-bonded charged associates (charge clusters) of impurity molecules. Taking into consideration the ionic character of the conductivity of insulating liquids, the formation of such clusters can be explained by interaction between the ions and the deformed outer shells of valence electrons of polar and polarized liquid molecules. The latter usually comes down to different models of multipole-multipole interaction [3] and to allowance for the degree of its attenuation with increasing distance between multipoles [4].

Qualitative consideration of the process leads to the notion of charged clusters formed by ions of electrolytic impurities and multilayer shells consisting of polar and polarized liquid molecules. The first shell is formed owing to the more pronounced monopole-dipole interaction, while the next shells are due to both monopole-dipole interaction and multipole interactions. As a result, structures with a close-packed core and a more loose peripheral part are formed. Since the interaction between an element of the molecular structure and the nearest environment is uncompensated, the centripetal forces and the forces imparting a spherical form to it emerge on the cluster periphery. On modeling such a structure and estimating the number of molecules entering a charge cluster, we can restrict ourselves to consideration, in a first approximation, of only ion-dipole interaction, whose energy is determined as

$$U_{\mathrm{de}} = \frac{q}{4\pi\varepsilon\varepsilon_0}\frac{\mathbf{r}\cdot\mathbf{p}}{r^3}, \tag{1}$$

where r is a radius vector, which begins in the cluster center and ends in the molecule centre. Dipoles and multipoles constituting a cluster also contribute to this energy but the energy of multipole interactions in it is considerably lower than that of ion-dipole interaction. The energy U_{de} depends on dipole orientation, which can be prescribed by the angle θ formed by r and p:

$$U_{\mathrm{de}} = qp/(4\pi\varepsilon\varepsilon_0 r^2)\cos\theta\,. \tag{2}$$

In the equilibrium state, the function of dipole distribution in the vicinity of a cluster is determined by the Boltzmann factor

$$W(r,\theta) = c\exp\left(-\frac{U_{\mathrm{de}}}{kT}\right). \tag{3}$$

The meaning of $W(r, \theta)$ is as follows: if dV is a volume element fixed by radius vector r, then WdV is the probability of finding a dipole with the prescribed orientation (angle θ) in this volume. In a spherical coordinate system we have

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$$dV = r^2 dr d\Omega \,, \tag{4}$$

where $d\Omega$ is an element of the space angle at which the volume dV is seen from the cluster center. Integration over all angles $d\Omega$ and averaging over all dipole orientations determine the probability of finding a dipole of an arbitrary orientation in a spherical frustrum $(r, r + dr)$:

$$dp = c \langle W \rangle r^2 dr \equiv f(r)\, dr \,, \tag{5}$$

$$\langle W \rangle = \frac{1}{4\pi} \int_0^{2\pi} d\varphi \int_0^{\pi} \sin\theta \, d\theta \exp\left(- \frac{qp}{4\pi\varepsilon\varepsilon_0 r_0^2} \cos\theta \right) , \tag{6}$$

where φ, θ are the angles of dipole orientation in a spherical coordinate system with the origin at the dipole center.

Calculations show that

$$\langle W \rangle = \xi^2 rh \xi^{-2} \,, \tag{7}$$

where $\xi = r/r_*$; $r_* = \sqrt{|q| p/\varepsilon\varepsilon_0 kT}$.

The radial function $f(r)$ of dipole distribution in the electric field of the cluster has a minimum at

$$r = r_*^{\text{cr}} = \xi_*^{\text{cr}} r_* \,, \tag{8}$$

where ξ_*^{cr} is a root of the equation

$$2\xi^2 = \text{cth}\, \xi^{-2} \,. \tag{9}$$

With accuracy to 1% the quantity

$$r_*^{\text{cr}} = 0.707 \sqrt{\left(\frac{|q| p}{\varepsilon\varepsilon_0 kT} \right)} \tag{10}$$

should be considered the critical size of the cluster (its dense part), i.e., at $r < r_*^{\text{cr}}$ dipoles are retained by electric charges of the cluster and at $r > r_*^{\text{cr}}$ dipoles are loose, i.e., the energy of their thermal motion exceeds that of interaction with the cluster. For instance, for solutions of butyl elcohol in transformer oil this gives

$$r_*^{\text{cr}} \simeq 7\sqrt{Z} \; [\text{Å}] \,. \tag{11}$$

Assuming, according to the data of x-ray analysis [2] that

$$r_*^{\text{cr}} \sim 50 \div 100 \; \text{Å} \,, \tag{12}$$

we obtain

$$Z \simeq 100 \,, \tag{13}$$

i.e., in its dense part the cluster contains more than 100 ions and $10^3 - 10^4$ neutral polar molecules of liquid (the size of one such molecule is ~ 6 Å). The stability of such a charged associate is sustained owing to the fact that the energy of Coulomb repulsion of ions surrounded by dipole shells of polar molecules (on the average, 10 molecules per ion):

$$\overline{U_{\text{ee}}} \sim \frac{1}{4\pi\varepsilon\varepsilon_0} \frac{e^2}{(5 \div 10)\, l} \sim (12 \div 15) \; \frac{\text{kJ}}{\text{mole}} \,, \tag{14}$$

is less than the energy of hydrogen bonds retaining polar molecules in the associated state

$$\overline{U_{\text{dd}}} \sim \frac{1}{4\pi\varepsilon\varepsilon_0}\frac{1}{2}\frac{e^2}{l} \sim (20 \div 30)\ \frac{\text{kJ}}{\text{mole}}, \tag{15}$$

since

$$\frac{U_{\text{dd}}}{U_{\text{ee}}} < \frac{2}{5}. \tag{16}$$

Here l is the dipole length, which coincides with the molecule size in order of magnitude; e is the electron charge.

Besides the dense central part, the cluster also contains a loose periphery, inside which the energy of interaction of a dipole with the central charge of the cluster is already less than the energy of its thermal motion but it is still insufficient to retain dipole orientation along mainly the radial direction starting from the cluster center. The minimum number of molecules contained in the loose part of a cluster is evaluated proceeding from the facts that:

1) in virtue of the spherical form of a cluster the interaction of dipole molecules of a liquid around a central charge can be described by spherical symmetry;

2) due to random thermal motion of molecules in a cluster the angle between the radial direction emanating from the cluster center and the dipole moment of molecules can be considered a random variable α obeying a normal law of distribution $P(\alpha)$ with variance σ.

We now find distribution of the angles between the dipoles of the n-th layer and the radial direction.

Let $\alpha_{n,k}$ be the angle between dipoles of the n-th and k-th layers. For the former layer, the distribution has the form

$$P(\alpha_1) = \frac{1}{(2\pi)^{1/2}\sigma_1}\exp\left(-\frac{\alpha_1^2}{2\sigma_1^2}\right). \tag{17}$$

For the latter layer it is

$$P(\alpha_2) = \int_{-\pi/2}^{\pi/2} P(\alpha_1)\,P(\alpha_{2,1})\,d\alpha_1\,. \tag{18}$$

Since $\alpha_{2,1} = \alpha_2 - \alpha_1$, $\sigma_2 \le \pi/2$, $P(\alpha)\,|_{|\alpha| > \pi/2} = 0$, expression (18) has the form

$$\begin{aligned}
P(\alpha_2) &= \int_{-\infty}^{\infty}\left(\frac{1}{(2\pi)^{1/2}\sigma_1}\right)^2 \exp\left(-\frac{\alpha_1^2}{2\sigma_1^2}\right)\exp\left(\frac{(\alpha_2-\alpha_1)^2}{2\sigma_1^2}\right)d\alpha_1 = \\
&= \int_{-\infty}^{\infty}\frac{1}{2\pi\sigma_1^2}\exp\left\{-\frac{1}{2\sigma_1^2}\left((\sqrt{2}\,\alpha_1 - \alpha_2/\sqrt{2}\,)^2 + \alpha_2^2/2\right)\right\}d\alpha_1 = \\
&= \frac{1}{2\pi\sigma_1^2}\exp\left(-\frac{\alpha_2^2}{4\sigma_1^2}\right)\int_{-\infty}^{\infty}\exp\left(-\frac{1}{2\sigma_1^2}(\sqrt{2}\,\alpha_1 - \alpha_2/\sqrt{2}\,)^2\right)d\alpha_1 = \\
&= -\frac{1}{2\pi\sigma_1^2}\exp\left(-\frac{\alpha_2^2}{2(\sqrt{2}\,\sigma_1)^2}\right)\sigma_1\pi^{1/2} = \frac{1}{(2\pi)^{1/2}(\sqrt{2}\,\sigma_1)}\exp\left(-\frac{\alpha_2^2}{2(\sqrt{2}\,\sigma_1)^2}\right).
\end{aligned} \tag{19}$$

Consequently, the distribution of the angles of dipoles of the latter layer relative to the radial distribution is determined by the expression

$$P(\alpha_2) = \frac{1}{(2\pi)^{1/2}\sigma_2} \exp\left(-\frac{\alpha_2^2}{2\sigma_2^2}\right), \tag{20}$$

where $\sigma_2 = \sqrt{2}\sigma_1$.

By mathematical induction it is easy to show that for the n-th layer the following expression is also valid

$$P(\alpha_n) = \frac{1}{2\pi^{1/2}\sigma_n} \exp\left(-\frac{\alpha_n^2}{2\sigma_n^2}\right), \tag{21}$$

where $\sigma_n = n^{1/2}\sigma_1$.

Indeed, taking into consideration that

$$\alpha_{n,n-1} = \alpha_n - \alpha_{n-1}, \tag{22}$$

$$P(\alpha_n) = \int_{-\infty}^{\infty} P(\alpha_n) P(\alpha_{n,n-1})\, d\alpha_{n-1},$$

we obtain

$$P(\alpha_n) = \frac{1}{2\pi\sigma_1^2 (n-1)^{1/2}} \int_{-\infty}^{\infty} \exp\left(-\frac{\alpha_{n-1}^2}{2\sigma_1^2 (n-1)}\right) \exp\left(-\frac{(\alpha_n - \alpha_{n-1})^2}{2\sigma_1^2}\right) d\alpha_{n-1} =$$

$$= \frac{1}{2\pi\sigma_1^2 (n-1)^{1/2}} \exp\left(-\frac{\alpha_n}{2\sigma_1^2 n}\right) \int_{-\infty}^{\infty} \exp\left\{-\frac{\left(\left(\frac{n-1}{n}\right)^{1/2} \alpha_n - \left(\frac{n}{n-1}\right)^{1/2} \alpha_{n-1}\right)^2}{2\sigma_1^2}\right\} d\alpha_{n-1}. \tag{23}$$

The integral is

$$\int_{-\infty}^{\infty} \exp\left\{-\frac{\left(\left(\frac{n-1}{n}\right)^{1/2} \alpha_n - \left(\frac{n}{n-1}\right)^{1/2} \alpha_{n-1}\right)^2}{2\sigma_1^2}\right\} d\alpha_{n-1} =$$

$$= \frac{\sqrt{2}\,\sigma_1 (n-1)^{1/2} \pi^{1/2}}{n^{1/2}}.$$

Therefore

$$P(\alpha_n) = \frac{1}{(2\pi)^{1/2}\sigma_n} \exp\left(-\frac{\alpha_n^2}{2\sigma_n^2}\right), \tag{24}$$

where $\sigma_n = n^{1/2}\sigma_1$.

If we assume that the last layer of the cluster is characterized by variance

$$\sigma_n = \frac{\pi}{2}, \tag{25}$$

the number of molecular layers in the cluster is

$$n = \left(\frac{\pi}{2\sigma_1}\right)^2. \tag{26}$$

Variance σ_1 is determined by counteracting ordering and disordering factors, namely, the binding energy (U) of a dipole molecule with the central charge and the energy of thermal motion of a molecule ($kT/2$), respectively. The standard deviation of the angle α_1 from zero (σ_1) is found by means of

$$\sigma_1 \approx \frac{kT}{2U}. \tag{27}$$

The binding energy of a dipole molecule with the central charge (q) is determined as

$$U = \frac{q\mu}{8\pi\varepsilon\varepsilon_0 r^2}. \tag{28}$$

From (26)–(28) we obtain the following expression for the number of layers in the cluster (n):

$$n = \left(\frac{q\mu}{8kT\varepsilon\varepsilon_0 r^2}\right)^2. \tag{29}$$

For the solutions of butyl alcohol in transformer oil the constants entering expression (29) are equal to:

$$q = 1.6\cdot 10^{-19}\ \text{(C)},\ \mu = 5.2\cdot 10^{-30}\ \text{(C}\cdot\text{m)},\ T = 300\ \text{(K)},\ \varepsilon = 2.2 \div 2.8,$$

$$r = 3\cdot 10^{-10}\ \text{(m)}. \tag{30}$$

Hence, for n we have

$$n \approx \left(\frac{1.6\cdot 10^{-19}\cdot 5.2\cdot 10^{-30}}{8\cdot 1.38\cdot 10^{-23}\cdot 300\cdot 2.5\cdot 8.85\cdot 10^{-12}\cdot 9\cdot 10^{-20}}\right)^2 \approx 160. \tag{31}$$

The number of molecules constituting a cluster is evaluated as

$$N \approx 4/3\cdot\pi\cdot n^3 \approx 2\cdot 10^7. \tag{32}$$

In the case of a "pure" nonpolar liquid, the numbers of layers and molecules in the cluster will naturally be smaller. Here, interaction of the central charge with polarized molecules of a nonpolar liquid is observed, the induced dipole moment of which is

$$|\mathrm{p}(r)| = \frac{3(\varepsilon - 1)\varepsilon_0 E(r)}{(\varepsilon + 2) n_0} = \frac{3(\varepsilon - 1) q}{4\pi\varepsilon(\varepsilon_0 + 2) n_0 r^2}, \tag{33}$$

In the case of pure transformer oil: $\varepsilon = 2.2$, $n_0 = 6\cdot 10^{27}$, $r \approx 5\cdot 10^{-10}$ (m).

For $\mathrm{p}(r)$ we have

$$|\mathrm{p}(r)| = \frac{3\cdot 1{,}2\cdot 1{,}6\cdot 10^{-19}}{4\cdot 3{,}14\cdot 2{,}2\cdot 4{,}2\cdot 6\cdot 10^{27}\cdot 2{,}5\cdot 10^{-19}}\ \mathrm{d}\ 3{,}3\cdot 10^{-30}\ (\mathrm{C}\cdot\text{м})$$

or according to formula (29):

$$n \approx \left(\frac{1.6 \cdot 10^{-19} \cdot 3.3 \cdot 10^{-30}}{8 \cdot 1.38 \cdot 10^{-23} \cdot 300 \cdot 2.2 \cdot 8.85 \cdot 10^{-12} \cdot 2.5 \cdot 10^{-19}} \right) \approx 11 , \tag{34}$$

which in terms of (32) yields

$$N \sim \frac{4 \cdot 3.14 \cdot (11)^3}{3} \sim 6 \cdot 10^3 , \tag{35}$$

i.e., the number of molecules in a cluster decreases by 3-4 orders of magnitude. Thus, despite its relative simplicity, the suggested model explains two basic properties of electric convection of low-conductivity liquids:

1) the possibility of transport of a large amount of neutral molecules of a liquid by a small amount of ions;
2) an extreme dependence of convection on impurity concentration [4].

NOTATION

q, cluster charge; p, induced dipole moment of polarized molecule; $\varepsilon\varepsilon_0$, dielectric permittivity of liquid; Z, charge number of cluster; U_{dd} and U_{de}, energies of dipole-dipole and dipole-ion interactions; r, cluster size; $d\Omega$, element of space angle; WdV, probability of finding a dipole with a prescribed orientation; φ, θ, angles of dipole orientation; σ, variance; μ, dipole moment of polar molecule; n_0, number of liquid molecules per unit volume; k, Boltzmann constant; T, absolute temperature; n, number of molecular layers; N, number of molecules in cluster; c, constant.

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