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Ionic conductivity and complexation in liquid dielectrics

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Abstract. **Electronic and ionic conductivity in nonpolar liquids is reviewed. Theoretical results on ionic complexation (formation of ion pairs and triplets, dipole – dipole chains, ion – dipole clusters) in liquid dielectrics in an intense external electric field are considered, and the relation between the complexation process and ionic conductivity is discussed. Experimental results supporting the possibility of complexation are presented and compared with theoretical calculations. Onsager's theory about the effect of an intense external electric field on ion-pair dissociation is corrected for the finite size of ions.**

1. Introduction

Liquid dielectrics (LD) represent a broad class of fluids whose physicochemical properties are so diverse that it is virtually impossible to given them a more or less comprehensive general definition. Here, we will deal with the class of nonpolar and weakly polar liquids, which exhibit high chemical stability and high breakdown voltage, and are physically close to simple liquids.

Traditionally, liquids have been studied by both chemical and physical methods, and this has resulted in certain inconsistencies in approaches and terminology. In the chemical literature, dielectric liquids are referred to as weak electrolytes, and the processes of recombination and dissociation are viewed as chemical reactions. Physical studies are mainly concerned with the threshold of electrical breakdown of high-resistivity liquids, that is, with the prebreakdown and breakdown phenomena. The purpose of both approaches, however, is to describe the behavior of the electrical conductivity and other properties of liquid dielectrics in a broad range of electric-field strengths.

In the physical literature, the field strengths are usually classified as low (under 1 kV cm^{-1}), medium (1 to 40 kV cm^{-1}), and high (> 40 kV cm^{-1}) [1 – 3]. In the low-field region, the current – voltage characteristic (CVC) is always linear, which is attributed to the incomplete dissociation of the dissolved salts (the so-called ion pairs A^+B^-) and to the equilibrium nature of the reversible dissociation – recombination reaction. This situation is entirely similar to the low-voltage conductivity in weakly ionized gases [4]. At this point, however, the analogy ends. The CVC in gases in medium fields exhibits a plateau, while in LD the linear segment is followed by a quadratic, which becomes exponential in strong fields [2, 3]. Such behavior is not universal, but the linear part of the CVC in liquid dielectrics is always followed by a nonlinear part, and there is no current saturation. We ought to recall an amusing historical incident, when Nikuradze [5] carelessly predicted the existence of a plateau in liquid dielectrics, and many years later Felici [6] branded Nikuradze's physics as 'imaginable' because of this. When the CVC becomes nonlinear, intensive flows begin to develop in liquid dielectrics. The study of these flows developed into a new physical discipline called electrohydrodynamics (EHD), pioneered in Russia by G A Ostroumov [7]. The importance of EHD for the intensification of heat exchange processes stimulated a considerable number of practical engineering studies [8]; however, even now the theories of EHD flows and nonlinear conductivity of liquid dielectrics are open to question. This is because the generation of charge carriers in medium and strong fields occurs through numerous concurrent mechanisms: dissociation of ion pairs and ion complexes; a contact generation at the liquid – electrode interface, which involves cold emission; electrochemical redox reactions; etc.

In this paper, we focus our attention on the dissociation – recombination processes in the bulk. As a matter of fact, with a view of intensifying the EHD flows, various ionizing agents

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having electron acceptor or donor properties, e.g., iodine, butyl alcohol, etc, are added to the liquid. Such solutions represent ion – dipole mixtures in a nonpolar medium. Therefore, it is important not only to know the structure of charge carriers (single ions, ion triplets, etc.), but also to give criteria for the transition from ion to cluster conductivity.

We believe that this problem has been underestimated or even totally ignored. For example, many calculations only consider the model of single ions [3, 7, 8]. At the other extreme, the decisive role is ascribed to the cluster ions. It is important therefore to gain theoretical understanding of formation of ion complexes and to validate theoretical findings with the experiment. Note that the nature of these processes depends considerably on the strength of an applied external field. In this paper, we analyze such processes in ion – dipole solutions in the low-voltage region, disregarding the electrode processes.

2. Liquid dielectrics: general description

The distinction between the two classes of liquid dielectrics (polar and nonpolar) is rather vague, and the current view is that the criterion of polarizability can be definitive only within a certain class of liquids, for example, for alcohols or halogenated aromatic hydrocarbons (bromobenzene, chlorobenzene, iodobenzene) [9]. Typical in this respect is dioxane $C_4H_8O_2$. On the one hand, it has all the properties of a nonpolar dielectric (electron polarizability and high electric resistivity); on the other hand, like most polar liquids, it is a good neutral solvent owing to the specific chemical activity of its molecule, which contains two active symmetrically arranged oxygen atoms.

Today, electron processes (mobility, electron capture, photoionization, etc.) in amorphous systems, from simple liquids and inert gases to amorphous glasses are well studied [10]. Here we are concerned with the processes of ion conductivity, so we first briefly touch upon the electron processes. These results will allow us to formulate the criteria for distinguishing between the electronic and ionic conductivity.

2.1 Mobility of electrons in disordered condensed media

It is usually assumed that the electrons in amorphous media may occur in three states: (1) quasi-free, or delocalized; (2) weakly bound, or continually bound; and (3) in the form of bubbles.

The electrons in a quasi-free or delocalized state display the highest mobility, which is only restricted by the process of scattering by the atoms of the inhomogeneous system. Such mobility is observed in liquid helium ^{4}He at low pressures (Fig. 1). The theoretical mobility of delocalized electrons versus the temperature of liquid T, the density of particles of liquid n, and the cross section of electron scattering by helium ions σ was expressed by Levine and Sanders [11, 12]:

$$\mu = \frac{2}{3}\left(\frac{2}{\pi m_e k_B T}\right)^{1/2} \frac{e}{n\sigma}\,, \tag{1}$$

where m_e and e are the mass and the charge of the electron, respectively; and k_B is the Boltzmann constant.

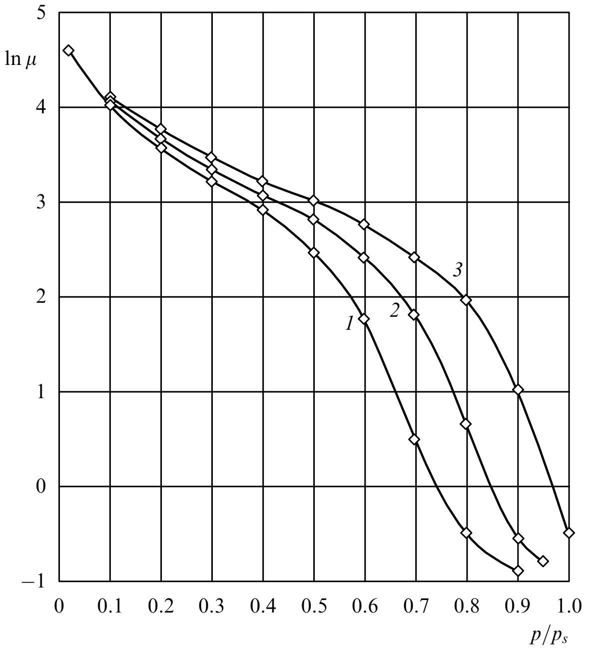

Figure 1. Mobility of electrons in ^{4}He at various temperatures and various pressures and [p_s is the saturation pressure, μ is measured in cm^2 (V s)$^{-1}$] [11]: *1*, $T = 4.10$ K; *2*, $T = 3.9$ K; and *3*, $T = 3.65$ K.

As the pressure increases, the mobility of electrons drops dramatically (by 4 or 5 orders of magnitude), which is explained by the transition of electrons first into the continually bound state, known as the Anderson localization, and then into the form of bubbles, i.e., cavities filled with electrons, whose typical radius R is about 12 Å [13, 14]. In the semihydrodynamic approximation, the mobility of bubbles is defined as [15]

$$\mu = \frac{e}{6\pi\eta R}\left[1 + \frac{9\pi\eta}{4nR(2\pi m_a k_B T)^{1/2}}\right], \tag{2}$$

where m_a is the mass of a helium atom, and η is the dynamic viscosity of the liquid.

Note that expressions (1), (2) are based on the simplest models. There are more accurate methods based on the quantum mechanical calculations of the energy states of quasi-free electrons and the kinetic Boltzmann equation (see Refs [16, 17] and review [10]). These calculations lead to results of the same type as (1) and (2), but take better account of the properties of the liquid via the model potentials of pair interaction and the two-particle correlation function. Nevertheless, the values calculated by formulas (1) and (2) are close enough to those measured experimentally (at least for ^{4}He; see Fig. 1), and can therefore be used for estimates.

A similar drop in electron mobility was also observed in gases: in hydrogen at 30 to 31.7 K [18] and in helium ^{4}He [19]; this drop, however, was later shown to be due to the capture of electrons by molecular oxygen with subsequent formation of negative ions O_2^- (see Ref. [10], p. 338).

As regards the state of quasi-free electrons in other liquefied inert gases (argon, krypton, and xenon), the quasi-free states have been proved theoretically [20] and experimentally [21] to be energetically more advantageous than the bubble states. This result applies also to nonpolar liquids, in particular for hydrocarbons, for which the electron work function is negative.

The mobility of electrons in nonpolar hydrocarbons is characterized by the following features [10] (Table 1).

(i) The mobility of electrons is highly sensitive to the structure of the hydrocarbon molecule. For example, in

Table 1. Mobility μ, activation energy E_A, threshold field strength E_* of the nonlinear dependence of the mobility on the field strength, and the work function for nonpolar hydrocarbons at different temperatures.

Liquid	μ_0, cm^2 (V s)$^{-1}$	E_A, kcal mol^{-1}	T, K	μ, cm^2 (V s)$^{-1}$	E_*, kV cm^{-1}	Work function, eV
Methane	—	~ 0	111	400	1.5	0
Ethane	170	2.1	200	0.8	80	—
Propane	210	2.6	208	0.4	—	—
Butane	—	—	296	0.4	50	—
n-Pentane	—	—	300	0.075	—	—
n-Hexane	67	4.06	296	0.09	80	0
Neopentane	—	—	296	67	5	−0.43
Cyclopentane	—	3.5	296	1.1	62	0.17
Cyclohexane	288.10	3.979	306	0.45	—	—
Toluene	10.17	2.95	304	0.54	3	−0.22
Benzene	10.17	2.95	300	0.6	3	−0.14
^{3}He	—	—	2.25	0.0406	—	0.9
^{4}He	—	—	4.2	0.0216	—	1.05
Ne	—	—	22	0.0016	—	0.5
Ar	—	—	82	475	—	−0.33
Kr	—	—	117	1800	—	−0.78
Xe	—	—	163	2200	—	−0.63
H_2, D_2	—	—	21	0.02, 0.01	—	−1.0

n-pentane $\mu = 0.07$ cm^2 (V s)$^{-1}$, whereas the mobility in neopentane is greater by three orders of magnitude: $\mu = 70$ cm^2 (V s)$^{-1}$. The rule of thumb is that the more compact and symmetrical the molecule, the higher the electron mobility.

(ii) In most hydrocarbons studied, the electron mobility obeys the Arrhenius law

$$\mu = \mu_0 \exp\left(-\frac{E_A}{k_B T}\right), \qquad (3)$$

where the activation energy E_A is determined by the collective dispersion interaction of the electron with the surrounding molecules and varies from $E_A = 0$ (for example, in methane [22] and neopentane [23, 24]) to $E_A = 0.2$ eV. The value of μ_0 is on the order of 100 cm^2 (V s)$^{-1}$.

(iii) The field strength E_* at which the mobility of electrons starts to show dependence on the field is extremely high, e.g., 80 kV cm^{-1} in ethane and 140 kV cm^{-1} in neopentane [25]. In the case of $E_A = 0$, the dependence of mobility on the field strength is the same as in the inert gases [22, 23].

(iv) In binary mixtures of hydrocarbons, the mobility obeys the Arrhenius law (3), in which the energy of activation is given by the relation characteristic of ideal solutions

$$E_A = x_1 E_{A_1} + x_2 E_{A_2} ,$$

where x_i is the molar part of the *i*th component, and E_{A_i} is the activation energy of an electron in pure *i*th liquid. This result indicates that the activation energy of an electron is determined by the collective interaction of the electron with the surrounding molecules.

(v) The small dipole moment of the molecules of the liquid ($\leqslant 0.3D$) has little effect on the mobility of electrons [23].

(vi) There is a correlation between the mobility and the work function of the electron: the mobility increases with decreasing work function [26–28].

(vii) The capture of electrons by impurity electronegative molecules, such as CCl_4 [29–31, 32], CH_3I, O_2 and C_2H_5Br [32], follows the scheme

$$X + e^- \xrightarrow{r} X^- ,$$

where X is the electron acceptor; e^- is the electron and r is the rate of pair recombination, which is limited by the process of approach of the electron and the molecule X and is described by the Langevin formula

$$r = \frac{e\mu_e}{\varepsilon} .$$

The results of measurements of the mobility of electrons and the rate of recombination for different electron acceptors and solvents according to Refs [29–32] are presented in Table 2. We see that with the concentrations of impurity molecules $n_0 \sim 10^{-7}$ mol typical of technical liquids, the characteristic recombination time is $\tau_e \simeq (rn_0)^{-1} \simeq 10^{-4}$ s. Because of this, in the absence of an external supply of electrons, they quickly recombine with the impurity electronegative molecules, and the charges in technical liquids only exist in the form of ions. The criterion of transition from electronic to ionic conductivity can be

Table 2. Recombination rates of electron–molecule reactions at $T = 23 \pm 1$ °C.

Reactant	Solvent	μ, cm^2 (V s)$^{-1}$	r, mol^{-1} s^{-1}
Oxygen	*n*-Hexane	0.078	0.11
	Cyclohexane	0.24–0.33	0.11
	Methyl cyclohexane	0.068	0.17
	Neopentane	70	1.2
Biphenyl	Ethanol	10^{-4}–10^{-3}	0.0043
	n-Hexane	0.078	0.77 ± 0.1
	Cyclohexane	0.24–0.33	2.6 ± 0.4
	Benzene	0.6–0.68	0.8
	Cyclopentane	1.1	3.5 ± 0.5
	2, 2, 4-Trimethyl pentane	7	11 ± 5
	2, 2-Dimethyl pentane	10.9	13 ± 4
CCl_4	*n*-Hexane	0.078	0.85
	n-Pentane	0.14	1.8
	Cyclohexane	0.24	1.8
	Cyclopentane	1.1	3 ± 1
	Neopentane	70	28.6
CH_3I	Cyclohexane	0.24–0.33	2.0
C_2H_5Br	*n*-Hexane	0.078	1.47
	n-Pentane	0.14	1.6
	2, 2, 4-Trimethyl pentane	7	6.3
	Neopentane	70	0.32

expressed as

$$\tau_e \simeq (rn_0)^{-1} \ll t_0 \,,$$

where t_0 is the characteristic time scale of the problem (electron's free path time, charge relaxation time, etc.).

2.2 Theoretical foundations of ionic conductivity in liquid dielectrics

Although each liquid is essentially a special object of study, it is possible to identify certain general features of ionic conductivity of liquid dielectrics. The electrical conductivity of 'technical' liquid dielectrics and their solutions depends on their ion components, which are formed in the liquid in redox reactions of the type

$$\mathrm{M} + \mathrm{X} \rightleftarrows \mathrm{M}\cdot\mathrm{X} \rightleftarrows \mathrm{M}^{+z}\mathrm{X}^{-z} \underset{\alpha_{11}}{\overset{k_2}{\rightleftarrows}} \mathrm{M}^{+z} + \mathrm{X}^{-z} \,. \qquad (4)$$

Here X is the electron acceptor molecule; M is the molecule of carrier liquid; $\mathrm{M}\cdot\mathrm{X}$ is the molecular complex [9]; $\mathrm{M}^{+z}\mathrm{X}^{-z}$ is the ion pair [33, 34]; M^{+z} and X^{-z} are the free ions; and z is the charge number of ions, which is linked with the ion charge e_i by the relation $e_i = ez$, where e is the charge of a proton.

Note that the ion 'doublets' ($\mathrm{M}^{+z}\mathrm{X}^{-z}$) are sometimes referred to as the molecular complex [35], although it is more commonly known as the ion pair [36]. According to Ref. [33], a molecular complex is defined as an intermediate state between the ion pair and free molecules that are bound in a molecular complex by weak dispersion forces.

The electrical conductivity of liquid dielectrics is described by the theory of weak electrolytes, whose experimental and theoretical foundations were laid in the first half of the last century [33–46] (for more details see Refs [33, 34]). Before proceeding to the main assumptions, it will be worthwhile to make some remarks concerning the notation. In the physical literature, the specific conductance is usually denoted by σ [1–8, 47, 51] or λ [36]; in the chemical literature, more commonly used is the concert of equivalent conductance defined as the ratio σ/c_0, where c_0 is the concentration of the dissolved salt. The equivalent conductance is denoted by λ [33] or Λ [36]. In the case of complete dissociation of the electrolyte, the equivalent conductance is proportional to the mean mobility of the positive and negative ions. According to the calculations of Blumentrits [38] and Falkenhagen [39] revised by Onsager and Fuoss [42] and by Debye [44], the mobility of ion μ depends on the ion concentration n as [33]

$$\mu_i = \mu_{0i} - \beta_i\sqrt{n} \,, \qquad (5)$$

$$\beta_i = \left(\frac{z_i e}{6\pi\eta} + \frac{z_1 z_2 e^2}{12\pi\varepsilon k_B T \rho_i}\,\frac{e z_i q}{1+\sqrt{q}}\right)\sqrt{\frac{2e^2}{\varepsilon k_B T}} \,, \qquad (6)$$

$$q = \frac{z_1 z_2}{z_1 + z_2}\,\frac{\mu_{01} + \mu_{02}}{\mu_{01} z_2 + \mu_{02} z_1} \,, \qquad \rho_i = 6\pi R_i \eta \,,$$

where z_i are the charge numbers of ions ($i = 1, 2$), η is the dynamic viscosity of the solvent, μ_{0i} is the mobility of the ith single ion in pure liquid, defined by the Arrhenius formula (3) via the activation energy, R_i is the effective radius of the ion of ith type. This relation shows that the ion atmosphere reduces the velocity of ion's motion in an external electric field owing to the so-called cataphoretic and relaxation effects [33, 48].

The mobility of a single ion of sort i is described well enough using the model of the ion as a sphere of radius R_i moving in a viscous continuum medium. In this case, the mobility in the Stokes approximation is given by the expression

$$\mu_{0i} = \frac{z_i e}{6\pi R_i \eta} \,. \qquad (7)$$

Formula (5) allows us to define a weak electrolyte as a poorly conductive liquid, in which the ion atmosphere has no effect on the motion of the ion:

$$\frac{\beta_i\sqrt{n}}{\mu_{0i}} \ll 1 \,. \qquad (8)$$

For example, for the transformer oil with $R_i \sim 3$ Å, $\eta = 0.2$ P, $\varepsilon = 2.2\varepsilon_0$, $T = 300$ K, conductivity $\sigma \leqslant 10^{-10}\ \Omega^{-1}\ \mathrm{m}^{-1}$, and singly charged ions of equal mobility, using the relation $\sigma = 2e\mu_{0i} n$, we obtain $\mu_{0i} \sim 1.4\times10^{-5}\ \mathrm{cm}^2\ (\mathrm{V\ s})^{-1}$, $\beta_i\sqrt{n}/\mu_{0i} \leqslant 10^{-3} \ll 1$. In other words, criterion (8) is satisfied in the range of typical conductivities of liquid dielectrics.

Thus, in liquid dielectrics the decisive role is played by paired interactions leading to the formation of ion pairs and complex ions [33, 43].

The theory of pair interactions in liquids was developed by Smoluchowski [37] under the assumption that the rates of the dissociation – recombination processes of the ions are limited by diffusion and migration of ions in the electric field. He also calculated the rate of recombination α_0 of neutral components [34, 37]:

$$\alpha_0 = 4\pi(D_1 + D_2)R_{12} \,, \qquad (9)$$

where D_1, D_2 are the coefficients of diffusion and R_{12} is the sum of the mean radii of the reactant molecules.

For charged reactants, Debye found that [44]

$$\alpha_{11} = \frac{4\pi(D_1 + D_2)\ell_B}{1 - \exp(-\ell_B/R_{12})} \,. \qquad (10)$$

Here, $\ell_B = 2r_B$, where r_B is the radius of the ion pair, defined in accordance with the Semenchenko – Bjerrum concept [33, 41] as

$$r_B = \frac{e_1 e_2}{8\pi\varepsilon k_B T} \,. \qquad (11)$$

Here, e_1, e_2 are the charges of the ions, ε is the permittivity of the medium, k_B is the Boltzmann constant, and T is the absolute temperature. Obviously, expression (10) reduces to (9) at $r_B \to 0$.

The expression for the dissociation rate constant k_{20} of ion pairs with a neglect of the effect of an external electric field is [49, 50]

$$k_{20} = (D_1 + D_2)\ell_B\left[\int_{R_{12}}^{r_B} \exp\left(\frac{\ell_B}{r}\right) r^2\,dr - \frac{1}{3}\left(r_B^3 - R_{12}^3\right)\right]^{-1} . \qquad (12)$$

For small ion radii ($R_{12} \ll r_B$), using the asymptotic representation

$$\int_\delta^{1/2} \exp\left(\frac{1}{s}\right) s^2\,ds = \delta^4 \exp\left(\frac{1}{\delta}\right)\left[1 + O(\delta^2)\right] , \qquad \delta \ll 1 \,, \qquad (13)$$

we obtain

$$k_{20} = 4(D_1 + D_2)\,\frac{r_{\mathrm{B}}^2}{R_{12}^4}\exp\left(-\frac{2}{\delta}\right), \qquad \delta = \frac{R_{12}}{r_{\mathrm{B}}}\,. \tag{14}$$

The ratio α_{11}/k_{20} is called the association constant and is denoted by $K_2 = K_{\mathrm{ass}}$ [34, 35]. Using (10) and (14), for the case of small ions ($\delta = R_{12}/r_{\mathrm{B}} \ll 1$), we can write

$$K_{20} = \frac{\alpha_{11}}{k_{20}} = 2\pi r_{\mathrm{B}}^3\delta^4\exp\frac{2}{\delta}\,, \qquad \delta = \frac{R_{12}}{r_{\mathrm{B}}}\,. \tag{15}$$

This expression differs from the known Fuoss formula [46] by the coefficient $3R_{12}/\ell_{\mathrm{B}}$ and coincides in the asymptotic limit (13) with the Bjerrum formula [33]. Such a situation is typical in physical chemistry, and is associated with different approximations. For example, if we rely on the concept of contacting ion pairs, we can use the method of partition functions to obtain the expression for K_{ass} that essentially coincides with Saha's formula (see, for example, Eqns (18.10) and (18.15) in Ref. [50]). Recall that Eqns (10) and (12) here are obtained by the kinetic method developed by Smoluchowski, and the size of the ion pair is estimated from the Semenchenko – Bjerrum concept.

The effects of an external electric field on the processes of recombination of ions and dissociation of ion pairs were first considered by Onsager [36]. Using the Smoluchowski method in conjunction with the Semenchenko – Bjerrum concept of ion pairs and assuming that the size of ions is small, he demonstrated that the rate of recombination does not depend on the external field strength E and is defined as

$$\alpha_{11} = 4\pi(D_1 + D_2)\ell_{\mathrm{B}} = \frac{e_1\mu_1 + e_2\mu_2}{\varepsilon}\,, \tag{16}$$

where μ_i are the coefficients of mobility of ions, which are linked with the diffusion coefficients by the Einstein relation $k_{\mathrm{B}}T/e_i = D_i/\mu_i$. Formula (16) follows from (10) at $r_{\mathrm{B}}/R_{12} \gg 1$ and was first expressed by Langevin in his studies of electrical conductivity in dense gases [52, 53].

According to Onsager, the dissociation rate is

$$k_2 = k_{20}F(p)\,, \tag{17}$$

where

$$F(p) = \frac{I_1(4p)}{2p}\,, \qquad p = \frac{e_1e_2}{2k_{\mathrm{B}}T}\left[\frac{(\mu_1+\mu_2)E}{4\pi\varepsilon(\mu_1e_2+\mu_2e_1)}\right]^{1/2}.$$

Function $F(p)$ is called the Onsager factor, and $I_1(s)$, $s = 4p$ is the modified Bessel function of the first order, which is defined by the series

$$I_1(s) = \sum_{n=0}^{\infty}\frac{(s/2)^{1+2n}}{n!(n+1)!}\,.$$

Function $F(p)$ at zero is equal to unity and grows monotonically with increasing argument, which indicates that the rate of dissociation of ion pairs in the electric field increases. For example, in nonpolar liquids ($\varepsilon \simeq 2\varepsilon_0$) for single-charged ions at room temperature ($T = 300$ K) in relatively weak fields ($E = 10$ kV cm^{-1}), we have $4p = 2$, and in strong fields ($E = 1$ MV cm^{-1}), $4p = 20$. In the latter case, we may set

$$F(p) = (32\pi p^3)^{-1/2}\exp 4p\,.$$

Hence, we see that in strong fields the dissociation rate has a tendency to grow exponentially.

As the concentration of ion pairs increases (to 10^{-5} mol l^{-1} and above [45]), ion triplets may form according to the reactions

$$\mathrm{A^+B^-} + \mathrm{A^+} \underset{k_3^+}{\overset{\alpha_{12}^+}{\longleftrightarrow}} \mathrm{A^+B^-A^+}\,, \qquad \mathrm{A^+B^-} + \mathrm{B^-} \underset{k_3^-}{\overset{\alpha_{12}^-}{\longleftrightarrow}} \mathrm{B^-A^+B^-}\,. \tag{18}$$

Conductivity that is accompanied by the formation of ion triplets $\mathrm{A^+B^-A^+}$ and $\mathrm{B^-A^+B^-}$ is called anomalous [33].

The elementary theory of calculation of the equilibrium constant K_{30} of reactions (18), developed by Fuoss and Krauss [43], is based on the following assumptions. It is assumed that the ion $\mathrm{B^-}$ can freely migrate near the 'rigid' ion pair $\mathrm{A^+B^-}$ with an effective size a (it could also be the $\mathrm{A^+}$ ion, but for definiteness we assume that it is the negative ion $\mathrm{B^-}$ that is free). In the state of equilibrium, the distribution of free ions in the neighborhood of the ion pair per unit volume is determined by the Boltzmann factor

$$n_{\mathrm{i}} = \bar{n}\exp\left(-\frac{U}{k_{\mathrm{B}}T}\right),$$

where $\bar{n}$ is the average equilibrium density of ions $\mathrm{B^-}$; U is the potential energy of interaction between the ion pair and a free ion (determined by only electrostatic interaction)

$$U = \frac{e^2}{4\pi\varepsilon}\left(\frac{1}{r} - \frac{1}{r_2}\right), \qquad r_2 = (a^2 + r^2 + 2ar\cos\psi)^{1/2}\,,$$

where r (r_2) is the distance between the bound ion $\mathrm{A^+}$ (bound ion $\mathrm{B^-}$) and the free ion $\mathrm{B^-}$, and ψ is the angle between the direction of the dipole in the ion pair and the vector that connects the bound and the free negative ions $\mathrm{B^-}$. At $\psi = 0$, the ions line up in the order $\mathrm{B^-A^+B^-}$.

Fuoss and Krauss [33, 43, 46] give the following expression for the association constant of ion triplets:

$$K_{30} = \frac{\alpha_{12}^+}{k_3^+} = \frac{\alpha_{12}^-}{k_3^-} = 4\pi\int_a^{r_{\mathrm{d}}}\exp\left(-\frac{U}{k_{\mathrm{B}}T}\right)r^2\,\mathrm{d}r\,, \tag{19}$$

where r_{d} is the size of a linear ion triplet defined as the extreme point of the radial distribution function at $\psi = 0$:

$$\frac{\mathrm{d}}{\mathrm{d}r}\left[r^2\exp\left(-\frac{U}{k_{\mathrm{B}}T}\right)\right] = 0\,. \tag{20}$$

Formula (19) assumes that the triplet is linear ($\psi = 0$); i.e., when a negative ion $\mathrm{B^-}$ approaches the ion pair $\mathrm{A^+B^-}$, all three ions line up in a row. Below, we will use the kinetic approach to demonstrate that taking into account the fluctuations of orientation of the ion pair in the limit $a \ll r_{\mathrm{d}}$ also leads to the asymptotic expression for K_{30}, which follows from (19). Moreover, formula (19) is derived in the approximation of a 'rigid' ion pair. If we assume, however, that the ions in the pair and the free ion only interact through electrostatic forces, then this approach is generally not consistent, since the ion pair cannot be considered as rigidly bound. Evidently, this approach only works for the case of a nonpolar solvent, when $R_{12} \ll r_{\mathrm{B}}$. Indeed, the radial distribution function of ions in the ion pair is proportional to $\exp(2r_{\mathrm{B}}/r)$, whence it follows that it is the contact arrangement of ions that is most likely to appear, so that $r \approx R_{12}$. In this case, the integral in (19) can be calculated approximately as

$$K_{30} = 2.6\pi r_{\rm B}^3 \delta^4 \exp\left(\frac{1}{\delta}\right), \qquad \delta \equiv \frac{R_{12}}{r_{\rm B}} . \tag{21}$$

From (15) and (21) it follows that

$$\frac{K_{30}}{K_{20}} = 1.3 \exp\left(-\frac{1}{\delta}\right) \ll 1 .$$

According to this relation, given that the ion size is $R_{12} \ll r_{\rm B}$, the constant of association of ion pairs is much greater than the constant of association of ion triplets. In other words, the probability of dissociation of ion triplets is much higher than the probability of dissociation of ion pairs, which is the consequence of a weakness of the ion – dipole interaction as compared with the ion – ion interaction. In view of this circumstance, we need to take into account the recombination reactions due to the strong ion – ion interaction [49, 53]:

$$\begin{aligned} &{\rm A^+B^-A^+ + B^-} \xrightarrow{\alpha_{13}^-} {\rm 2A^+B^-} , \\ &{\rm B^-A^+B^- + A^+} \xrightarrow{\alpha_{13}^+} {\rm 2A^+B^-} , \\ &{\rm A^+B^-A^+ + B^-A^+B^-} \xrightarrow{\alpha_{33}} {\rm 3A^+B^-} . \end{aligned} \tag{22}$$

The inclusion of these reactions leads to conclusions that differ somewhat from the Fuoss – Krauss theory.

Let us consider this in greater detail, paying attention first of all to the effects of processes (18) and (22) on the ionic conductivity in liquid dielectrics. As is known, the coefficient of electrical conductivity is written as

$$\sigma = e \sum_i z_i \mu_i n_i , \tag{23}$$

where the sum is taken over all types of ions; n_i is the bulk concentration of ions; and the subscripts $i = 1$ to 4 correspond, respectively, to the ions $\rm A^+$, $\rm B^-$, $\rm A^+B^-A^+$, and $\rm B^-A^+B^-$. In the equilibrium state, the concentrations are determined by the balance between the production and annihilation of ions in reactions (8), (18), and (22):

$$k_2 N - \alpha_{11} n_1 n_2 + k_3^+ n_3 - \alpha_{12}^+ n_1 N - \alpha_{13}^+ n_1 n_4 = 0 , \tag{24}$$

$$k_2 N - \alpha_{11} n_1 n_3 + k_3^- n_4 - \alpha_{12}^- n_2 N - \alpha_{13}^- n_2 n_3 = 0 , \tag{25}$$

$$\alpha_{12}^+ n_1 N - k_3^+ n_3 - \alpha_{13}^- n_2 n_3 - \alpha_{33} n_3 n_4 = 0 , \tag{26}$$

$$\alpha_{12}^- n_2 N - k_3^- n_4 - \alpha_{13}^- n_1 n_4 - \alpha_{33} n_3 n_4 = 0 , \tag{27}$$

where N is the concentration of ion pairs $\rm A^+B^-$.

The following relations result from these equations:

$$K_3 = \frac{\alpha_{12}^+}{k_3^+} = \frac{\alpha_{12}^-}{k_3^-} , \qquad n_1 = n_2 , \qquad n_3 = n_4 . \tag{28}$$

Here K_3 is the constant of association of reactions (18).

The balance of mass of ion components together with these last relations gives us the closing equation

$$N = N_0 - n_1 - 3n_3 , \tag{29}$$

where N_0 is the initial concentration of ion pairs $\rm A^+B^-$, when there are no single ions or ion triplets.

Equations (24) and (25) allow validating the asymptotic expressions (35), (36) (see below). For example, with a low concentration of ion pairs ($K_3 N_0 \ll 1$) and noting that $n_1 = n_2 = n$, from (24) and (25) we obtain a quadratic equation in the concentrations of single ions:

$$K_{20} n^2 + n - N_0 = 0 , \qquad K_{20} = \frac{\alpha_{11}}{k_{20}} ,$$

whose solution at $K_{20} N_0 \ll 1$ is $n = N_0$, which points to the complete dissociation of ion pairs. At the other extreme, when $K_3 N_0 \ll 1$, $K_{20} N_0 \gg 1$, we observe weak dissociation of ion pairs, and the concentration of ions is $n = \sqrt{N_0 / K_{20}}$. Finally, when $K_{20} N_0 \gg 1$ and $K_3 N_0$ is arbitrary, we have weak dissociation of ion pairs and insignificant concentration of triplets as compared to the concentration of ion pairs:

$$\xi_1 = \frac{n_1}{N_0} \ll 1 , \qquad \xi_3 = \frac{n_3}{N_0} \ll 1 . \tag{30}$$

Of the four equations (24) – (27), only Eqns (24) and (26) are independent, which together with (29) in the approximation (30) have the solution

$$\xi_1 = \left[K_2 N_0 \left(1 + \frac{\alpha_{13}^+ + \alpha_{13}^-}{\alpha_{11}} K_3 N_0 \right) + \frac{\alpha_{33}}{\alpha_{11}} (K_3 N_0)^2 \right]^{-1/2} \tag{31}$$

$$\xi_3 = K_3 N_0 \xi_1 , \qquad K_2 = \frac{\alpha_{11}}{k_2} . \tag{32}$$

Making use of (31) and (32), from (23) we obtain the following expression for the coefficient of electrical conductivity in the presence of complexation and weak dissociation of ion pairs:

$$\sigma = e \big[\mu_1 + \mu_2 + (\mu_3 + \mu_4) K_3 N_0 \big] \xi_1 N_0 . \tag{33}$$

Note that the equivalent conductance in the Fuoss – Krauss theory (33) is given by

$$\lambda = \frac{\sigma}{N_0} \sim C_1 N_0^{1/2} + C_2 N_0^{-1/2} .$$

As follows from (33), the inclusion of the recombination processes (22) leads to a more sophisticated dependence of λ on N_0. Note also that formula (33) holds for arbitrary values of the product $K_3 N_0$ (but given that the dissociation of ion pairs is low!). However, the condition of sedimentation stability (see below) imposes the restriction $K_3 N_0 < 1$.

2.3 Experimental studies of electrical conductivity in solutions of liquid dielectrics

A review of the experimental works concerned with the cataphoretic and relaxation effects and the Wien effect in weak solutions of electrolytes (as a rule, water solutions with a conductivity $10^{-5} - 10^{-2}$ Ω^{-1} cm^{-1}) can be found in the monograph [33] and Onsager's classical paper [36]. In early studies the CVC was measured with a bridge circuit. To eliminate Joule heating, a high voltage was applied as a microsecond pulse (usually, by discharging a capacitor). In modern installations, a pulse from a pulse generator is applied to the gate of a thyristor, which sends a powerful pulse to the primary of a high-voltage transformer, whose secondary feeds a voltage multiplier [47].

The experimental measurements of CVC of liquid dielectrics brought about some nontrivial results.

(i) The voltage drop across the electrodes immersed in dielectrics was found to be small, and so the CVC can be measured using a conventional constant-voltage supply (Fig. 2). Because of this, the CVC of liquid dielectrics are

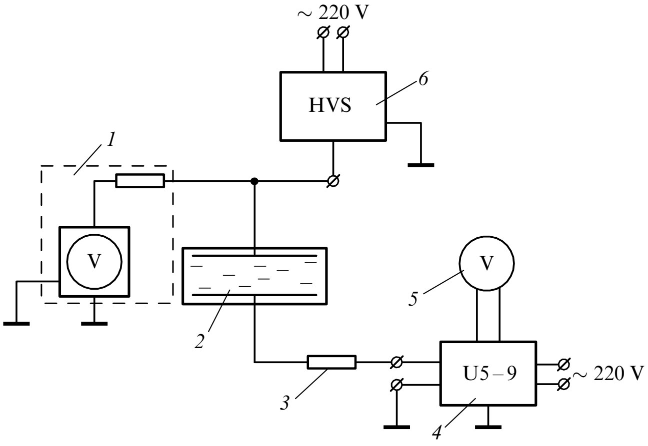

Figure 2. Circuit diagram of the installation for measuring the CVC of dielectric liquids: *1*, kilovoltmeter; *2*, measuring cell; *3*, ballast resistor; *4*, dc amplifier; *5*, digital recorder; and *6*, high-voltage source.

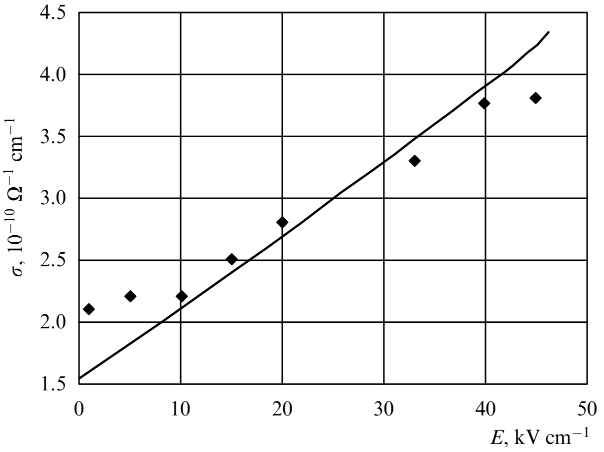

Figure 3. Electrical conductivity vs. field strength for a solution of 1% picric acid, 5% ethyl alcohol, and 1% mineral oil in benzene [54]. Solid line, theoretical curve.

almost always measured using direct current [1–3, 5–7, 35, 36, 47, 49–57].

(ii) In many cases, the electrical conductivity of nonaqueous solutions in high-voltage fields does not agree with Onsager's theory, as was noted by Onsager himself [36] (see the results of Gemant [54, 55] shown in Figs 3, 4). For example, there is agreement for the solutions of I_2 and $SbCl_5$ in pyralene, but no agreement for the solutions of oxygen, SF_6, or anthraquinone [35, 36] (Figs 5, 6).

(iii) The role of the contact ionization processes on the electrode surfaces in relatively weak electric fields is important.

Let us explain this last statement, considering separately the cases of polar and nonpolar liquids.

Polar dielectrics (nitrobenzene, bromobenzene, iodobenzene, chlorobenzene, pyridine, acetone, alcohols, etc.) exhibit a high degree of self-dissociation. Because of this, even the highly refined liquids (with a conductivity as low as $\sim 10^{-13}$ Ω^{-1} cm^{-1} [6, 56]) within a few days will restore their conductivity to typical values of $\sim 10^{-11}$ Ω^{-1} cm^{-1}. Very well developed in such liquids are electrode processes. Probe measurements [47, 58] and measurements using the Kerr effect [59, 61, 62] indicate that electrochemical injection of charges occurs in strong fields and that cathode injection is, as a rule, much stronger than anode injection. In this way, it was demonstrated that there are two regimes of electrical conductivity in polar liquids: dissociative conductivity obeying Ohm's law in weak fields ($E \leqslant 1$ kV cm^{-1}), and injection conductivity in strong fields ($E \geqslant 10$ kV cm^{-1}), when the majority of conduction ions are produced in the electrode redox reactions. The injection conductivity can be controlled by adding various agents to the liquid; this may also reduce the intensity of electrochemical decomposition of molecules of the carrier liquid on the electrodes (the so-called electrochemical protection of liquids by redox systems [63]). Another interesting method of controlling conductivity is based on the use of ion-exchange membranes [64]. In particular, covering one of the electrodes, e.g., the cathode, with a cationite membrane, one can achieve intense unipolar injection of ions into a polar dielectric like nitrobenzene or pyralene [65].

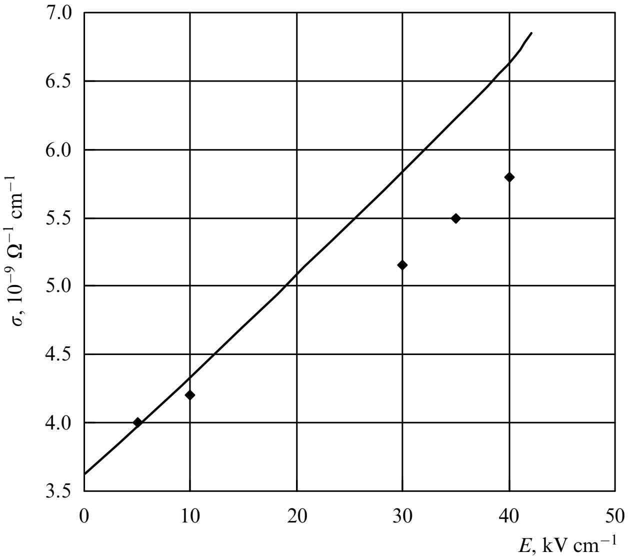

Figure 4. Electrical conductivity vs. field strength for a solution of 1% picric acid, 8% ethyl alcohol, and 3% mineral oil in benzene [55]. Solid line, theoretical curve.

Nonpolar dielectrics can be purified to an extremely low conductivity (achievable values as low as 10^{-19} Ω^{-1} cm^{-1} [3]). Conductivity of the order of 10^{-14} Ω^{-1} cm^{-1} is easily achieved simply by filtering through paper and then through glass filters, with subsequent drying in a desiccator. Note that even at this level the conductivity of nonpolar liquids is sensitive to the absorption processes (absorption of air and water vapor through the free surface), and to the quality of the electrode surface such as the presence of microscopic inhomogeneities [66–68], oxide film, and adsorption layers. The effects of the structure of the electrode surface are especially manifest in strong fields ($E \geqslant 100$ kV cm^{-1}), which stimulate cold emission of electrons from the cathode. It turns out that in this case the electrons are mainly emitted from the microscopic inhomogeneities, which even on well polished electrodes (aluminum or steel [66]) may have the size of about 1 μm, with a surface density of 10^8 cm^{-2}. The study of high-voltage conductivity dominated by the cold emission of electrons from microspikes (the so-called ectons) has currently become a special discipline in high-voltage electrophysics [67, 68].

Of special interest is the region of conductivity of nonpolar liquids in the range of 10^{-12}–10^{-11} Ω^{-1} cm^{-1}. On

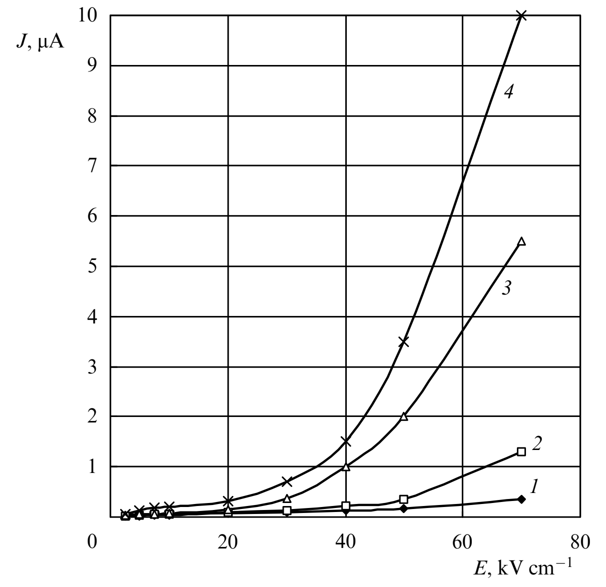

Figure 5. CVC of pyralene solutions with various additives: *1*, pure chlorobiphenyl liquid (pyralene); *2*, saturated with SF_6; *3*, 1 ppm anthraquinone; *4*, saturated with O_2.

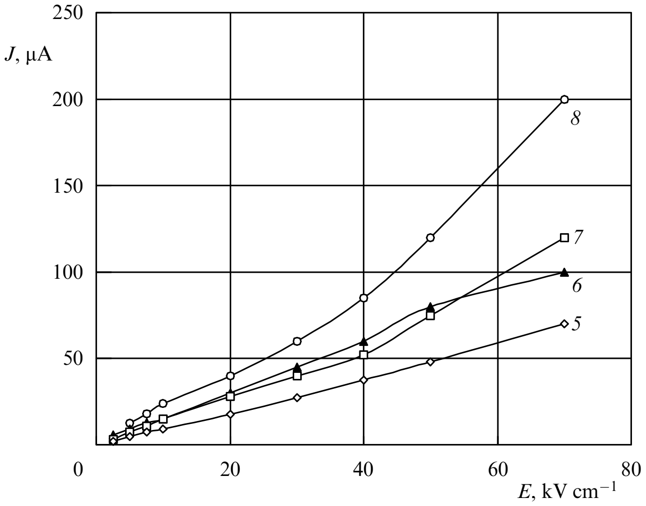

Figure 6. CVC of pyralene solutions with various additives: *5*, 1 ppm I_2; *6*, 1 ppm $SbCl_5$; *7*, 2 ppm I_2; and *8*, 3 ppm I_2.

the one hand, such is the conductivity of the so-called technical insulating liquids (transformer oil or mineral oil, and the like); on the other hand, the EHD flows in this range are especially intensive [7, 8, 47, 49, 69 – 76]. Note that, owing to the processes of electrocleaning, the electroconvection is usually unstable and fades out with time. Therefore, in order to obtain stable results, the liquid is purified to the conductivity of $\sim 10^{-14}\ \Omega^{-1}\ \text{cm}^{-1}$, with subsequent addition of special ionizing agents (molecular iodine, butyl alcohol, etc.) to increase the conductivity by 2 or 3 orders of magnitude. This procedure is essentially similar to the electrochemical protection of polar liquids with redox systems. There are, however, some important differences.

First of all, the addition of electronegative agents (strong oxidizers I_2, O_2, etc.) leads to a considerable increase in the dissociative ionization according to scheme (4). The degree of dissociation is usually extremely low and amounts to $\xi = n/N_0 \approx 10^{-5}$ [49, 50], where n is the equilibrium concentration of positive (or negative) ions, and N_0 is the initial concentration of the dissociating salt (neutral oxidizer).

Another important circumstance is the electrochemical redox reactions at the electrodes, which occur even in relatively weak fields $E \geqslant 1$ kV cm^{-1} [57, 60, 69, 70]. For example, according to the results of Refs [69, 70], the conductivity in the mixture of transformer oil with iodine is ohmic in the fields $E < 1$ kV cm^{-1}, mixed dissociation – injection type at $E = 1 - 10$ kV cm^{-1}, and injection type at $E \geqslant 10$ kV cm^{-1}. The level of cathode injection in terms of electric current is at least one order of magnitude greater than the level of anode injection. In Ref. [60] it was experimentally demonstrated that bipolar injection occurs in mixtures of transformer oil with aromatic halocarbons (iodobenzene, bromobenzene, and chlorobenzene), and the cathode injection was at least four times stronger than the anode injection. Note that a good amount of care is required in such experiments: the initial oil must be fresh; it must be free from contamination with products of oxidation, gases, water, and the like; and the ionizing additives must be chemically pure. As a matter of fact, neglect of these obvious rules has led to a considerable inconsistency in the results of measurements, and even to the persistent disbelief in the possibility of obtaining consistent data on the electrical conductivity of high-resistivity liquids [1, 7, 8]. There is also another circumstance that affects the results of measurements and, in our opinion, leads to inaccurate measurements. Rather often, the chemical activity of the additive is not taken into account in experiments with solutions. In Ref. [69] it was demonstrated, for example, that copper iodite is formed on copper electrodes in the iodine solutions in transformer oil, with subsequent rather quick adsorption of iodine by the electrode surface, whereas there is no such effect with titanium electrodes. It is quite likely that the so-called bipolar charged electrode structures [47, 58] are associated with the adsorption processes.

A systematic study of the effects of ionizing additives on EHD flows led to the discovery of bipolar electrode structures by a team of researches from Leningrad [47, 58]. The method of formation of unipolar injection conductivity in polar liquids using ion-exchange membranes was developed in the Laboratory of Electrostatics and Dielectric Materials (Grenoble) [57, 64, 65, 73]. Theoretical and experimental validation of the definitive role of redox reactions involving neutral components in polar liquids (liquid crystals) is given in Ref. [72], and in nonpolar liquid dielectrics in Refs [60, 61, 69]. Further experiments confirmed the dissociation – injection mechanism of conductivity of liquid dielectrics [74], and revealed a number of more delicate effects. It was demonstrated that bipolar structures may form in the absence of adsorption on the electrodes, but only if the mobility of the injected ions is very low compared with the mobility of single impurity ions resulting from the decomposition of ion pairs [74, 75]. According to numerical experiments, under these conditions the bipolar structures are also coordinated with the structure of EHD flows [76]. These results, combined with knowledge of electrochemistry of solutions, have prompted the idea of the existence of ion complexes in the solutions of nonpolar liquids [49, 51, 76]. Currently this view prevails [51, 77], which emphasizes the expedience of studying the formation of complexes in liquid dielectrics.

We believe that to date there has been no systematic study of complex formation in nonpolar liquid dielectrics. So we set to study the complexation in iodine solutions in transformer oil using the titration method [33].

The experimental setup is shown in Fig. 2. The source of high voltage was an IVN-50 current-stabilized high-voltage power supply manufactured by the Special Design Bureau of the Institute of Applied Physics of the Academy of Sciences of Moldavia (Kishinev). Additional overcurrent protection was installed at the input of the U5-9 electrometer amplifier. For the base liquid we used T-750 fresh transformer oil (GOST 982-80). The transformer oil was carefully filtered through paper and glass filters (POR15 type), with subsequent vacuum degassing and dehydration in a desiccator filled with $CaCl_2$ adsorbent. The measuring cell was made from Plexiglas, and the electrodes were two plane-parallel steel plates 15×40 mm separated by $d = 3.5$ mm. Steel was selected because of its inertness toward iodine.

The behavior of the electrical conductivity of pure transformer oil is quite consistent with what has been reported earlier [3, 35]. Figure 7 shows the ampere–time characteristics reflecting the effect of training of the electrodes. We see that the conductivity increases for about 1 h and then decreases. This behavior is especially manifest in strong fields (curves *3–5*). We associate such behavior with the following processes: (1) the surface electrode conductivity, when the molecules of water and oxygen adsorbed by the surface of the electrode enter into electrochemical reactions and disappear in the course of time (the so-called electrocleaning of the electrodes [3]); (2) accumulation of ions in the double electric layer; and (3) passage of ion waves in the presence of complex ions (see below). After the passage of electric current through the cell for about 2 h, the repeated measurements of CVC stabilize, and the spread of readings becomes small. This feature is clearly visible in Fig. 8, where the stable CVC is shown as a solid line.

The electrical conductivity of solutions of molecular iodine in transformer oil was measured using titration with a saturated solution from a microburet. The concentration of iodine molecules I_2 in the saturated solution of transformer oil was 4.2×10^{18} cm^{-3}, the drop volume $v_0 = 0.178$ cm^3, and the number of molecules in a drop $N_k = 7.5 \times 10^{16}$.

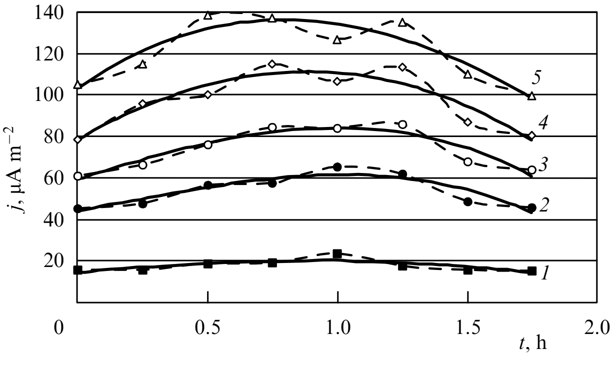

Figure 7. Ampere–time curves for transformer oil dried for 48 hours: *1*, $E = 7.26$ kV cm^{-1}; *2*, $E = 14.52$ kV cm^{-1}; *3*, $E = 18.15$ kV cm^{-1}; *4*, $E = 21.78$ kV cm^{-1}; and *5*, $E = 25.41$ kV cm^{-1}.

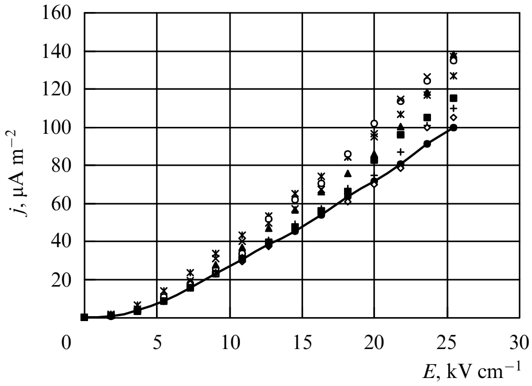

Figure 8. CVC curves for transformer oil dried for 48 h, with 15 min intervals between consecutive CVCs.

The results of the measurements were processed as follows. Let i be the order number of a series of measurements; k_i be the number of drops; and $U_i = x_i U_0$ and $J_i = y_i J_0$ be the voltage and the total current, respectively ($J_0 = 10^{-7}$ A and $U_0 = 127$ V being the scale divisions; x_i and y_i, the readings of the instruments). The conductivity σ_i and the concentration of iodine c_i are found from the relations

$$\sigma_i = \sigma_0 \frac{y_i}{x_i}, \qquad \sigma_0 = \frac{J_0 d}{S U_0} = 4.6 \times 10^{-11}\ \Omega^{-1}\,\mathrm{cm}^{-1},$$

$$c_i = \frac{k_i N_k}{v_i},$$

where S is the area of the electrode, $v_i = V_0 + i v_0$ is the volume of liquid in the cell, and $V_0 = 26.88$ cm^3 is the initial volume of pure transformer oil.

The results of measurements are conveniently represented in terms of $s_i = (\sigma_i/\sigma_0) \times 10^3$, $\alpha_i = (\lambda_i/\lambda) \times 10^3$, $\lambda_i = \sigma_i/c_i$, $\lambda_0 = \sigma_0 V_0/N_k$, $\beta_i = s_i\sqrt{c_1/c_i}$, where $c_1 = 2.8 \times 10^{15}$ cm^{-3} is the concentration of iodine in the liquid when one drop is added.

k_i......1	2.5	5	10	20	50	100	200	300
s_i......6	15	22	32	46	78	126	180	220
α_i......6	6	4.4	3.2	2.3	1.6	1.3	0.95	0.9
β_i......6	9	10	10.3	10.3	11	13	13.5	14

Strictly speaking, by the equivalent conductance one ought to mean the ratio σ_i/N_i, where N_i is the concentration of ion pairs that are formed in the reaction

$$I_2 \cdot M \rightleftarrows M^+ I_2^- . \qquad (34)$$

Here, M is the molecule of the carrier liquid. Then, $N_i = K_0 c_i$, where K_0 is the constant of equilibrium of reaction (34), which is to be determined.

These results agree rather well with the features of electrical conductivity due to the components of reactions (4) and (18), i.e., single ions and ion complexes. This is easily demonstrated by selecting three asymptotic limits:

(1) region of low impurity concentration ($N_i K_{20} < 1$):

$$\sigma_i = e(\mu_1 + \mu_2) N_i, \qquad (35)$$

(2) region of single-ion conductivity ($N_i K_{20} \gg 1$, $N_i K_{30} \ll 1$):

$$\sigma_i = e(\mu_1 + \mu_2) \sqrt{\frac{N_i}{K_{20}}}, \qquad (36)$$

Table 3. Mobility of positive μ_+ and negative μ_- ions in nonpolar liquids, 10^{-4} cm^2 (V s)$^{-1}$.

Liquid	Method of ion generation									
	X-rays		Ref.	Photoemission	Ref.	Cold emission of electrons	Ref.	Dissociation of ion pairs		Ref.
	μ_+	μ_-		μ_-		μ_-		μ_+	μ_-	
n-Hexane	4.4	8.27	[78]	11	[87]	1–14	[92]			
	13	4	[79]	10	[88]	1.5	[93]			
	9.2	5.8	[80]	10	[89]	1.5	[94]			
	13	6.8	[81]	10	[90]	6–8	[95]			
	9.1	8.5	[82]	7.5	[91]					
	20	10	[83]	1.5	[91]					
	2–2.5	2–2.5	[84]							
	10	5	[85]							
	6	—	[85]							
	2	2	[85]							
	10	—	[86]							
	6.6	4.2	[80]	11	[87]	2.4	[93]			
n-Octane	5.2	2.9	[80]	7	[89]	3	[93]			
n-Nonane	3.8	2	[80]							
n-Decane	2.7	1.5	[80]	3	[89]	2.1	[93]			
Benzene				4.5	[88]			5	5	[96]
CCl_4								0.61	0.19	[96]
Dioxane									2.1	[95]
Technical transformer oil								~ 0.01 Single ions		

(3) region of mixed conductivity by single ions and ion triplets ($N_i K_{30} \leqslant 1$), in which the conductivity is determined by relations (31) and (33).

Formally, it follows from (31) and (33) that one may consider the case $N_i K_{30} \gg 1$, when the equivalent conductance approaches the asymptote $\sigma_i / N_i = \text{const}$. However, it is difficult to realize this situation experimentally because of the sedimentation instability at $N_i K_{30} > 1$ (see Section 3.6).

Comparing relations (35) and (36) with the results of measurements, we see that upon addition of one drop the conductivity is described by asymptotic relation (35):

$$\frac{\sigma_i}{c_i} = 0.006\lambda_0 = e(\mu_1 + \mu_2) K_0 \,, \tag{37}$$

and upon addition of 20 drops, by asymptotic relation (36)

$$\frac{\sigma_i}{\sqrt{c_i}} = \frac{0.0103\sigma_0}{\sqrt{c_1}} = e(\mu_1 + \mu_2)\sqrt{\frac{K_0}{K_{20}}} \,. \tag{38}$$

We see from (37) and (38) that to express the equilibrium constants K_0, K_{20} we need information about the charges of the ions and their mobilities. In view of this, the problem of measuring mobilities of ions in liquid dielectrics becomes important.

Information about the mobilities of ions in nonpolar liquid dielectrics is very controversial. This issue is discussed in detail in monograph [3] and review [35]. As follows from Table 3, the mobility of ions depends not only on the type of liquid, but also on the way of generating them in the liquid, and the results differ considerably from one source to another. In our view, the spread of the experimental results may be due, first, to the solvation of ions, which depends on the conditions of formation of ions in the liquid, and, second, to the hydrodynamic instability of the ion cloud [49]. This latter factor seems to be the decisive one, because a hydrodynamic instability of the ion wavefront is often detected in the experiment and can even give rise to turbulence [73].

In Ref. [74] the mobility of ions was measured in weak solutions of iodine in the transformer oil using the method of transit of an ion wave. The experimental setup is shown in Fig. 9. The criterion of existence of an ion wave in the case of incomplete dissociation of ion pairs is expressed in Ref. [74] as

$$\frac{\sigma d}{(\mu_1 + \mu_2)\varepsilon E_0} \leqslant 1 \,, \tag{39}$$

where $E_0 = U/d$ is the external field strength in the cell, and σ is the low-voltage ohmic conductivity.

Like in Refs [95, 96], we observed a peak on the ampere–time characteristics and associated it with the transit time of the ion wave (see Figs 8 and 10). According to our data, the

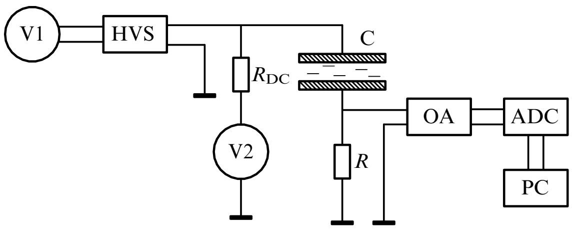

Figure 9. Circuit diagram of the installation for measuring ion waves: V1, V2, voltmeters; HVS, high-voltage source; C, measuring cell; OA, operational amplifier; ADC, analog–digital converter; R_{DC}, ballast resistor; R, protective resistor and PC, computer.

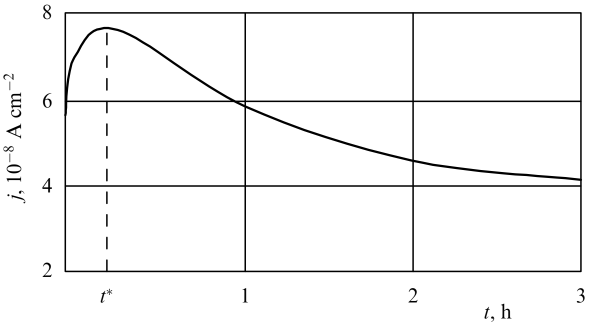

Figure 10. Ampere – time curve for a solution of iodine in transformer oil, with a copper anode and a titanium cathode at $E_0 = 2.7$ kV cm^{-1}. Conductivity of the solution for the linear portion of the CVC is $\sigma = 7 \times 10^{-11}\ \Omega^{-1}$ cm^{-1}.

mobility of ions in pure transformer oil is about $\sim 10^{-6}$ cm^2 (V s)$^{-1}$. In these experiments there was no reproducibility of the results. We believe that this can be explained by two factors: first, the above-mentioned hydrodynamic instability of the liquid, and second, the generally unfounded identification of the current peak with the time of transit of the ion wave. As a matter of fact, the current peak in the ampere – time curve may be due to electrode processes. Therefore, to produce reliable results, the measurements must be carried out in pulsed fields [10], and the pulse length must be much less than the characteristic time of buildup of ions on the electrodes and must be adjusted empirically.

Even at this stage, the results of measurements allow making estimates of the equilibrium constant of ionization K_0, ion pairs K_2, and ion triplets K_3. As follows from the results of measurements, the mobilities of negative and positive ions in viscous liquids are close (Table 4). In our calculations we assume that the mobilities of negative and positive ions are the same and that formula (7) holds. Using the characteristics of transformer oil (see Table 4) and the viscosity $\eta = 0.2$ P, we express the mobility via the effective radius of ions R as follows:

$$\mu = \mu_1 = \mu_2 = \frac{0.42}{R} \times 10^{-4}\ \mathrm{cm}^2\ (\mathrm{V\ s})^{-1}\,. \tag{40}$$

Here and further, the radius R is expressed in angstroms.

Substituting (40) into (37), we obtain for the polarization constant

$$K_0 = 7.46 \times 10^{-6} R\,. \tag{41}$$

Relation (38) allows expressing K_2 via K_0 and the concentration of iodine c_1 upon addition of one drop:

$$K_2 = \frac{0.34}{K_0 c_1}\,. \tag{42}$$

Using (41) and (42), from (15) we obtain the equation for finding the effective radius of a single ion in the form

$$3.1 \times 10^{-15} R^5 \exp\frac{252}{R} = 1\,.$$

The solution of this equation gives us the estimate of the effective radius of single ions $R = 12$ Å, and formulas (40), (41), (15) and (61) allow us to evaluate the mobilities of single ions and equilibrium constants:

$$\begin{aligned} &\mu = 3.5 \times 10^{-6}\ \mathrm{cm}^2\ (\mathrm{V\ s})^{-1}\,, \qquad K_0 = 8.95 \times 10^{-5}\,, \\ &K_2 = 6.3 \times 10^{-12}\ \mathrm{cm}^3\,, \qquad K_3 = 6.93 \times 10^{-15}\ \mathrm{cm}^3\,. \end{aligned} \tag{43}$$

From these results we can find the critical concentration of iodine at which the formation of complexes affects the conductivity. For example, for a 10% contribution we must set $K_3 N_0 \sim 0.1$, then $N_0 \sim 1.6 \times 10^{13}$ cm^{-3}. Eventually, using the relation $N_0 = K_0 c_i$, we obtain $c_i \sim 1.8 \times 10^{17}$ cm^{-3}; that is, in our case the complexation starts to play a significant role after addition of 1000 drops of iodine.

The association constants K_2 and K_3 for different liquids are presented in Table 4, from which we see that the constants K_2 and K_3 decrease with increasing dielectric constant (and fixed size of the ions), or with increasing size of the ions (and fixed ε). This is logical, because in both cases the binding energy between the ions decreases, which leads to an increase in the dissociation rate of ion complexes, while the recombination rates remain the same.

Finally, let us discuss the accuracy of our measurements and calculations. Figure 11 illustrates the accuracy margins of the field strengths applied to the cell (horizontal bars), and the fluctuations of the measured currents (vertical bars). All measured current – voltage characteristics and the related conductivities correspond to the mean values for these ranges. As to the accuracy of the calculated estimates for the parameters R, μ, K_0, K_2, K_3, we must first prove the validity of the asymptotic relations (37) and (38). This can easily be done using the following numerical results: for one drop, $K_{20} N_1 = K_{20} K_0 c_1 = 0.34 < 1$; for 20 drops $K_{20} N_{20} = K_{20} K_0 \times 20 c_1 = 6.8 > 1$.

Table 4. Correlation between the electrophysical parameters of liquid dielectrics and their polarizability.

Characteristic	Benzene C_6H_6	Iodobenzene C_6H_5I	Butyl alcohol $CH_3(CH_2)_3OH$	Acetone $(CH_3)_2CO$	Nitrobenzene $C_6H_5NO_2$	Transformer oil with iodine
ρ, g cm^{-3}	0.88	1.84	0.81	0.79	1.22	0.98
$\varepsilon/\varepsilon_0$	2.23	5.3	16.8	18.7	32.9	2.2
r_i, Å	3.27	3.5	3.3	3	3.4	12
r_B, Å	126	52	16.7	14.8	8.4	126
$\delta = R_{12}/r_B = 2r_i/r_B$	0.052	0.13	0.39	0.41	0.81	0.1
E_*, kV cm^{-1}	3.1	7.6	23.4	26.7	47.3	3.1
$4p$, $E = 10$ kV cm^{-1}	1.8	1.15	0.65	0.61	0.46	1.8
$4p$, $E = 1$ MV cm^{-1}	18	11.5	6.5	6.1	4.6	18
K_{20}, cm^3	4.6×10^{-6}	1.2×10^{-15}				$\sim 6.3 \times 10^{-12}$
K_{30}, cm^3	2.7×10^{-14}	7.0×10^{-19}				$\sim 7 \times 10^{-15}$

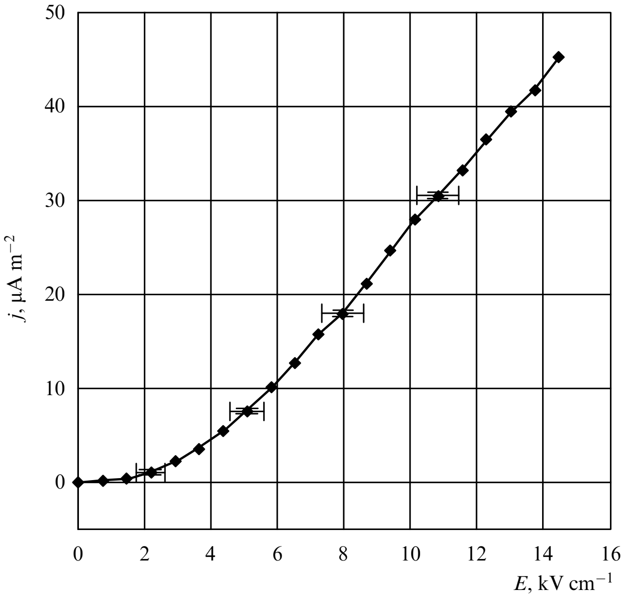

Figure 11. Evaluation of the accuracy of CVC measurements.

3. Kinetics of complexation in liquid dielectrics

Based on the main principles of reaction kinetics in solutions [37], we carried out a theoretical analysis of complex formation in solutions of liquid dielectrics [98]. Here, we briefly present the conclusions of this analysis, and describe our view on the role of complex formation in realistic situations.

Analyzing the process of complexation, one must pay attention to one important circumstance, namely, to the inclusion of the finite size of ions into the calculation of reaction rate constants. We have already seen this when drawing a comparison between experimental and theoretical values of the constant of association of ion pairs. Note that the importance of this was always clear to the researchers [33], but, unfortunately, has not always been taken into account [36].

The kinetic theory is based on the following assumptions: (1) the limiting stage of the reaction is the process of approaching (withdrawing) of the reacting particles, controlled by diffusion and migration; and (2) the reaction occurs according to the scheme of interaction between a single particle (ion, dipole) and a complex object (ion pair, triplet, etc.). It can be proved that the particle-location distribution function can be represented as $f_n = W_{n-1}(\mathbf{r}_1, \ldots, \mathbf{r}_{n-1}) f(\mathbf{r})$, where W_{n-1} describes the distribution of $n-1$ particles within the complex, $f(\mathbf{r})$ is the probability for a single particle to be located in the neighborhood of a complex consisting of $n-1$ particles, and $\mathbf{r}$ is the position vector of the single particle (with the origin in the center of the complex).

The method of moments has been used to express the equation for the function $f(\mathbf{r})$:

$$-(D_{n-1} + D_1)\,\Delta f + \operatorname{div}\big[f(\mu_1 + \mu_{n-1})\,\langle \mathbf{F}_{n-1,1}\rangle + \mu_{n-1}\,\langle \mathbf{F}_{n-1}\rangle - \mu_1\langle \mathbf{F}_1\rangle\big] = 0\,. \tag{44}$$

Here, D_1, μ_1, and $\mathbf{F}_1$ (D_{n-1}, μ_{n-1}, and $\mathbf{F}_{n-1}$) are, respectively, the coefficient of diffusion, the mobility, and the external force related to a single particle (complex); and $\mathbf{F}_{n-1,1}$ is the force of interaction between the complex and the particle. Angle brackets denote averaging with respect to all orientations of the complex.

The boundary conditions for the function f in the case of recombination are

$$r = R_{12}:\ f = 0\,; \qquad r \to \infty:\ f \to 1\,, \tag{45}$$

and in the case of dissociation

$$\int_{V_*} f\,\mathrm{d}V = 1\,, \qquad r \to \infty:\ f \to 0\,, \tag{46}$$

where V_* is the region embracing the complex (in which the particles are regarded as bound).

The rate constants of dissociation k and recombination α are written in the form

$$k = \int_S \mathbf{i}\cdot\mathbf{n}\,\mathrm{d}S\,, \tag{47}$$

$$\alpha = -\int_S \mathbf{i}\cdot\mathbf{n}\,\mathrm{d}S\,. \tag{48}$$

Here,

$$\mathbf{i} = -(D_{n-1} + D_1)\,\nabla f + f\big[(\mu_1 + \mu_{n-1})\langle \mathbf{F}_{n-1,1}\rangle + \mu_{n-1}\langle \mathbf{F}_1\rangle - \mu_1\langle \mathbf{F}_1\rangle\big]$$

is the vector of the relative density of the flow of probability, and $\mathbf{n}$ is the external normal to the sphere S that symmetrically embraces the complex.

We give the results of the calculations, following Ref. [98].

3.1 Kinetics of dissociation of ion pairs

For the rate of dissociation of ion pairs, we have

$$k_2 = 4\pi(D_1 + D_2)\,l_{\mathrm{B}} A\,F(p)\,, \tag{49}$$

where $l_{\mathrm{B}} = 2r_{\mathrm{B}}$, and $F(p)$ is the Onsager function [see (10)]. The constant A is given by

$$A^{-1} = 2\pi l_{\mathrm{B}}^3 \int_0^{\theta_*}\int_{\delta_1}^{S_*(\theta)} \exp\left[\frac{1}{s} + 4p^2(1-\cos\theta)\right] \times I(s,\cos\theta)s\,\mathrm{d}s\sin\theta\,\mathrm{d}\theta\,, \tag{50}$$

$$I(s,\cos\theta) = \int_0^1 I_0(\mu\sqrt{t})\exp\left(-\frac{t}{s}\right)\mathrm{d}t\,, \qquad \mu = 4p\cos\frac{\theta}{2}\,,$$

$$S_*(\theta) = \frac{1}{1+\sqrt{1+4p^2\cos\theta}}\,.$$

Here, the angle θ_* is found from the equation

$$\cos\theta_* = -\frac{1}{4p^2}\,,$$

the parameter $\delta_1 = \delta/2$, where $\delta = R_{12}/r_{\mathrm{B}}$ is defined in (15), and I_0 is the modified Bessel function of zero order.

Integral (50) can be calculated approximately in the limiting case $\delta_1 \ll 1, p \leqslant 1$:

$$A^{-1} = 4\pi l_{\mathrm{B}}^3 \delta_1^4 \exp\left(\frac{1}{\delta_1}\right). \tag{51}$$

Substituting (51) into (49), we obtain Onsager's result (17).

In another limiting case, where $\delta_1 \ll 1$, $4p \gg 1$, but $4p^2\delta_1^2 \ll 1$, for Onsager's function we find the correction to Onsager's asymptotics

$$F(p) \to \frac{\exp 4p}{4p\sqrt{2\pi p}} \left[1 + \frac{\exp(-1/\delta_1)}{4p\sqrt{2\pi p}\,\delta^4} \int_{1/\sqrt{2}}^{1} \frac{S_*^2(x)\exp 4px}{\sqrt{x}}\,\mathrm{d}x\right]^{-1}. \tag{52}$$

As demonstrated in Ref. [98], Onsager's approach only applies to point ions ($\delta_1 \to 0$). For ions of small but finite dimensions, when $\delta_1 \ll 1$, formulas (50) and (52) are a refinement to Onsager's theory. In particular, from (52) we see that in strong fields the dissociation rate does not grow as fast as predicted by Onsager's theory. It is quite likely that this circumstance explains the disagreement between the theory and the calculations [99]. The effects of an external field on the processes of dissociation and recombination can be determined by the parameter $4p = \sqrt{E/E_*}$, where $E_* = e/(64\pi\varepsilon r_B^2)$ for singly charged ions. If $E \geqslant E_*$, then the effects of the external field must be taken into account, at $E \ll E_*$ the effects of the field are small and can be neglected.

The limits of applicability of Onsager's approach and the typical values of the parameters can be inferred from the data in Table 4, presented for room temperature ($T = 300$ K). From these results it follows that Onsager's calculations are not valid for nonpolar solvents ($\varepsilon/\varepsilon_0 \geqslant 5$) and sufficiently strong fields. Note that in these calculations of the radii of ions we assumed that the neutral molecule and the corresponding ion had the same radius (this is a rather coarse approximation, just as the assumption of a spherical ion shape).

3.2 Rate of recombination of two ions

Onsager's theory predicts that the recombination rate of the ion α is independent of the field strength. The result is different if we take into account the finite size of the ions at $4p^2\delta_1^2 \ll 1$:

$$\alpha = \alpha_0 \left[1 + \exp\left(-\frac{1}{\delta_1}\right) F(p)\right], \tag{53}$$

where α_0 is defined according to (10), and $F(p)$ is the Onsager factor. From this relation we see that in strong fields the recombination rates tend to grow, while in the limit of point ions $\delta_1 \to 0$ the recombination rate does not depend on the external field strength.

3.3 Rate of recombination of an ion and a dipole

It can be demonstrated [98] that the effects of an external electric field on the processes of dissociation of a triplet into an ion pair and a single ion and their recombination are determined by the parameter $q = p^2 r_d/r_B$, where r_d is the characteristic statistical size of an ion triplet defined as

$$r_d = \sqrt{\frac{ed_0}{4\pi\varepsilon k_B T}}. \tag{54}$$

Here, d_0 is the dipole moment of an ion pair.

Simple estimates indicate that up to the breakdown field strength the parameter q is negative, and so in the first approximation the effects of external field can be neglected.

In the case of recombination, it suffices to use the asymptotic expression for the mean force of the ion–dipole interaction [98]:

$$\langle \mathbf{F}_{1,2} \rangle = -2\,\frac{ed_0}{4\pi\varepsilon}\,\frac{L(\xi)}{r^2}\,\mathbf{r}^0, \qquad \xi = \frac{d_0 E_i}{k_B T}, \qquad \mathbf{r}^0 = \frac{\mathbf{r}}{r}, \tag{55}$$

where $L(\xi) = \coth\xi - \xi^{-1}$ is the Langevin function, and $E_i = e/4\pi\varepsilon r^2$ is the field of the ion.

Substituting (55) into (44) and noting that $\langle \mathbf{F}_1 \rangle = \langle \mathbf{F}_2 \rangle = 0$, we obtain the ordinary differential equation, which can be easily integrated. After simple calculations, we obtain the following expression for the coefficient of recombination of a single ion and a dipole:

$$\alpha_{12} = \frac{4\pi(D_1 + D_2)\,r_d}{Q_1}, \qquad Q_1 = \int_0^{1/\delta_3} \frac{x^2\,\mathrm{d}x}{\sinh x^2}, \qquad \delta_3 = \frac{R_{13} + R_{12}}{r_d}. \tag{56}$$

Here, R_{ik} is the sum of radii of the ith and kth ions (ions 1 and 3 are assumed to be bound, ion 2 is free).

3.4 Rate of dissociation of an ion triplet into an ion pair and a single ion

In the case of dissociation of a triplet, the single ion moves in the mean field of the dipole close to the latter, and therefore it is necessary to calculate the total mean force of interaction between the ion and the dipole. After some cumbersome algebra, we arrive at the following expressions:

$$k_3 = \frac{D_1 + D_2}{r_B^2 Q_2}, \tag{57}$$

$$Q_2 = \int_{\delta_3}^{\delta_D} \exp\Pi(s)\,H(s)\,\mathrm{d}s, \tag{58}$$

$$H(s) = \int_s^\infty \frac{\exp\Pi(s)}{s^2}\,\mathrm{d}s, \qquad \Pi(s) = \int_s^\infty f_{12}(s)\,\mathrm{d}s,$$

$$f_{12}(s) = C(s)\int_{-1}^{1} W(s,x)\,\frac{s - \delta_1 x}{R(s,x)}\,\mathrm{d}x,$$

$$W(s,x) = \exp\frac{2}{R(s,x)}, \qquad R(s,x) = (s^2 + \delta_{13}^2 - 2s\,\delta_{13}x)^{1/2},$$

$$C(s) = \frac{1}{\int_{-1}^{1} W(s,x)\,\mathrm{d}x}, \qquad \delta_{13} = \frac{R_{13}}{r_B},$$

$$\delta_D = \frac{r_d}{r_B}, \qquad \delta_3 = \frac{R_{13} + R_{12}}{r_d}.$$

Integral (58) at $\delta_3 \ll \delta_D \ll 1$ can be calculated approximately:

$$Q_2 = \frac{1}{4}\sqrt{\frac{\pi}{2e}}\,\frac{(\delta_{13} + \delta)^4\delta^2}{(\delta_{13} + 2\delta)\delta_{13}^{3/2}}\exp\left(\frac{1}{\delta}\right). \tag{59}$$

Here, $e = 2.718...$ is the Naperian logarithm base, and $\delta = R_{12}/r_B$.

Useful for making estimates are the following expressions for the case of ions having the same radius:

$$k_3 = \frac{D_1 + D_2}{r_B^2}\,\delta^{-7/2}\exp\left(-\frac{1}{\delta}\right), \qquad \delta = \frac{R_{12}}{r_B}, \tag{60}$$

$$K_{30} = \frac{\alpha_{12}}{k_3} = 3.7\pi r_B^3\delta^4\exp\left(\frac{1}{\delta}\right). \tag{61}$$

Note that the last relation obtained by the kinetic method differs from expression (21) obtained from the model considerations only by a numeric coefficient.

3.5 Kinetics of four-member ion complexes

The four-member ion complexes $A^+B^-A^+B^-$ may result from the recombination of ion triplets and free ions, or the recombination of ion pairs:

$$\begin{aligned} &A^+B^-A^+ + B^- \xrightarrow{\alpha_{13}^-} A^+B^-A^+B^- , \\ &B^-A^+B^- + A^+ \xrightarrow{\alpha_{13}^+} A^+B^-A^+B^- , \end{aligned} \qquad (62)$$

$$A^+B^- + A^+B^- \xrightarrow{\alpha_{22}} A^+B^-A^+B^- . \qquad (63)$$

Reactions (62) are due to the strong ion – ion interaction, and therefore the recombination coefficients α_{13}^+ and α_{13}^- can be found using the Debye formula (10), or the refined formula (53). The recombination coefficient α_{22} of reaction (63) is determined by the weak dipole – dipole interaction. Coefficient α_{22} can be calculated from equation (44). Somewhat cumbersome calculations yield the following expression:

$$\alpha_{22} = 4\pi(D_1 + D_2)\, r_{\rm dd} , \qquad (64)$$

$$r_{\rm dd} = \left(\frac{d_1 d_2}{4\pi\varepsilon k_{\rm B} T}\right)^{1/3} . \qquad (65)$$

Here, in formula (64) we have dropped a coefficient of the order of unity (equal to 1.07); the parameter $r_{\rm dd}$ defines the statistical size of the linear four-member ion complex, d_1 (d_2) are the dipole moments of the recombinant dipoles [in the case of reaction (63), we have $d_1 = d_2$].

Note that formula (64) holds also for the recombination of two magnetic dipoles. In this case, $r_{\rm dd} = (\mu m_1 m_2/4\pi k_{\rm B} T)^{1/3}$, where μ is the absolute magnetic permeability of the carrier media (which may be liquid or solid); and m_1, m_2 are the magnetic moments of the dipoles.

The four-member complexes may decompose into a free ion and an ion complex, or into two ion pairs:

$$\begin{aligned} &A^+B^-A^+B^- \xrightarrow{k_4^-} A^+B^-A^+ + B^- , \\ &A^+B^-A^+B^- \xrightarrow{k_4^+} B^-A^+B^- + A^+ , \end{aligned} \qquad (66)$$

$$A^+B^-A^+B^- \xrightarrow{k_4} A^+B^- + A^+B^- . \qquad (67)$$

For calculating the rate constants of these reactions, one needs to know the static structure of the four-member complex. When the ions in the ion pair are additionally linked with a chemical bond, the dipoles in a four-member complex are most likely arranged in a linear array. This conclusion was proved theoretically [100] and verified experimentally for magnetic dipoles in magnetic colloids [101]. In the case of ions that are held together only by electrostatic forces, the most likely configuration is determined from the condition of maximum binding energy. Such configuration is obviously a square with the ions of the same sign located in the opposite corners. The maximum static size of a four-member complex (the diagonal of the square) is $r_4 = (4\sqrt{2} - 2) r_{\rm B}$, where $r_{\rm B}$ is the size of an ion pair (11). In the general case, the calculation of the reaction rate constants of the four-member complexes (66), (67) is a formidable task but deserves special attention.

For a linear dipole chain, the equilibrium constant of reactions (63) and (67) can be estimated by the Fuoss – Krauss method using formula (19):

$$K_{40} = 4\pi \int_{R_{12}}^{r_{\rm dd}} \exp\left(-\frac{U}{r_{\rm B} T}\right) r^2\, {\rm d}r , \qquad U = -\frac{2 d_1 d_2}{4\pi\varepsilon} \frac{1}{r^3} ,$$

where R_{12} is the minimum distance of approach of two parallel dipoles aligned on the same line, and U is their energy of interaction.

At $R_{12} \ll r_{\rm dd}$, we approximately have

$$K_{40} \approx \frac{2\pi}{3} r_{\rm dd}^3 \delta_4^6 \exp\left(\frac{2}{\delta_4^3}\right) , \qquad \delta_4 = \frac{R_{12}}{r_{\rm dd}} . \qquad (68)$$

Using the relation $\alpha_{22}/k_4 = K_{40}$, we can calculate the rate constant for the dissociation of the four-member complex into two dipoles

$$k_4 = \frac{\alpha_{22}}{K_{40}} = 1.5(D_1 + D_2)\, r_{\rm dd}^{-2} \delta_4^{-6} \exp\left(-\frac{2}{\delta_4^3}\right) . \qquad (69)$$

This formula, with the appropriate definition of $r_{\rm dd}$, describes the rate of decomposition of a two-member magnetic chain into two magnetic dipoles.

3.6 Kinetics of ion – dipole clusters

In concentrated solutions of polar liquids in nonpolar solvents (for example, butyl alcohol in transformer oil), the so-called ion – dipole clusters of the type $A^+(AB)_m$, where AB is a polar molecule (which can also be an ion pair) and m is the number of polar molecules, can be formed. Such structures may play the definitive role in the development of EHD flows and in the formation of the so-called bipolar electrode structures [47, 58]. The kinetics of the formation of ion – dipole clusters is determined by the sequence of reactions

$$\begin{aligned} &A^+ + AB \underset{k_{12}}{\overset{\alpha_{12}}{\rightleftarrows}} A^+(AB) , \\ &A^+(AB) + AB \underset{k_{22}}{\overset{\alpha_{22}}{\rightleftarrows}} A^+(AB)_2 , \\ &\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \\ &A^+(AB)_{m-1} + AB \underset{k_{m2}}{\overset{\alpha_{m2}}{\rightleftarrows}} A^+(AB)_m . \end{aligned} \qquad (70)$$

Here, we use a different notation for the reaction constants: α_{i2} and k_{i2} are, respectively, the rates of recombination and dissociation in the ith reaction.

To derive the criterion of the existence of ion – dipole clusters, we assume that dipoles only occupy the first coordination shell around an ion A^+ and that the effects of dipoles in the ion – dipole cluster on the processes of dissociation and recombination in the ith reaction can be ignored. In this case, according to (56) and (60), we obtain

$$\begin{aligned} &\alpha_{n2} = 2.7\pi(D_{n-1} + D_2)\, r_{\rm d} , \\ &k_{n2} = (D_{n-1} + D_2)\, r_{\rm B}^{-2} \delta^{-7/2} \exp\left(-\frac{1}{\delta}\right) , \qquad \delta = \frac{R_{12}}{r_{\rm B}} , \end{aligned} \qquad (71)$$

where R_{12} is the minimum distance between the ion A^+ and the dipole, $r_{\rm d} = \sqrt{2 R_{13}\, r_{\rm B}}$ is the effective size of the ion – dipole cluster, and R_{13} is the length of the dipole.

From (71) it follows that the association constants of all reactions (70) are the same and equal to the constant K_{30} described by formula (61). By N we denote the concentration of dipole molecules AB; n is the concentration of free ions A^+; and n_i is the concentration of ion–dipole complexes $A^+(AB)_i$. According to chemical kinetics, the concentrations n_i are defined by the following set of equations:

$$\begin{aligned} \frac{dn_1}{dt} &= \alpha_{12}\, nN - k_{12}\, n_1 \,, \\ \frac{dn_2}{dt} &= \alpha_{22}\, n_1 N - k_{22}\, n_2 \,, \\ &\ldots\ldots\ldots\ldots\ldots\ldots\ldots \\ \frac{dn_m}{dt} &= \alpha_{m2}\, n_{m-1} N - k_{m2}\, n_m \,. \end{aligned} \tag{72}$$

From (72) it follows that the characteristic time of the completion of the ith reaction is

$$\tau_i = \frac{1}{k_{i2}} = \frac{r_d^2}{D_2 + D_{i-1}}\, \delta^{7/2} \exp\left(\frac{1}{\delta}\right). \tag{73}$$

For the typical values $R_{12} \sim R_{13} \sim 7$ Å, $r_B \sim 126$ Å, and $D_2 \sim 10^{-6}$ cm^2 s^{-1}, the characteristic times τ_i are very short ($\tau_i \sim 10^{-4}$ s), and so in experiments the steady-state concentration distribution sets in almost instantaneously and only depends on the degree of stirring of the solution.

At equilibrium, from (72) we have

$$n_1 = (K_{30}N)n\,, \qquad n_i = (K_{30}N)\, n_{i-1} = (K_{30}N)^i n\,, \qquad i \geqslant 2\,. \tag{74}$$

Hence, we see that at $K_{30}N < 1$ the equilibrium concentrations of ion–dipole clusters containing i dipoles decrease in geometrical progression, and at $K_{30}N > 1$ we have sedimentation instability. In this case the ion–dipole complexes evolve into drop-like macromolecules, which coagulate and precipitate. Such sedimentation instability is often observed in experiments and is responsible for the poor solubility of polar liquids in nonpolar solvents.

4. Conclusions

Finally, let us formulate a few general conclusions.

(1) We have a sufficiently clear knowledge of the features of electronic conductivity in amorphous nonpolar media and of the criteria of transition from electronic to ionic conductivity.

(2) The ionic conductivity can be uncontrollable (due to the absorption of oxygen, moisture, etc. from the atmosphere), or controllable, when a cleaned and dried liquid is doped with special ionizing agents like molecular iodine, alcohols, etc. This latter case is especially important both practically and theoretically. In particular, the ionization of a liquid in this case occurs according to the mechanism of redox reactions in two stages. At the first stage, molecular complexes are formed, with subsequent formation of ion pairs (this reaction is characterized by the ionization constant K_0). At the second stage, the ion pairs dissociate into free ions (this reaction is characterized by the association constant K_2).

(3) The importance of the complexation process for the ionic conductivity of liquid dielectrics is well appreciated. The types of ion reactions of complex formation and the corresponding rates of reactions (dissociation and recombination) are summarized in Table 5. From Table 5 we see that the rates of dissociation of ion complexes obey the Arrhenius law $k = k_0 \exp(-E_A/k_B T)$, where E_A is the binding energy between the interacting components separated by a minimum distance. Note that this distance is definitive for the calculation of the rates of dissociation and must be calculated with due account for the interaction between the charged components with the medium (solvation). It is obvious that in this case the effective radius of the ion is much greater than its effective radius without solvation (the radius of free ions). This may be the origin of the discrepancy between the reaction rates calculated by statistical methods (for example, the method of partition functions [102]) and by kinetic methods. Currently, this circumstance is being recognized; for example, the local polarization of the medium is the key factor in the calculations of mobilities of both electrons [103] and ions [104].

Note that formulas for the recombination coefficients also have the same structure: a constant times the sum of the diffusion coefficients times the effective size of the complex.

(4) The constants of ionization K_0 and of the association into ion pairs K_2 and ion triplets K_3 can be inferred from the measurements of the low-voltage ohmic conductivity as the dielectric is titrated with its saturated solution.

(5) In the nonpolar media having a concentration of ion pairs N_0 and satisfying the condition $K_{30}N_0 \ll 1$, the electrical conductivity depends only on single ions, at $K_{30}N_0 \leqslant 1$ on

Table 5. Types of complexation reactions and the corresponding reaction rates.

Reaction	Recombination coefficient α	Dissociation rate k	Characteristic size of ion complexes	Small parameter
$A^+B^- \rightleftarrows A^+B^-\vert$	$8\pi(D_1 + D_2)\, r_B$	$\frac{D_1 + D_2}{4r_B^2}\, \delta^{-4} \exp\left(-\frac{2}{\delta}\right)$	$r_B = \frac{e^2}{8\pi\varepsilon k_B T}$	$\delta = \frac{R_{12}}{r_B}$
$A^+B^- + A^+ \rightleftarrows A^+B^-A^+$	$2.7\pi(D_1 + D_2)\, r_d$	$\frac{D_1 + D_2}{r_B^2}\, \delta^{-7/2} \exp\left(-\frac{1}{\delta}\right)$	$r_d = \sqrt{2\delta}\, r_B$	$\delta = \frac{R_{12}}{r_B}$
$A^+B^- + A^+B^- \rightleftarrows A^+B^-A^+B^-$	$4\pi(D_1 + D_2)\, r_{dd}$	$\frac{1.5(D_1 + D_2)}{r_{dd}^2}\, \delta_4^{-6} \exp\left(-\frac{2}{\delta_4^3}\right)$	$r_{dd} = \left(\frac{d_0^2}{4\pi\varepsilon k_B T}\right)^{1/3} = (2R_{12}^2 r_B)^{1/3}$	$\delta_4 = \frac{R_{12}}{r_{dd}}$
$A^+(AB)_{n-1} + AB \rightleftarrows A^+(AB)_n$	$2.7\pi(D_{n-1} + D_2)\, r_d$	$\frac{D_{n-1} + D_2}{r_B^2}\, \delta^{-7/2} \exp\left(-\frac{1}{\delta}\right)$	$r_d = \sqrt{2\delta}\, r_B$	$\delta = \frac{R_{12}}{r_B}$

single ions and ion complexes, and at $K_{30}N_0 > 1$ we have sedimentation instability.

(6) It is important to take into account the effects of the external high-voltage field on dissipation – recombination processes. Onsager's theory certainly has its limitations, and only holds in the approximation of point ions. Corrections for the finite size of the ions indicate that the rate of recombination of ions increases in the presence of an external field (in Onsager's theory, the recombination is not affected by the external field), while the rate of dissociation exhibits a more sophisticated dependence on the external electric field strength and differs considerably from Onsager's factor.

(7) Full understanding of the electrical conductivity of liquid dielectrics is impossible without due regard for the contact processes on the interface between the liquid dielectric and the electrode, such as the formation of a double electric layer, the effects of the interface on the dissociation – recombination processes in the near-surface region (through the image forces, etc.), the emission of electrons from the microspike surface features, redox processes associated both with the injection and discharge of ions, and the effects of adsorption films on the electron exchange between the electrode and the ion component. These problems currently attract considerable interest and call for special treatment.

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