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The Solvated Electron in Polar Organic Liquids

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The spectroscopic characteristics and the mechanism of the motion of solvated electrons in polar organic liquids are examined. It is shown that the part of the spectrum where solvated electrons absorb is determined by the polarity of microregions in the liquid. The intensity and half-width of the absorption band depend on the region of the spectrum in which absorption occurs. The theoretical concepts concerning the nature of the solvated electron and the mechanism of its motion are considered. The bibliography includes 65 references.

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I. INTRODUCTION

The study of excess electrons in liquids (solvated electrons) is of particular interest for the understanding of their behaviour as chemically reactive species giving rise to a wide variety of reactions and determining the fundamental step in electrochemical, radiation-chemical, and other processes. These processes are determined by the nature of the localised state and the diffusion characteristics of the electrons. The possibility of the dissolution of alkali metals in ammonia was first discovered by Weyl[1]. Kraus[2] suggested that the colour of the resulting solution is associated with the solvated electron formed on association of the metal atom to the cation and an electron. A brief unstable colour was also observed on dissolution of alkali metals in polar solvents, for example alcohols, at a low temperature[3]. By analogy with ammonia, it was attributed to solvated electrons. A new stage in the study of solvated electrons began after the detection of hydrated electrons by pulse radiolysis[4]. The subsequent employment of this method made it possible to obtain quantitative characteristics of solvated electrons (e_s) in various liquids where their lifetime amounts to a fraction of a second. The study of such electrons in a wide variety of organic liquids led to fundamentally new results, which are important for the understanding of the nature of the solvated state of the electron.

The principal method for detecting solvated electrons involves the measurement of absorption spectra, which characterise mainly the localised state of e_s. There have been only a limited number of investigations of the relaxation currents associated with the motion of solvated electrons. For this reason, the mechanism of their transport in polar liquids has been least thoroughly studied compared with their other characteristics. The spectroscopic characteristics of solvated electrons have now been measured in a large number of pure organic liquids, both polar and non-polar, and in mixtures of organic liquids with different proportions of the components; the experimental wavelength range in which solvated electrons absorb extends from 250 to 3000 nm. The temperature range of the measurements of the e_s spectra extends from the temperature of liquid helium[5] to temperatures in excess of critical values (in the case of water)[6]. The influence of pressure up to several kilobars on the absorption spectra of solvated electrons has been studied. The time interval corresponding to the investigation of the formation of and changes in the absorption spectra of solvated electrons is between 10^{-11} and 10^{-3} s. In some cases stable spectra of solvated electrons were recorded. Much attention has been devoted to the investigation of a large number of reactions of solvated electrons with various additives and also to the investigation of the influence of certain compounds which do not interact chemically with e_s, on the ways in which the latter are stabilised, which is reflected by a change in the characteristics of the absorption spectra. Systematic accounts of the results have been given in reviews and monographs[7-12] and reference data have been published[13,14].

II. CERTAIN THEORETICAL MODELS OF THE SOLVATED ELECTRON

Despite the abundance of experimental data, there is at present no generally accepted theoretical model which would explain all the experimental results for solvated electrons. The current aim of the main fundamental approaches to the understanding of their nature is to explain the principal parameters of the optical absorption spectra of solvated electrons, namely the half-width of the absorption band, its asymmetry, intensity, the coefficient of the temperature shift of the wavelength of the absorption maximum (λ_{max}), and the dependence of the position of λ_{max} on the macroscopic and microscopic characteristics of the medium.

The theoretical models discussed in various studies can be conventionally divided into two groups. In those of the first group an attempt is made to calculate, by considering real characteristics of the liquid, the parameters of the potential well in which the electron is localised, the distribution of the discrete energy levels in it, and the limit of the continuous spectrum of levels. In models of this group account can be taken of various types of interactions between the electron and the condensed medium. The simple polaron model considers the medium as a macroscopically continuous dielectric[15-18]. In semicontinuous or molecular-cavity models account is taken of

the molecular structure of the solvent, in contrast to the polaron model[19,20]. Consideration of the excess electron in a polar medium within the framework of the adiabatic approximation with simultaneous examination of the electronic energy and the energy of solvent rearrangement has proved to be the most successful approach[19]. In structural models it is assumed that the electron is bound to the nearest solvent molecules sufficiently strongly to neglect long-range interactions and the localisation of the electrons at several molecules[21], dimers, trimers[22], clusters[23], and structural defects[24] is considered. The principal achievement of this group of studies is agreement between the theoretically calculated and experimental λ_{max} for solvated electrons in water and ammonia. On passing to more complex organic molecules, such agreement cannot be attained. In these investigations the spectra are interpreted almost exclusively as due to a transition between two discrete levels, usually the $1s \rightarrow 2p$ transition (i.e. the electron remains bound in the excited state).

The other approach involves the selection of a form of potential whereby an agreement between the theoretically calculated absorption band of solvated electrons and the experimental band can be achieved by a suitable choice of a definite number of parameters. Thus, when the hydrogen-like potential is used and two parameters are adjusted, it is possible to reach[25] complete agreement between the calculated and experimental absorption curves for solvated electrons in various liquids over a wide range of pressures and temperatures. However, the parameters obtained in the mutual adjustment of these spectra can be in no way related to the real characteristics of the liquid and therefore the predictive value of this approach is slight. The experimental data obtained in recent years leads to the conclusion[26,27] that optical absorption is determined mainly by the transition to a continuous spectrum. On the basis of this assumption, it can be shown[28] that, by specifying the simplest form of the potential curve, namely a rectangular well, it is possible to achieve a satisfactory agreement between the theoretical and experimental absorption curves when certain parameters are chosen. Certain important characteristics of solvated electrons have been calculated[29] from the shape of their absorption line using threshold formulae and it was concluded that the lower energy side of the absorption band corresponds to photoionisation, the effective interaction in the final state being short-lived.

Evidently the development of theoretical concepts concerning the nature of the solvated electron is determined in both approaches by the possibility of a more specific allowance for the fundamental forms of interaction between the electron and the liquid medium. In its turn this entails a systematic treatment of the available experimental data and the determination of the general characteristics of the behaviour of these electrons in various liquids.

III. SPECTROSCOPIC CHARACTERISTICS IN POLAR LIQUIDS

In a number of studies, attempts were made to relate the spectroscopic characteristics of the solvated electron to the properties of the liquid in which it is solvated. A correlation has been observed[30] between the static dielectric constant (D_{st}) and λ_{max} in methanol, ethanol, propanol, and ethylene glycol. However, measurements of the absorption spectra of solvated electrons in twenty straight-chain and branched-chain alcohols[31,32] showed unambiguously that no such correlation exists. These investigations showed, for alcohols, that there is also no correlation between λ_{max} and the fundamental parameter of the polaron theory $\beta = 1/D_{opt} - 1/D_{st}$. Analysis of the absorption spectra of solvated electrons in a large number of organic liquids of different structures leads to the conclusion[31,33] that the localised state of the electron in a polar liquid is probably determined by the interaction with the polar groups of a small number of molecules of the liquid.

It is noteworthy that the question of whether or not λ_{max} is determined by the interaction of the electron with a large number of molecules of the liquid (i.e. by the dielectric characteristics of the medium) or with the first solvation layer (i.e. by short-range forces) cannot be answered by studying two-component systems[34,35], since a gradual substitution of one mixture component by another also produces a smooth change in the dielectric constant. For this reason, the spectra of solvated electrons were studied by pulsed radiolysis in monoethanolamine (MEA), a bifunctional compound, and in an equimolar ethanolamine mixture[36]. MEA and the mixture have similar chemical compositions but differ appreciably in their dielectric constants: $D_{st} = 57.7$ for MEA and $D_{st} = 10.5$ for the mixture at 20°C. The wavelength corresponding to the optical absorption maximum of solvated electrons in MEA is 910 nm [36]; it occupies an intermediate position between λ_{max} for ethanol (700 nm [30]) and ethylamine (1300 nm [37]) and is close to λ_{max} for the mixture (880 nm), although the dielectric constants of MEA and the mixture differ by a factor greater than 5. Thus the position of the absorption maximum of solvated electrons for liquids having similar chemical compositions is determined by the presence of functional groups, in the present case OH and NH_2, and is independent of the macroscopic characteristics of the liquid.

For liquids with appreciably different molecular structures, it is also impossible to observe a correlation between λ_{max} and D_{st}. The same applies to the parameter $D_{st}\rho$ (where ρ is the density), which is correlated with the changes in λ_{max} or E_{max} (the energy corresponding to λ_{max}) as a function of pressure and temperature in alcohols but not in other liquids[38]. An attempt to take into account in a more complex manner the influence of the structure of the liquid on the position of E_{max} has been made[39]. Assuming that the structure of the liquid plays a major role in determining E_{max}, the author calculated the values of the correlation parameter g_c in the Kirkwood equation for various liquids:

$$[(D_{st.} - 1)(2D_{st.} + 1)/9D_{st.}](M/\rho) = (4\pi N/3)[\alpha + (g_c\mu^2/3kT)], \quad (1)$$

where M is the molecular weight, α the molecular polarisability, and μ the dipole moment. Values of g_c greater than unity indicate a greater local polarity in microscopic regions within the liquids than might have been expected from the molecular dipole moment.

A satisfactory correlation has been observed between E_{max} and the parameter $D_{st}\rho g_c^3\alpha_p$ (α_p is the polarisability of the polar group in the molecule) for a number of amines, ethers, alcohols, water, and ammonia[39]. However, subsequent measurements of the spectra of solvated electrons in amides[40] failed to confirm the general applicability of the observed relation. For example, E_{max} for *NN*-dimethylacetamide is smaller by a factor of three than might have been expected from the relation. This is because the parameter $D_{st}\rho g_c^3\alpha_p$ is largely determined by the macroscopic characteristic D_{st}; since amides are characterised by relatively high values of D_{st} (30–40), there is a sharp

inconsistency between the similar values of E_{max} observed for amides and for example weakly polar amines, on the one hand, and the widely different values of $D_{st}\rho g_c^3 \alpha_p$ for the same liquids, on the other.

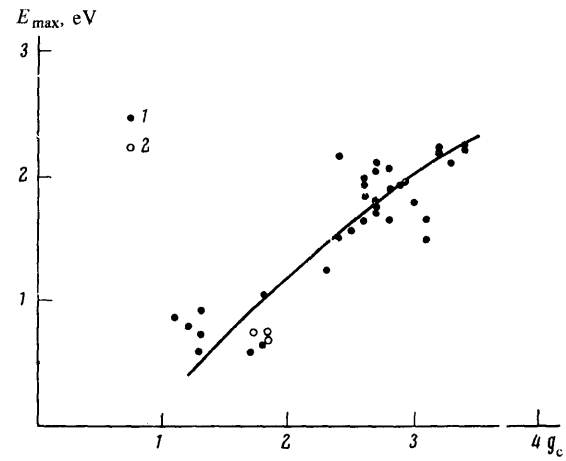


Figure 1. Variation of E_{max} (e_S) with the correlation parameter g_C of polar liquids: 1) liquids considered by Freeman[39]; 2) liquids investigated by Galvas et al.[40].

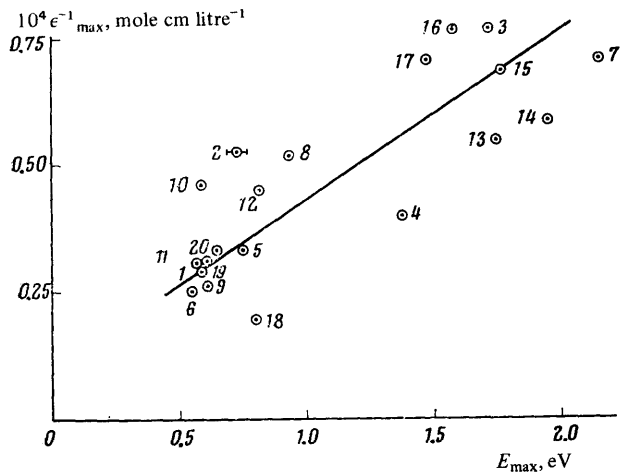


Figure 2. Variation of ϵ_{max} for the solvated electron with E_{max} in different liquids: 1) hexamethylphosphoramide[41]; 2) dimethyl sulphoxide (the upper limit of ϵ_{max} calculated from the data of Cooper et al.[63] is quoted); 3) 2-methoxyethanol[40]; 4) ethyl methyl ketone[46]; 5) squalane[64]; the remaining points were calculated from data quoted by Dorfman and Jou[42]; 6) ethyl ether; 7) ethylene glycol; 8) ethylenediamine; 9) tetrahydrofuran; 10) methyltetrahydrofuran; 11) diethylamine; 12) 1,3-propylenediamine; 13) water; 14) methanol; 15) ethanol; 16) 1-propanol; 17) isopropyl alcohol; 18) ammonia; 19) dimethoxyethane; 20) diglyme.

It was shown above that macroscopic characteristics have only a weak influence on the mechanism of the formation of the solvated electron and E_{max}. If the interaction of the electron with the nearest polar groups is regarded as the main one, a correlation may be expected between E_{max} and g_C. Indeed, Fig. 1 shows that, for all the liquids considered[39,40], including amides (open circles), the same functional relation holds between E_{max} and g_C.

There are few experimental data for the variation of the shape of the e_S absorption band on passing from one liquid to another. For ammonia[35], hexamethylphosphoramide[41], and 2-methoxyethyl ether[42], the absorption band is satisfactorily represented by a combined Lorentzian–Gaussian profile; the long-wavelength component of the absorption band is then described by the Gaussian function and the descent from the maximum in the direction of short-wavelengths obeys the Lorentzian function. In other liquids such analysis is difficult, particularly because of the inadequate accuracy of the recording of the e_S spectrum. However, it is possible to find a relation between simpler parameters characterising the spectrum and the position of the spectrum on the wavelength scale. Fig. 2 presents the variation of the reciprocal of the extinction coefficient at the maximum (ϵ_{max}) with E_{max}. Evidently, the extinction coefficient increases for all liquids with decrease of E_{max}. If one remembers that the oscillator strength of the e_S absorption band changes little (in the range 0.5–0.9), then the above finding reflects the fact that the e_S infrared absorption bands are narrower and more intense than the bands at short wavelengths.

IV. INTERACTION WITH POLAR LIQUIDS

Thus the region of the spectrum in which the solvated electron should absorb and the spectral characteristics can be predicted beforehand, albeit very approximately, for any organic liquid, subject to the condition that the electron is solvated in this liquid, i.e. does not react with the molecules of the liquid before solvation. The lifetime of the solvated electron in a particular organic liquid is usually inferred from the rate constant for the reaction of the hydrated electron with the molecules of the liquid. However, it is clear from the foregoing that in each liquid the solvated electron exhibits specific properties which do not allow the simple assumption that the properties are the same as those of the hydrated electron.

The factors governing the stabilisation of electrons in various organic liquids can be found by considering the results of a study of the interaction of low-energy (~1 eV) electrons with organic molecules in the gas phase[43,44]. This shows[46] that solvated electrons are formed in liquids whose molecules interact with electrons in the gas phase to form extremely short-lived negative ions ($10^{-15} \leq \tau \leq 10^{-12}$ s) and are characterised by a negative electron affinity. The rate constants for the e_S annihilation reactions in these liquids are $\leqslant 10^7$ litre mole^{-1} s^{-1}.

The results of the gas-phase measurements have been compared[44] with the rate constants for the interaction of hydrated electrons with the molecules of the above organic compounds in aqueous solutions. This leads to conclusions which are difficult to account for, for example when ketones are considered. Forming only extremely short-lived ions in the gas phase, they nevertheless react with hydrated electrons and the reaction is characterised by a high rate constant ($k = 6 \times 10^9$ litre mole^{-1} s^{-1}). Without considering in detail the mechanism of this reaction, the above considerations might have suggested that solvated electrons can be detected in pure liquid ketones, in view of the results of the gas-phase measurements. Indeed, a species has been detected in ethyl methyl ketone, whose

properties, such as the position of the absorption band (λ_{max} = 900 nm), its shape, its extinction coefficient ($\epsilon_{max} = 2.5 \times 10^4$ litre mole^{-1} cm^{-1}), and its half-width (0.5 eV) are quite similar to the spectroscopic characteristics of solvated electrons in other organic liquids [33,45]. Here we may note that the mobility of solvated electrons in ethyl methyl ketone (EMK) greatly exceeds the mobility of molecular ions in the same liquid [46]. Similar results were obtained in other investigations [40]. The rate constant for the reaction of electrons solvated in ethanol with dimethylformamide ($k = 1.1 \times 10^9$ litre mole^{-1} s^{-1}) suggests that in pure dimethylformamide (DMF) solvated electrons are not formed (the lifetime $\tau < 5 \times 10^{-11}$ s). In practice it was found that solvated electrons with an infrared spectrum having a lifetime of about 1 μs are formed in pure DMF. Naturally the specific features of the condensed state, particularly the association of molecules in the liquid, have an appreciable influence on the mechanism of the reaction of solvated electrons with the organic liquid molecules, as will be shown below.

Depending on the method of generation, solvated electrons can be obtained both in equilibrium with the surrounding medium (electrochemical generation, dissolution of metals) and in a non-equilibrium state (radiation-induced generation and photoionisation). In the latter case the lifetime of the solvated electron can be determined by its recombination with an ionised parent molecule or with radiolysis (photolysis) side products. However, for any method of generation, the maximum possible lifetime of the solvated electron is determined by the rate of its reaction with the molecules of the organic liquid in which it was solvated.

Despite the extensive experimental data obtained in studies of the kinetic characteristics of solvated electrons in various organic media, a comparative study of the influence of the molecular structure of liquids on the reaction of the electron with the medium has not been made. Nevertheless, the latter is one of the most important reactions [8,9]. The influence of the structure of the matrix on this reaction was studied for aliphatic monohydric alcohols with different hydrocarbon chain lengths and also for glycols and glycerols [46,47]. Using the method of pulse radiolysis, measurements were made of the rate constants for the reaction

$$ROH + e_s \xrightarrow{k} RO^- + H. \qquad (2)$$

Fig. 3 presents the values of k as a function of the number of carbon atoms n in the hydrocarbon chain in alcohols, iso-alcohols, and glycols at room temperature. The values of k for methanol and ethanol were taken from Rzad and Fendler [48] and a second, lower value for methanol from Iha and Freeman [49]. The Figure shows that k increases monotonically with increase of the hydrocarbon chain length and the constant is higher for alcohols with the iso-structure and glycols than for straight-chain alcohols. In conformity with this relation, $k = 2.4 \times 10^5$ litre mole^{-1} s^{-1} was obtained in glycerol, which agrees with the value quoted by Kajiwara and Thomas [50], but greatly exceeds the k values for propanol and propylene glycol.

Examination of the possible reaction mechanisms leads to the conclusion that the electron most probably reacts with monomeric matrix molecules which are not associated by hydrogen bonds [46]. In this case the activation energy for the reaction is related to the dipole relaxation of the liquid molecules, leading to the dissociation of the hydrogen bond, and amounts to several kcal mole^{-1}. The dependence of the rate constant on the hydrocarbon chain length of the alcohol molecules can be naturally explained, since it is known [51] that in the lower alcohols–higher alcohols series the degree of association diminishes. This also happens on passing from straight-chain to branched-chain alcohols, in agreement with the experimental results.

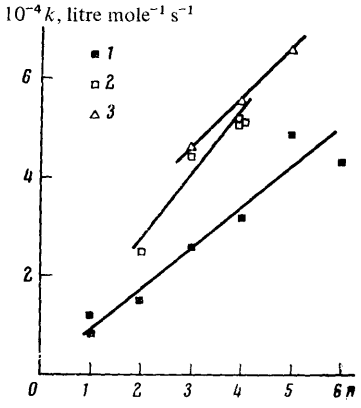


Figure 3. Variation of k with the number of carbon atoms n in the hydrocarbon chain: 1) straight-chain alcohols; 2) glycols (ethylene glycol, 1,2-propylene glycol, and 1,3-, 1,4-, and 2,3-butylene glycols); 3) iso-alcohols (isopropyl, isobutyl, and isopentyl alcohols).

The change in the rate constant on increasing the number of hydroxy-groups per molecule in the series 1-propanol, 1,2-propylene glycol, and glycerol is of interest, these being 2.6×10^4, 4.5×10^4, and 2.4×10^5 litre mole^{-1} s^{-1} respectively. When the rate constant is recalculated relative to the concentration of OH groups, it is found to increase only for glycerol: 2.6×10^4; 2.3×10^4; 8×10^4. This implies that the concentration of unassociated hydroxy-groups does not change on passing from the alcohol to the glycol and increases for glycerol, but the degree of association increases in this sequence with the corresponding variation of viscosity (2.2, 45.6, and 960 cP). Experimental confirmation of this would constitute valuable support for the hypothesis that the solvated electron reacts with the medium.

However, one cannot assume that the reaction of solvated electrons with monomeric molecules is diffusion-controlled, since, when the rate constant is calculated in terms of the concentration of monomeric molecules, which constitute only a few per cent of the total number of molecules, it is nevertheless still several orders of magnitude lower than the diffusion limit.

V. THE CHARACTERISTICS OF TRANSPORT IN POLAR LIQUIDS

Despite their importance, the reactions of solvated electrons with the molecules of liquids by which they are solvated have been studied much less than those of solvated electrons with the acceptors introduced into the liquids. Being one of the most chemically reactive species, the solvated electron reacts in many instances with organic molecules at rates controlled by the diffusion

limit. The rate constants for these reactions are determined by the mobility of the solvated electron and can be calculated using the latter. The study of solvated electron transport phenomena is important for the elucidation of the mechanism of the motion of electrons in non-ordered liquid media, for the determination of the nature of the interaction of solvated electrons with acceptors, and for the elucidation of the mechanism of oxidation-reduction reactions.

The mobilities of solvated electrons were previously measured reliably only in water[52,53] and in ammonia[54]. In water the mobility $\mu(e_S)$ of the solvated electrons generated by the ionising radiation pulse was obtained from electrical measurements, since the mechanism of the ionic process initiated by ionising radiation in water is known in detail. From this standpoint, organic liquids have been much less thoroughly investigated. Furthermore, in polar organic liquids the lifetime of the solvated electron is as a rule 10^{-4}–10^{-8} s owing to its interaction with the molecules of the liquid or the acceptor, and it is impossible to use standard methods for the determination of mobilities by measuring the time of flight of the electron between the electrodes. For this reason, a method has been developed for the measurement of the mobility of solvated electrons in which pulse measurements of their optical and electrical characteristics are combined[33].

The mobilities of solvated electrons, protons, and ions in certain polar liquids.

Liquid	D_{st}	T, °C	μ (H+), cm^2 V^{-1} s^{-1}	μ (m.i.), cm^2 V^{-1} s^{-1}	$\mu(e_S)$, cm^2 V^{-1} s^{-1}	η, cP	References
Water	81	20	$4\cdot10^{-3}$	$1\cdot10^{-3}$*	$2\cdot10^{-3}$	1.0	52
Methanol	31	20	$1.4\cdot10^{-3}$	$9\cdot10^{-4}$*	$2.8\cdot10^{-3}$	0.58	46,55
Hexamethyl-phosphoramide	30	20	—	$6\cdot10^{-5}$	$5.5\cdot10^{-4}$	3.6	33
Ammonia	22	−60	$1.3\cdot10^{-3}$	$1.8\cdot10^{-3}$*	$1\cdot10^{-2}$	0.37	54,56
1-Propanol	20	20	$3.6\cdot10^{-4}$	$1.8\cdot10^{-4}$	$4.6\cdot10^{-4}$	2.39	47,46
Isopropyl alcohol	19	20	$2.4\cdot10^{-4}$	$1.5\cdot10^{-4}$	$4.5\cdot10^{-4}$	3.95	47,46
Dimethoxyethane	13	−90	—	$4\cdot10^{-5}$*	$4\cdot10^{-4}$	32.3	57,58
Monobutylamine	5	20	—	$2\cdot10^{-3}$	$2.7\cdot10^{-3}$	0.35	33

*The average mobilities of alkali metal and halide ions.

Spectroscopic measurements showed that in the organic liquids investigated solvated electrons generated by high-energy electron pulses disappear via a pseudofirst-order reaction. By reacting with acceptors or matrix molecules, the electron passes from the solvated state, detected by means of the optical absorption and characterised by the lifetime $\tau = k_{opt}^{-1}$, to a bound state. This entails a change in the mobility of the charged species. Numerical values of $\mu(e_S)$ were obtained by treating the current relaxation curves in terms of the equations[33]:

$$I_{max} = FG(e_s)PS[\mu(e_s) + \mu((m.i.)]/100;$$
$$\frac{I(t)}{I_{max}} = 2\left[\frac{\mu(e_s)}{\mu(m.i.)} + 1\right]^{-1} + \left\{\frac{[\mu(e_s)/\mu(m.i.)] - 1}{[\mu(e_s)/\mu(m.i.)] + 1}\right\} e^{-k_{opt}\cdot t}, \quad (3)$$

where $G(e_S)$ is the radiation-chemical yield of solvated electrons, P the dose in the pulse, $\mu(e_S)$ and μ(m.i.) are the mobilities of solvated electrons and molecular ions, F is the electric field strength, S the area of the electrodes, and I_{max} the maximum amplitude of the relaxation current. The Table lists the mobilities of solvated electrons, protons, and ions for certain polar liquids.

The data quoted by Vannikov et al.[33] first led to the conclusion that the mobility of solvated electrons in various polar media is inversely proportional to their viscosities. Recently this conclusion was confirmed in a study[55] where it was shown that the Walden rule holds for solvated electrons, and $\mu(e_S)\eta = C$. Fig. 4 presents the known mobilities of solvated electrons as a function of the viscosity of the polar liquid. The straight line corresponds to the Walden rule with $C = 2 \times 10^{-3}$ cm^2 cP V^{-1} s^{-1}. The values of $\mu(e_S)$ are quoted for room temperature, with the exception of ammonia (−60°C) and dimethoxyethane (−90°C). Since the relation $\kappa = \mu kT/e$ holds between the mobility and the diffusion coefficient κ, one can assume that a relation analogous to that illustrated in Fig. 4 holds between $\kappa(e_S)$ and η.

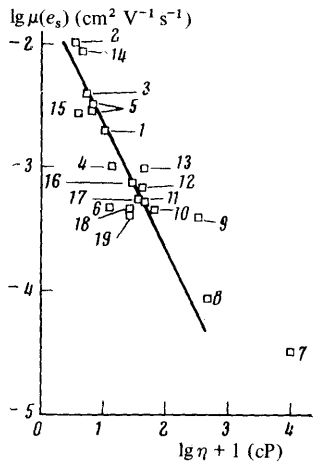


Figure 4. Variation of the mobility of the solvated electron with viscosity in polar liquids: 1) water[52]; 2) ammonia[54]; 3) n-propyl ether[55]; 4) ethanol[55]; 5) methanol[46,55]; 6) ethanol[65]; 7) glycerol[50]; the data for the remaining limits were taken from Refs. 33, 46, 47, and 57: 8) 1,2-propylene glycol; 9) dimethoxyethane; 10) hexanol; 11) 1-pentanol; 12) isobutyl alcohol; 13) isopentyl alcohol; 14) ethyl methyl ketone; 15) monobutylamine; 16) 1-butanol; 17) hexamethylphosphoramide; 18) 1-propanol; 19) isopropyl alcohol.

The results obtained for polar liquids, referring to various classes of organic compounds, show that in all cases the mobility of solvated electrons is much higher than that of molecular ions, with the exception of water, where the mobilities of electrons and hydroxide ions are the same; however, one should note that hydroxide ions exhibit anomalous mobility. Thus the mechanism of the motion of solvated electrons differs from that of the usual diffusion of ions. The activation energy for mobility measured for solvated electrons in hexamethylphosphoramide is 1.6 kcal mole^{-1} and is smaller than the activation energy for ionic mobility (4.4 kcal mole^{-1}).[59] On the other hand, the specific characteristics of the diffusion of solvated electrons distinguish it from the mechanism of the motion of protons (it has been suggested[60] that the same mechanism applies to hydrated electrons and H^+ ions), which in

certain liquids, for example in water and alcohols, leads to anomalous mobilities, since high values of $\mu(e_S)$ relative to ionic mobilities are observed also in liquids where there is no anomalous proton mobility.

In principle it is possible to postulate a mechanism for the motion of e_S based on the transition of the electron to a quasifree state with a high mobility and its subsequent solvation. Estimates based on experimental results, [19,61] have shown [46] that the minimum activation energy for the process exceeds 10 kcal mole^{-1}, which is much more than the experimental value quoted above and makes this mechanism of the motion of e_S unlikely in polar organic liquids. The jump mechanism of the motion of the electron between local regions in the liquid where orientation polarisation corresponds to a minimum in the overall electron energy appears to be more realistic [62]. The diffusional jump is accompanied by a reorientation of the liquid molecules and one may expect a correlation between the viscosity and the mobility $\mu(e_S)$, which is in fact observed, as shown above.

Thus empirical relations and gas-phase data for the interaction of electrons with organic molecules as well as macroscopic characteristics of the organic liquid and its molecular parameters make it possible to determine approximately beforehand whether solvated electrons will be formed in the given liquid and to indicate the part of the spectrum where the e_S absorption band should occur, the parameters of the spectrum, and the expected mobility and diffusion coefficient of e_S. Theoretical proof of the above characteristics will promote a significant advance in the understanding of the nature of the solvated state of electrons in polar organic liquids.

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