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Electrochemistry

SOLVATED ELECTRON IN POLAR ORGANIC LIQUIDS

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Solvated electrons are the simplest chemical entities that are involved in the various reactions to determine an elementary act in radiation chemistry, photochemistry and electrochemistry. The nature of the localized electron state in polar liquid is visible in the absorption spectra. The diffusion characteristic of solvated electron is obtained by the measurement of conductivity of the solvated electron solutions.

In the present paper, general correlations between the optical transition energy and the polarity of microdomains of liquid, the extinction coefficient of absorption band of solvated electron and the optical transition energy, the diffusion coefficient of solvated electron and the viscosity of liquid, the position of maximum of the optical absorption band and the chemical structure of the mono and bifunctional molecules of the solvent are discussed. The correlations found are determined in general by the interaction of electron with the first solvating layer and are independent of macroscopic dielectric characteristics of the liquid. The diffusion of solvated electron is explained by hopping between the local sites with equal orientation polarisations. The study of change of molecular characteristics of liquid under e_s generation gives the additional information on the nature of solvated electron. In the deformation of the chemical bonds of the molecules, solvating electron is determined by the appearance of excess electron density on bonds due to the creation of states with charge transfer between electron in cavity and molecules of the first solvating layer. One can consider the optical e_s absorption to correspond to a charge transfer from cavity to an expanded intermolecular orbital and solvated electron ground state to be a linear superposition of these two limiting structures.

Laser photolysis (Q-switched neodimium laser, 20ns duration of pulse) method has been used in a study of the influence of light on electrochemically generated solvated electron solution in hexamethylphosphortriamide. In this organic liquid, the complex electron associations, particularly dielectron localized on Na^+ cation, are formed. Laser photolysis allows to determine the nature of excited state of dielectrons and mechanism of its formation from two solvated electrons and degradation after a laser pulse.

Keywords : Solvated Electron; Polar Organic Liquids; Laser Photolysis; Absorption Spectra

INTRODUCTION

INVESTIGATION of excess electrons—solvated electrons—in liquids is of particular interest for understanding their behaviour as chemically active particles participating in diverse transformations, and in defining the elementary act in electrochemical, radiation-chemical and other processes. These processes are determined by the localized state nature and diffusion characteristics of electrons. Nowadays, a special branch of electrochemistry is developing the electrochemistry of solvated electron (Krishtalik & Alpatova, 1975).

Weyl (1864) was the first to establish the fact that alkali metals can be dissolved in ammonia. Kraus (1908) suggested that colour is associated with the solvated electron formed upon electrolytic dissociation of a metal atom into cation and solvated electron (e_s). The appearance of a temporary unstable colour was also observed upon dissolution of alkali metals in polar solvents, e.g., in alcohols at low temperature. By analogy with ammonia, it was attributed to solvated electron. The detection of hydrated electron by pulse radiolysis marked a new stage in investigation of solvated electron (Hart & Boag, 1962). Later on by the use of this method it became possible to obtain quantitative characteristics of e_s^- in various liquids in which the life-time of e_s^- is some fractions of a second. Investigation of e_s^- in diverse organic liquids led to radically new results of great importance for understanding the nature of the solvated state of electron.

Analysis of the absorption spectra of e_s^- in a large number of organic liquids leads to the conclusion (Vannikov *et al.*, 1972) that the localized state of electron in polar liquids seems to be determined by interaction with polar groups of a small number of liquid molecules.

INVESTIGATIONS AND RESULTS

We studied the absorption spectra of e_s^- in a bifunctional compound of monoethanolamine (MEA) and an equimolar mixture of ethanol and amine. MEA and the mixture have similar chemical composition but differ widely in their dielectric characteristics : for MEA $D_0 = 57.7$ and for the mixture $D_0 = 10.5$ at 20 °C. The wavelength corresponding to the maximum of the optical absorption band of e_s in MEA [is 910nm (Vannikov & Marevtzev, 1973), it] occupies an intermediate position between λ_{max} in ethanol (700nm) and in ethylamine (1300nm), being close to λ_{max} in the mixture (880nm), though the dielectric constants of MEA and mixture differ more than five times. Thus for liquids of similar chemical composition the position of the absorption maximum of e_s^- is determined by the presence of functional groups, in this case OH and NH_2-groups, and does not depend on the macroscopic characteristics of liquids.

Assuming the liquid structure to play a significant role in determining E_{max} (energy at the maximum of optical density spectrum), we can calculate the values of the correlation parameter g_k in the Kirkwood equation (1) for different liquids. The values of g_k greater than unity indicate that the microscopic regions of liquids have a larger local polarity than it would be expected from the dipole moment values of the molecule,

$$\frac{(D_0 - 1)(2D_0 + 1)M}{9D_0\rho} = \frac{4\pi N}{3}\left(\alpha + g_k\frac{\mu^2}{3kT}\right), \qquad ...(1)$$

where μ and α are respectively dipole moment and polarizability of molecule, D_0 and ρ are dielectric constant and density of liquid respectively.

If the interaction of electron with the nearest polar groups is assumed to be of chief importance, g_k and E_{max} may be expected to correlate. In fact, as shown in Fig. 1 for all liquids at different temperatures and pressures there is the same functional dependence of E_{max} on g_k. A certain scatter of points seems to be due to the insufficiency of using only the parameters and in taking account for the influence of the properties of molecules. For this reason, it was of interest to check the relation between different values of E_{max} and g_k for a liquid by varying the temperature. As it follows from Fig. 2, and Table I there is a linear dependence of E_{max} on g_k in the case of methapole.

TABLE I

T (°c)	3	20	57	83	127	148	208
g_k	3.22	3.15	3.00	2.84	2.53	2.37	1.90
E_{max}, eV	1.98	1.94	1.86	1.78	1.64	1.58	1.37 ± 3.02

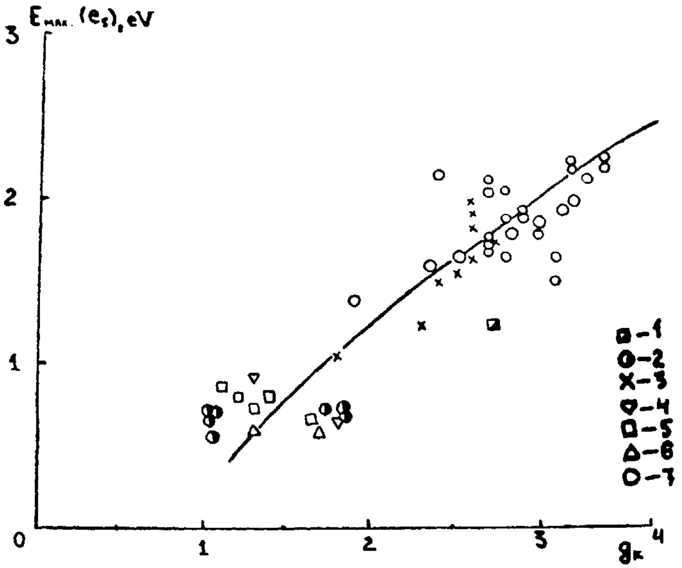

FIG. 1. Relationship between E_{max} and g_k : 1. hydrazine (Seddon *et al.*, 1976); 2. amide (Galvas *et al.*, 1974); 3. H_2O (Seddon *et al.*, 1976; and Freeman, 1973); 4. amines (Seddon *et al.*, 1976; and Freeman, 1973); 5. ammonia (Seddon *et al.*, 1976; and Freeman, 1973); 6. ethers (Freeman, 1973); 7. alcohols (Freeman, 1973; and Chubakova & Bach, 1978).

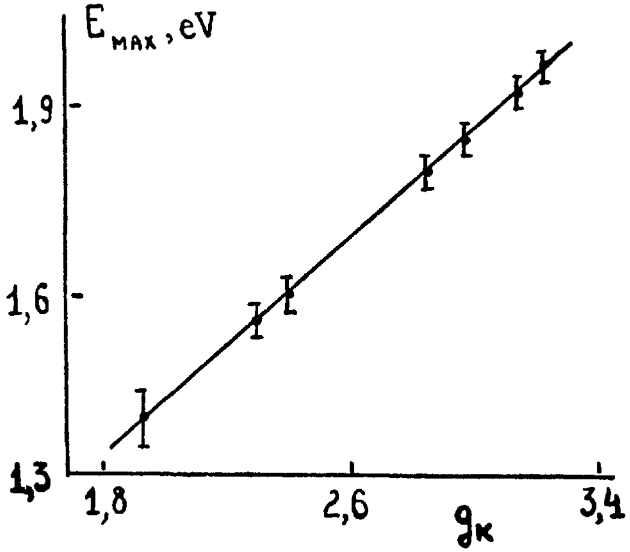

FIG. 2. Relationship between *E*max and g_k methanol (Chubakova & Bach, 1978).

For a detailed study of localization processes, of particular importance are the liquids in which stable solutions of e_s^- are formed. Among organic polar liquids hexamethylphosphortriamide (HMPA) holds a unique position. In this liquid it is possible to generate electrochemically e_s forming stable solution. In HMPA e_s^- is in equilibrium with complexes of the stoichiometry—two electron a sodium cation.

Laser photolysis was used to study the electrochemically generated solvated electrons in HMPA (Mal'tsev & Vannikov, 1977).

Solvated electrons were generated in special electrochemical quartz cells. A cathodic chamber designed as a spectrophotometric vessel allowed us to conduct simultaneous irradiation and optical measurements. If a platinum electrode placed in this electrochemical cell is cathodically polarized it is possible to attain conditions at sufficiently high negative potentials such that electrons escape from the electrode surface into the solution to form solvated electrons. This process was investigated earlier (Krishtalik & Alpatova, 1975). A schematic diagram of the apparatus used in laser photolysis is given in Fig. 3.

The analysiug light from a 1000W xenon lamp supplied with current stabilization enters the cell at right angle to the laser beam and passes through a monochromator to a photomultiplier. The signals were displayed on an oscilloscope and photographed. A Q-switched neodymium laser producing pulses of less than 20ns full width at half maximum was used as the photolysis source. The second mode (λ = 530nm) corresponding to the short wavelength side of the complex absorption band was used in the present work.

After the electrochemical polarization an equilibrium is reached in the solution between solvated electrons and cationelectron associates. The absorption spectra in

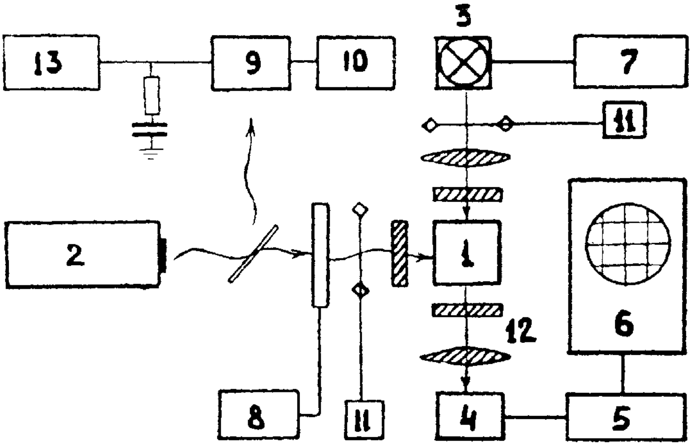

FIG. 3. Schematic diagram of laser photolysis apparatus. 1. Electrochemical cell. 2. Q-switched neodymium laser. 3. 1000W xenon lamp. 4. Monochromator. 5. Photomultiplier. 6. Oscilloscope. 7. Current stabilize. 8. Calorimeter. 9. Pulse form control. 10. High voltage supplier. 11. Shutter. 12. Lens. 13. Pulse voltmeter.

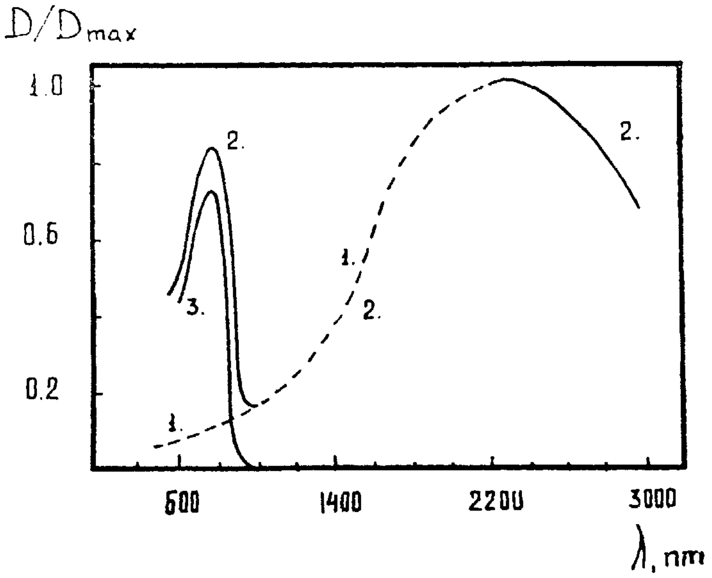

FIG. 4. Optical absorption spectra of e_s^- solutions in HMPA. see text.

this solution are shown in Fig. 4. Curve 1 is an e_s spectrum obtained by pulse radiolysis, 2-spectra of e_s species (Na^+, e_s^{-2}) spectrum obtained by subtraction of e_s^- band from complex band 2. It is seen that the absorption band of e_s^-, overlaps the spectrum of the complex in the region of $\lambda \simeq 600 + 900$nm. The transient absorption band of solvated electrons obtained in pure HMPA on pulse radiolysis allowed one to obtain the absorption band with long wave edge at $\lambda = 960$nm belonging to the complex.

The observed gradual decrease of the blue colour of solvated electron solutions is due to reactions of e_s^- with HMPA molecules or with possible acceptors. The decay curve of e_s differs from the kinetic curve of the complex decay, as it is shown in Fig. 5. However ,the ratio D_{750}/D^2_{980} remains constant and equals 24.5 in a cell of 0.3cm length, as it is shown in Fig. 6.

The observed dependence indicates that the equilibrium between e_s^- and complex is attained long before the beginning of the measurements. On the other hand, the linear dependence of D^2_{980} *vs.* D_{750} unequivocally confirms that two electrons take part in the formation of the complex. A species consisting of two sodium cations and two e_s^- is, in principle, also possible; however, it has been shown in experiments with varying sodium ion concentration that only one cation takes part in the formation of the complex. The obtained data are a direct proof of the existence of equilibrium between e_s^- and complex is attained above composition which we denote (Na^+, e_2^{-2}) without ascribing to it a definite structure as yet. These results allow to determine an equilibrium constant K, that is equal to $4.5 \times 10^3 dm^3 mole^{-1} (Na^+ = 0.2 mole\ dm^{-3})$:

$$e_s^- + e_s^- (Na^+) \underset{k_2}{\overset{k_1}{\rightleftarrows}} (e_2^{-2}, Na^+), K = \frac{k_1}{k_2} \qquad ...(2)$$

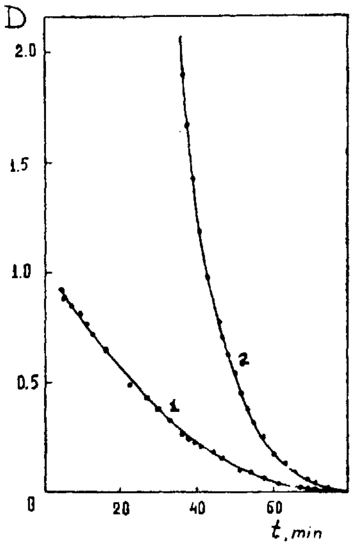

FIG. 5. Decrease of optical absorption $e_s^-(D_{980})$ and (Na^+, e_2^{-2}) (D_{750}) band in 0.2 mol dm^{-3} NaBr solutions after electrochemical generation in HMPA. 1—decay of e_s^- absorption spectrum at 980nm; 2 — decay of (Na^+, e_2^{-2}) band at 750nm.

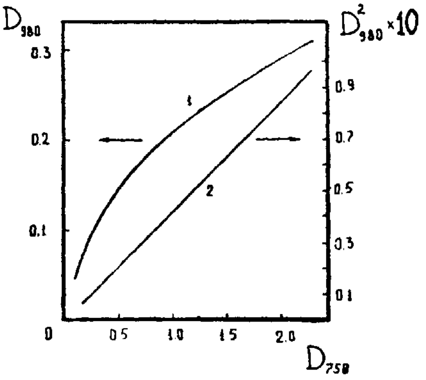

FIG. 6. A plot of e_s^- optical absorptions D_{980} and D^2_{980} v.s. D_{750} of (Na^+, e_2^{2-}) absorption.

Under the action of a laser pulse on 0.2 molar NaBr solution in HMPA containing e_s^- and a complex, the optical density of the complex spectrum shows a transient partial bleaching followed by rapid recovery of the absorption (Fig. 7, curve 2). Simultaneously, a transient increase of optical density in the e_s^- range occurs, which decays as shown in Fig. 7, curve 1. Obviously, the decay rate of (Na$^+$, e_2^{-2}) under the influence of a laser pulse depends on their configuration. There may be different structural forms corresponding to the stoichiometry of the species (Na$^+$, e_2^{-2}. First, it could be a formation of two solvated electrons stabilized in the vicinity of a sodium cation. However, the absence of the ESR spectrum and optical absorption band of solvated electrons in the case of complex formation and the appearance of characteristic spectrum of complex do not support this structure. On the other hand, we may consider that in this case, photodissociation of bielectron complex should occur during the laser pulses on the way (3) with the formation of two e_s^- or on the way (4) with the formation of e_s^- and noncontact ion pair :

$$(\mathrm{Na}^+, e_2^{-2}) \xrightarrow{h\nu} \begin{cases} \nearrow 2e_s^- + \mathrm{Na}^+ & \qquad \ldots(3) \\ \searrow e_s^- + (\mathrm{Na}^+, e_s^-) & \qquad \ldots(4) \end{cases}$$

However, we cannot discriminate between reactions (3) and (4) since the spectrum of e_s^- and noncontact ion pairs (Na$^+$, e_s^-) are practically indistinguishable (Mal'tsev & Vannikov, 1977). Finally, the species (Na$^+$, e_2^{-2}) may be a sodium anion Na$^-$ dissociating in a two-stage process under the action of a laser pulse : i.e., after the first transient step (5) induced by laser pulse, one should expect to observe as a

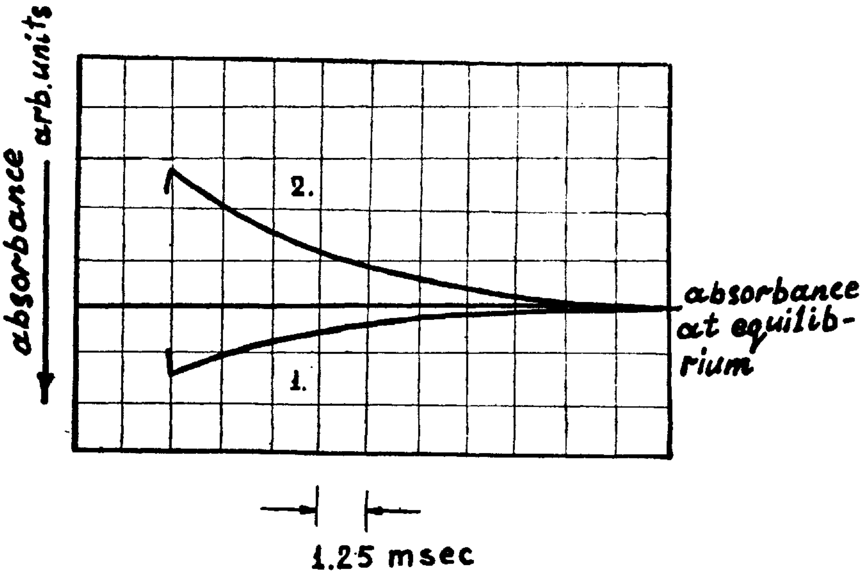

FIG. 7. Typical oscillograms observed by laser photolysis. 1. Change of e_s^- absorption at 1060 nm. 2. Change of (Na$^+$, e_s^{-2}) band absorption at 750nm. horizontal axis — 1m/div., vertical axis-arb. units.

comparatively slower second stage (6) the appearance of the same amount of solvated electrons limited by thermal dissociation of sodium atoms.

$$\mathrm{Na}^- \xrightarrow{h\nu} \mathrm{Na} + e_s^- \qquad \ldots(5)$$

$$\mathrm{Na} \xrightarrow[\text{therm.}]{} \mathrm{Na}^+ + e_s^- \qquad \ldots(6)$$

Possibly because of the comparatively long time of resolution (10ns of laser apparatus), the second stage was not observed and the existence of this reaction (6) during a much shorter time is not excluded. It should be noted that the ESR spectrum of sodium atom Na was not observed when the same solution was exposed to light in stationary conditions. So we believe that complex has a structure of bielectron stabilized on sodium cation, but not anion Na^-.

The extinction coefficient of (Na^+, e_2^{-2}) at $E_{\max}$ was directly estimated from the optical densities of e_s^- and bielectron determined at the end of the laser pulse, taking into account that the decay of bielectron leads to the formation of the e_s^- according to reaction (3) or (4) :

$$\mathcal{E}_{750}^{(\mathrm{Na}^+,\, e_2^{-2})} = 2\mathcal{E}_{1060}^{e^-s} \cdot \Delta D_{750}^{(\mathrm{Na}^+,\, e_2^{-2})} / \Delta D_{1060}^{es^-}$$

$$= 4 \times 10^4 \mathrm{dm}^3\mathrm{mol}^{-1}\mathrm{cm}^{-1},$$

The oscillator strength of bielectron band was found to be 0.7.

Laser photolysis on the high energy side of the (Na^+, e_2^{-2}) absorption band causes a decrease of its density, whilst its shape remains unchanged, revealing that it is homogeneously broadened as it is shown in Fig. 8. The wavelength of a laser pulse is 530nm. The quantum yield of bielectron decay was obtained as 0.075.

The low quantum yield indicates that the generation of excited states and their autoionization occurs when light of $\lambda = 530$nm is absorbed by bielectron, so that the probability of direct excitation from the ground state into the continuum is small.

As demonstrated above, a considerable amount of e_s^- and bielectron exists in equilibrium (2) in solutions of NaBr in HMPA. The appearance of excess solvated electrons in the solution after the action of a laser pulse ($\lambda = 530$nm) causes a disturbance of this equilibrium. The process of re-establishing the former equilibrium in this system is described by kinetic equation (7) and is shown in Fig. 9 :

$$\ln\left[\frac{[e_s^-]_{in}\,(a - \Delta\,[e_s]_t)}{a\,([e_s^-]_{in} - \Delta\,[e_s^-]_t)}\right] = 4(a - [e_s^-]_{in})\, k_1 t$$

$$a = \frac{4K([e_s^-]_{in} + \Delta\,[e_s^-]_{\mathrm{laser}}) + 1}{4K} - [e_s^-]_{in}. \qquad \ldots(7)$$

where $[e_s^-]_{in}$, $\Delta\,[e_s^-]_{\mathrm{laser}}$, $\Delta\,[e_s^-]_t$ are the initial equilibrium concentration of e_s^- after electrochemical generation, the additional concentration of e_s^- due to laser pulse, the concentration of e_s^- changing in accordance with (2).

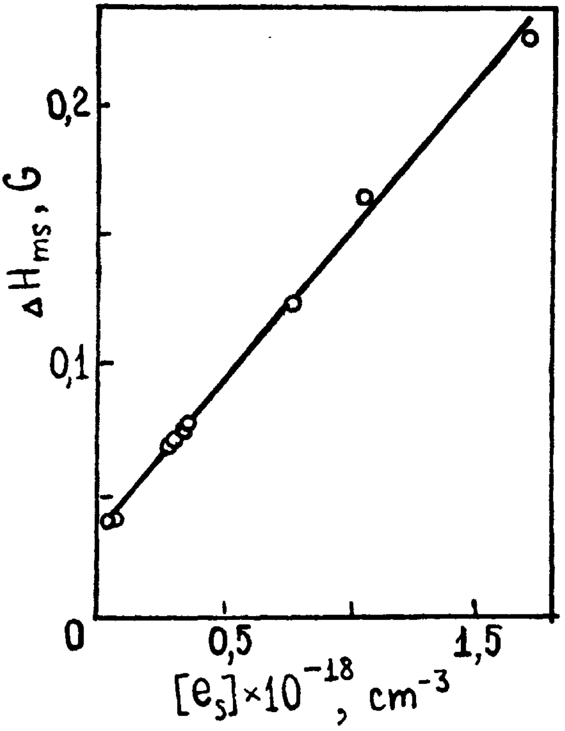

FIG. 8. Influence of laser light ($\lambda = 530$nm) on (Na^+, e_2^{-2}) absorption band (electrochemical generation. Upper curve snows the bielectron spectrum before laser action. Lower curve refers to the spectrum of these species right after a laser pulse (10ns).

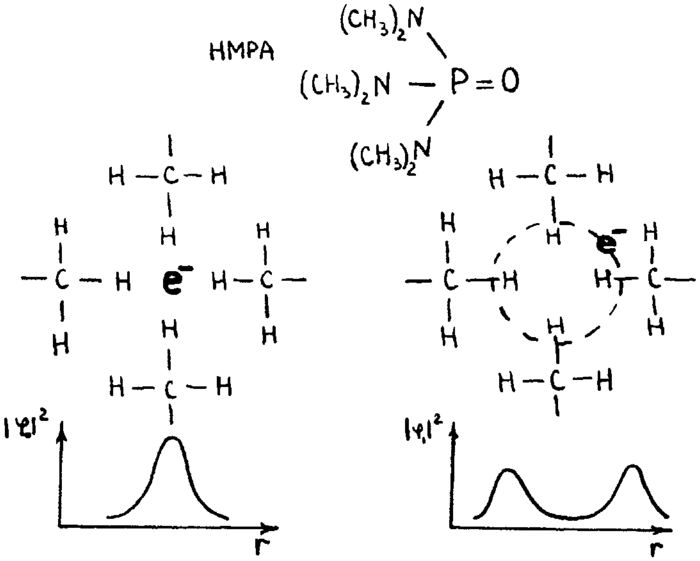

FIG. 9. Signals observed at 1060nm in e_s^- solution after laser pulse. — Observed trace, 0 — calculated according to (7).

Taking from the oscilloscope trace of e_s^- decay at any moment after a laser pulse the corresponding value of e_s^- concentration and substituting it into equation, we get the rate constant of bielectron formation $k_1 = 1.2 \times 10^6\ \mathrm{dm^3mol^{-1}s^{-1}}$.

The rate constant for the complex decay (k_2) was found to be $k_2 = k_1/K = 2.7 \times 10^2\mathrm{S^{-1}}$.

The next step in the development of these studies was to investigate the molecular structure of e_s^- in HMPA. As the first result it was found by active laser Raman spectroscopy (Achmanov *et al.*, 1979) that there is a change in the vibration frequency of the C-H bond ($1436\mathrm{cm^{-1}}$) in HMPA in the presence of e_s^-. This effect is explained by the appearance of additional electron density δe at the C-H bonds of HMPA molecules forming the first solvation layer of e_s^- (Fig. 10). This led to the assumption that the electron in HMPA in the ground state (wave function $\psi_N(e_s^-)$, energy E_N) is a charge transfer complex described by two limiting structures; electron localized in the cavity ψ_0, and electron residing on the extended intermolecular arbital composed of the first solvation layer molecules

$$\text{Ground state } e_s^- : \psi_N\,(e_s^-) = a\,\psi_0 + b\,\psi_1$$

The value of the charge transfer is determined by coefficients a and b

$$\delta e = \frac{b^2}{a^2 + b^2}$$

In the excited state (wave function $\psi_V\,(e_s^*)$, energy E_V) electron is mainly localized on the intermolecular orbital and the absorption spectrum of e_s ($E_{\max}$) is the band corresponding to charge transfer between these two states :

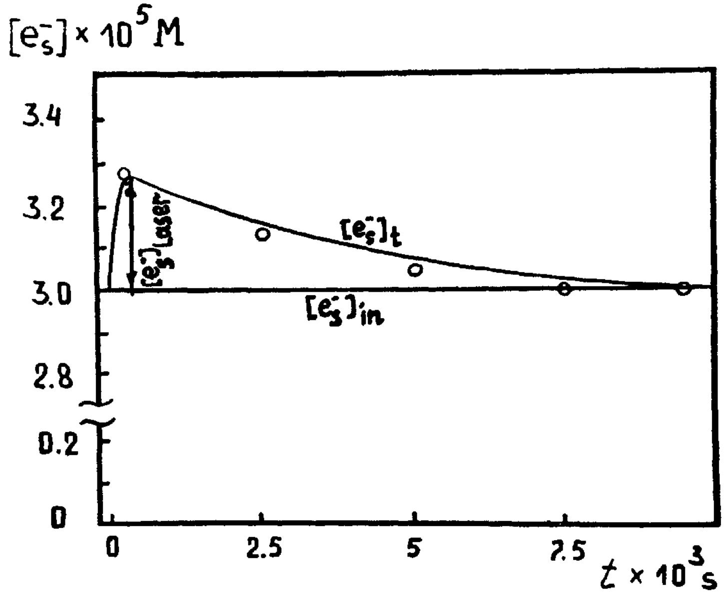

FIG. 10. Solvated electron in HMPA. ψ_0 — wave function of electron localized in the cavity. ψ_τ — wave function of electron residing on the extending intermolecular orbital.

$$\text{Excited state } e_s^* : \psi_V(e_s^*) = b^*\psi_0 + a^*\psi_1$$

$$E_{max} = h\nu_{max} \, . \, e_s^- = E_V = E_N$$

In order to compare quantitatively E_{max} of the absorption band of e_s^- with the molecular characteristics of liquids it is necessary to determine the level of e_s^- relative to vacuum, which so far has not been done for polar organic liquids.

In HMPA ESR spectrum of e_s^- is characterized by a single line of the Lorenz shape and width, which depends on the concentration e_s^- (Grishina *et al.*, 1978). It can be seen from Fig. 11 that the line width increases linearly with the concentration of e_s^- and that the initial width is 0, 037 Causs. Experimental dependence is given by

$$\Delta H_{ms} = 0.037 + 67 \, [e_s^-]$$

$$(G) \qquad (\text{mole dm}^{-3}) \qquad \ldots(8)$$

If the linewidth is controlled by the frequency (ν_s) of spin reorientation in double collisions, then (13)

$$\nu_s = (7/T_2 - 7/T_2) = 7.5.10^7 \, (\Delta H_{ms} - \Delta_{ms,\,0}) \qquad \ldots(9)$$

where H_{ms} and T_2 are the linewidth and the spin-spin relaxation time, $H_{ms,0}$ and $T_{2,\,0}$ are the same entities extrapolated to zero concentration of e_s^-. ν_e is connected with the paramagnetic particle collision frequency (ν_d) by the relation

$$\nu_e = f\nu_d \qquad \ldots(10)$$

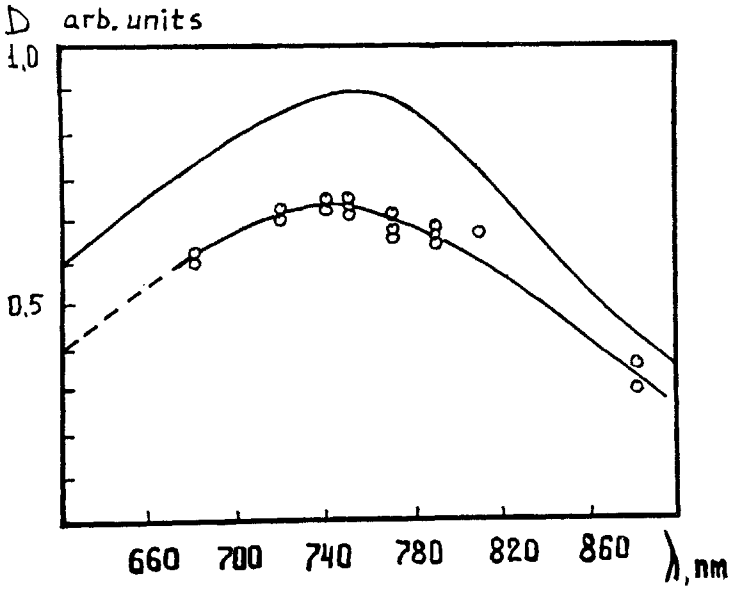

FIG. 11. Relationship between ΔH_{ms} and $[e_s^-]$.

where p is the collision reorientation probability, the maximum p value is 0.5.

The frequency of double collisions of single charged ions (solvated electrons) is

$$\nu_d = k_d\,[e_s^-] \qquad \text{...(11)}$$

where diffusion constant k_d is

$$k_d = \frac{4\pi\mu e N_0}{1000 D_0}\left\{\exp\left(\frac{e^2}{zD_0KT}\right) - 1\right\} \qquad \text{...(12)}$$

Taking into account that mobility μ is equal $5,5 \times 10^{-4}\mathrm{cm}^2\mathrm{V}^{-1}\mathrm{S}^{-1}$ the reaction radius r is $r = 2r\,(e_s^-)$ 8Å (Mal'tsev & Vannikov, 1977) we find $k_d = 1,25 \times 10^9$ $\mathrm{mole}^{-1}\mathrm{S}^{-1}\mathrm{dm}^3$.

Thus for e_s in HMPA one should expect, from (9)–(12), the relationship

$$\Delta H_{ms} = \Delta H_{ms\cdot 0} + 82p\,[e_s^-] \qquad \text{...(13)}$$

Relation (9) is close to the theoretical equation (13) within the accuracy of $[e_s^-]$, $r(e_s^-)$. μ evaluations, if the spin reorientation probability during collisions is a maximum. It shows that the ESR linewidth of e_s^- is determined by the frequency of mutual collisions of e_s^-.

We have discussed some properties of e_s^- in organic liquids. We believe that the knowledge of these properties is necessary for better understanding of electrode processes with participation of e_s^-, such as cathodic generation of electrons, photoemission of electrons from metal into solution and so on.

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Discussion

N. SUBRAMANYAN (*Central Electrochemical Research Institute, Karaikudi*) : Does the life of solvated electron vary with the nature of the solvent ?

A. V. VANNIKOV (*Instituie of Electrochemistry, Academy of Sciences of USSR, Moscow*) : Yes. It does.