ENERGY CHARACTERISTICS OF SURPLUS ELECTRONS IN POLAR MEDIA

UDC 541.13

R. R. Dogonadze, L. I Krishtalik,
and Yu. V. Pleskov

A qualitative examination of the energy characteristics of electrons in polar liquids, in particular, the energies of solvation of localized and delocalized electrons, the energies of reorganization of the solvent, and the spectra of the solvated electrons, is given, and the photoemission and thermal emission of electrons from solutions in polar solvents are discussed. The available experimental data are analyzed thoroughly and estimates of some of the energy characteristics of the electrons in various polar liquids are given.

The important role that is ascribed to solvated electrons in radiochemical, photoelectrochemical, and some electrochemical processes explains the interest displayed in the last decade in the structure, properties, and reactivity of the solvated electron in polar media [1, 2]. The photoemission investigations carried out in recent years have yielded important information regarding both localized (solvated) and delocalized electrons. The present communication includes an attempt to represent the energy pattern of the electron-polar medium system (for example, an electrolyte solution) and, on the basis of published data, to estimate some energy characteristics of electrons in the major solvents.

QUALITATIVE DESCRIPTION

We will examine the energy relationships for different states of the electron using Fig. 1.

Level V, 0 corresponds to the electron in vacuo and to the solvent in the equilibrium state. It is implied that the conducting liquid phase as a whole does not bear a charge, so that the electrical field is absent in vacuo; however, if this condition is not satisfied, then, as is usually done [3], it is assumed that the electron is found near the liquid surface at a distance that is small but large enough so that one can disregard the field of the double layer and the image forces.

Let us transfer the electron into the liquid and give it the possibility of moving so rapidly that orientation polarization will not have time to interact with it. The energy effect (A_{el}) of this sort of process will be determined by the energy of interaction of the electron with a practically inertia-free (with respect to the electron under consideration) electronic polarization (A_e)* and by the work required to transport the electron through the surface potential difference (χ). Level e,0 in Fig. 1 corresponds to this state – an electron interacting only with the electronic polarization. Actually, as noted above, the state in which interaction with the orientation polarization is absent is accomplished only by virtue of the rapid motion of the electron, and the electron consequently has a definite kinetic energy K, i.e., it is found at some level above the

---

* More precisely, A_e includes not only the interaction with the electronic polarization but also the nonelectrostatic interaction with the molecules of the medium.

Institute of Electrochemistry, Academy of Sciences of the USSR, Moscow. Translated from Élektrokhimiya, Vol. 10, No. 4, pp. 507-514, April, 1974. Original article submitted January 24, 1973.

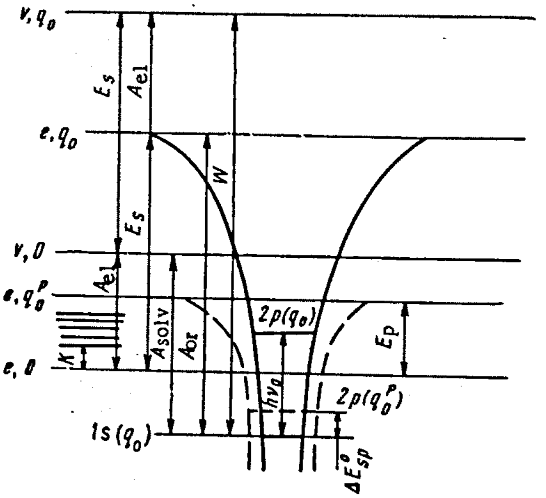

Fig. 1. Energy levels in the electron-polar liquid system.

e,0 level. The latter can be considered to be an analog of the bottom of the conductivity zone.* It follows from the definition of A_{el} that this is a "real" energy (in analogy with the real work of solvation).

The electrons in the conductivity zone are delocalized. The localization of electrons, i.e., their transition to the bonded state, is caused by the formation of a potential well induced by reorientation of the dipoles. The creation of the appropriate configuration of dipoles requires the expenditure of energy E_s. In expending this energy, we convert the system from the V,0 state to the V,q_0 state: an electron in vacuo and the solvent with the corresponding configuration, i.e., with oriented dipoles and (possibly) the formation of a cavity or other changes in the liquid structure; the state of the solvent is represented schematically by coordinate q_0. Introducing the electron into the solution now, we gain, in addition to energy $A_{el} = A_e - e\chi$ ($e > 0$ is the absolute magnitude of the electron charge), the electron energy in the potential well (A_{or}). The total real work of solvation is $A_{solv} = A_{el} + A_{or} - E_s$.† It is easy to see that, depending on the ratio of the A_{or} and E_s values, the total work of solvation may be both greater and less than the work of solvation of the delocalized electron (A_{el}). In precisely the same way, A_{solv} may be both greater and less than A_{or}.

The A_{or} value is similar to the ionization energy of the atom. This is the energy of detachment of an electron from the ground level to form a delocalized electron in the medium rather than in vacuo, i.e., an electron in the conductivity zone. If there are other levels in addition to the ground level in the potential well, transition from the ground level to excited levels (of the 1s → 2p type) may be observed. The maximum in the absorption spectrum of the solvated electron is usually linked with a transition of this type.‡ In this case it is important to emphasize that this transition, in conformity with the Franck-Condon principle, occurs for invariable coordinates of the heavy subsystem, i.e., the solvent molecules. The potential well shown in Fig. 1 by means of the continuous line corresponds to a solvent configuration that is an equilibrium one for the 1s state. This configuration is not an equilibrium one for the 2p state (different size and symmetry of the electron cloud), but as noted above, light absorption occurs precisely for this configuration. The equilibrium potential well for the 2p state (dashed line) differs in both form and spacing of the energy levels [different work of formation of the corresponding solvent configuration of the solvent (E_p)]. It is easy to see that the energy of the absorbed quantum ($h\nu_0$) is not directly associated with the difference in the equilibrium energies in the 1s and 2p states (ΔE_{sp}^0). Of course, energy $h\nu_0$ cannot exceed A_{or} but may be not only less than but also larger than A_{solv} or A_{el}. One cannot therefore identify the energy of solvation of the electron with the energy corresponding to the absoprtion band maximum.

The maximum energy on the $W = A_{or} + A_{el}$ diagram is the work expended in the transition of the electron from equilibrium level 1s to a vacuum, during which the configuration of the solvent in solution remains constant. In other words, this is the work function of the electron, which, in principle, might have been determined by means of photoemission in vacuo (more accurately, of course, in the solvent vapors) from a solution of solvated electrons, since the configuration of the solvent does not have time to relax to a new equilibrium state during this rapid process.

---

* In contrast to an ideal crystal, the energy zones do not have sharp boundaries in such a disordered system as a solvent. However, diffusion of the bottom of the conductivity zone does not interfere with the definition of A_{el} from the photoelectric work function (see below) by extrapolation of the photocurrent from the region of sufficiently high energies, i.e., the region in which the effect of erosion becomes nonessential.

† Strictly speaking, the nonelectrostatic interaction with the molecules of the medium is different for the localized and delocalized electrons. In the latter equation, this change is formally included in the A_{or} value, which is basically determined by the interaction of the electron with the oriented dipoles.

‡ According to another point of view (see [4], for example), to which our attention was directed by A. M. Brodskii, the principal band in the absorption spectrum of the solvated electron corresponds to the transition from the 1s level to the zone.

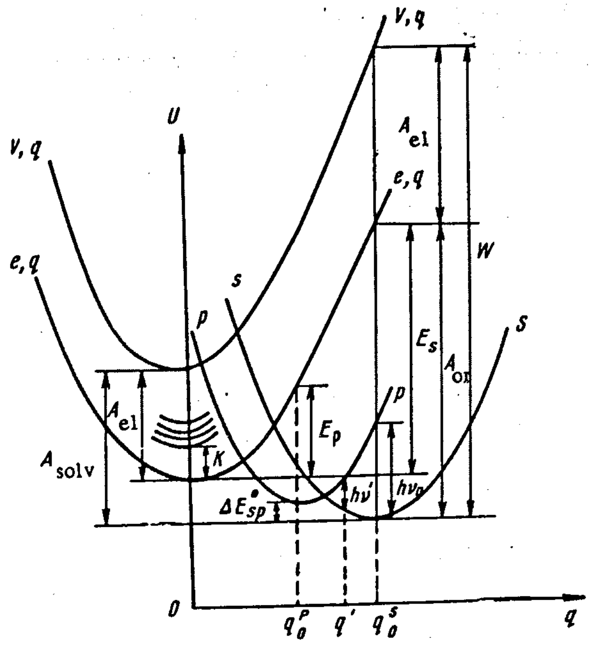

Fig. 2. Energy terms of the electron–polar solvent system.

The construction in Fig. 1 was carried out only for two solvent configurations – q_0 and q_0^p, which correspond to the equilibrium solvation of the electron in the 1s and 2p states. However, the solvent configuration may also be a nonequilibrium one, and an analogous energy diagram with its E_s, A_{or}, and $h\nu_0$ values can be constructed for each of these possible configurations (q). A large selection of possible $h\nu_0$ values determines, at least partially, the diffusion of the spectral line into a broad band, the maximum of which corresponds to the most probable starting state, i.e., q_0.

The corresponding ratios are seen more graphically in Fig. 2, in which the energy is plotted as a function of the generalized coordinate q, which, as in the theory of charge-transfer reactions, describes the state of orientation polarization of the solvent [5].* Curve V,q corresponds to changes in the energy of the system owing to fluctuations in the solvent (electron in vacuo), while curve e,q has the same significance but the electron is found in the liquid and interacts only with its electron polarization. The orientation polarization of the solvent ($q = 0$) corresponds to the equilibrium state (the minimum of the curves). The q_0 value corresponds to the equilibrium configuration of the solvated electron in the 1s state. The work expended in the formation of this solvent configuration (E_s) has the same significance as the reorganization energy used in the theory of chemical reactions [5]. The s and p curves show changes in the energy of the system during fluctuation of the configuration of the solvent about the equilibrium values for the s and p states (q_0 and q_0^p). Light absorption – transition from the 1s to the 2p state – occurs with an invariable solvent configuration. If it corresponds to the starting equilibrium state, quantum $h\nu_0$ is absorbed at any arbitrary q value, for example, h_{ν}' is absorbed for q'. The nonequilibrium values and other energy characteristics can be similarly found.

As noted above, the nonequilibrium work function (W) can be determined from data on the photoemission of electrons from solution. The real heat of solvation can, in principle, be determined from the temperature dependence of the current of thermoelectronic emission† from a solution of solvated electrons. If the equilibrium between the localized and delocalized electrons is not disrupted during the emission process and the energy distribution of the latter electrons remains an equilibrium value, the temperature dependence of the thermal emission will be determined by the equilibrium "thermal work function" of the electron, i.e., what amounts to the same thing as the real heat of solvation. However, if the rate of emission is sufficiently high and the equilibrium is disrupted, the experimentally determined heat of thermal emission

---

* The representation of the energy as a function of only one coordinate was done for the sake of convenience in the qualitative examination. In actuality, of course, the picture is multidimensional; however, this is not reflected in the qualitative conclusions of the present study. We note that the motion of the system along coordinate q is considered to be classical.

† In this determination, it is assumed that the contribution of the change (with temperature) in the potential difference on the liquid–vapor boundary is small.

TABLE 1. Energy Characteristics of the Electron (eV)

Solvent	H_2O	NH_3	HMPT	Methanol	Ethanol	DME	Propylene carbonate
A_{solv}	1,47	1,7 [illegible]	(1,0) * [illegible]	–	–	–	–
A_{el}	1,3	–	(0,9) **	(0,9) [14] ** 0,4 ***	(0,75) [14] **	(0,55) [14] ** –0,1 ***	(1,0) **
$h\nu_0$	1,72 [illegible]	0,88 [illegible]	0,45 [illegible]	1,98 [illegible]	1,77 [illegible]	–	–
W	–	(1,4–1,8) [illegible] (1,42–1,6) [illegible] (1,85) [illegible]	(1,34–1,4) [illegible]	–	–	–	–
V_{ms} for Hg	0,26 [16]	–	–	0,53 [17]	–	0,63 [19]	–
at the zero							
point	1,33 [illegible]	1,33 [illegible]	1,46 [illegible]	1,33 [illegible]	1,36 [illegible]	1,43 [21]	–

* The less reliable data are in parentheses.
† No correction for the Volta potential was introduced.
‡ Conversion of the data in [14].

will no longer be an equilibrium value but rather a certain effective activation energy that is greater or equal to the real heat of solvation. Its value depends on the mechanism of the process.

Let us compare two possible paths – direct transition of the electron, due to fluctuations of the orientation polarization of the solvent, from the bonded 1s state into a vacuum and (a more complex path) transition of the electron initially into the zone and then acquisition by it of kinetic energy sufficient for emergence from the liquid. The activation energy for direct emergence into a vacuum (this corresponds to the intersection of the s, and V, q terms) is always greater than the activation energy for transition into the zone (intersection of the s and e,q terms), and it therefore can be shown that the second path is preferred. However, one must take into account that the acquisition of kinetic energy by delocalized electrons from the medium is an extremely slow process, due to the weak interaction of the electrons with thermal phonons. The first variant – direct transition of the electron from the bonded state into a vacuum with bypassing of the zone – may therefore be the primary path.

The emergence into a vacuum from the bonded state may also be realized by different means. For example, transition from term s to term p and from the p state into a vacuum is the more favorable path for the arrangement of potential curves depicted in Fig. 2. However, if the minimum of term p were, for example, shifted to the right of term s (which is, in principle, possible), direct transition into a vacuum from the s state would be more favorable. In addition, one should bear in mind the possibility of the difference in the terms of the bonded states of the electron in the depths of the liquid and near its surface.

Apropos of this we note that in the scheme (Fig. 2), a substantial difference between the activation energies for thermal transition of the electron into the zone and for its excitation by light (A_{or}) is distinctly apparent – the latter value is generally greater.* It is also seen from Fig. 2 that the thermal activation energy is greater or equal to the distance between the 1s level and the bottom of the conductivity zone.

In concluding this discussion, it should be emphasized that the figures presented above are illustrative in character. Although the principal qualitative results of our reasoning do not depend on the arbitrary character of the construction of these schemes, the quantitative relationships between the different values and different systems may vary over broad limits.

COMPARISON WITH EXPERIMENT

The values of a number of energy characteristics of the electron in several solvents are presented in Table 1. We will initially examine the methods used to obtain these values.

Solvation Energy

The real standard energy of hydration of the electron was calculated on the basis of the thermodynamic cycle;

$$H_{gas} \rightarrow H^+_{gas} + e^-_{gas} \quad H^+_{gas} + H_2O \rightarrow H^+_{aq}; \quad e^-_{gas} + H_2O \rightarrow e^-_{aq}; \quad H^+_{aq} + e^-_{aq} \rightarrow H_{aq};$$
$$H_{aq} \rightarrow H_{gas} + H_2O.$$

---

* Within limits, A_{or} may be equal to the thermal activation energy. A similar situation is realized in barrierless charge transfer (see [5], for example).

It is 1.57 eV [6].* This value is relative to the standard state (1 mole/liter). It is necessary to exclude the concentration term (~ RT ln 1/55) for its subsequent comparison with A_{el}, which is determined from the photoemission data and is the concentration-independent difference in the energy levels. The thus corrected A_{solv} value is 1.47 eV.

The chemical heat of solvation of the electron for liquid ammonia was calculated [8] from the heats of dissolving of the alkali metals. The value obtained (1.7 eV) differs from the free energy of solvation by the magnitude of the entropy term, which probably does not exceed 0.1 eV [2]. The correction for the surface potential difference (χ) was not taken into account in this estimate.

While the error in the determination of A_{solv} for water scarcely exceeds 0.1 eV, it may be even higher for hexamethylphosphoric triamide (HMPT). We present the experimentally found value of 1.0 eV as the real heat of solvation for HMPT; this value was found by Delahay and co-workers [9] as the energy of activation of the thermoelectronic emisson from a solution of solvated electrons (obtained by dissolving sodium metal in HMPT). However, this activation energy may, as discussed above, exceed A_{solv}. In addition, the activation energy measured in [9] includes a term associated with the change in the potential difference (due, in particular, to specific adsorption of sodium) on the surface of HMPT, from which emission of electrons proceeds, as the temperature changes.

Energy of the Bottom of the Conductivity Zone

The energy of the bottom of the conductivity zone was determined on the basis of measurements of the photoelectric work function of the electron (W_{ms}) from a metal (mercury) to the corresponding solvents. The work function for HMPT and propylene carbonate was determined in the present study; the details of the experiment will be published separately. The electrocapillary maxima were taken from [10, 11].

As Frumkin has shown [12] (see also [13]), $A_{el} = W_{mv} - W_{ms} - eV_{ms}$, where W_{mv} is the work expended in removing the electron from a metal into a vacuum, and V_{ms} is the Volta potential of the metal-solution.† Both W_{ms} and V_{ms} are linearly dependent on the electrode potential, so that one does not need to know the electrocapillary maximum in a given solvent for the calculation of A_{el} but can perform the calculation for an arbitrary potential. Unfortunately, at present the Volta potentials are known only for a few solvents. The accuracy in the determination of A_{el} for water was ± 0.1 eV, but it is probably lower for other solvents.

Energy $h\nu_0$ is determined from the corresponding maximum in the absorption spectrum of a solution of solvated electrons. The latter is obtained either by dissolving an alkali metal or by electrochemical generation of electrons in a solvent [19]. The $h\nu_0$ values are usually presented with an accuracy of no less than 0.1 eV.

The nonequilibrium work required to remove an electron from the solvated state into a vacuum can be determined as the threshold of photoelectronic emission from a solution of the solvated electron in the appropriate solvent. Unfortunately, threshold measurements are usually extremely sensitive to the method of extrapolation of the dependence of the photocurrent on the energy of the light quantum. There is still no precise theory of photoelectronic emission from electrolyte solutions that would render this sort of extrapolation reliable. Delahay [20], on the basis of model concepts, has proposed a formula for extrapolation, has determined the work function for HMPT, and has also converted the experimental data of Hasing [21] for liquid ammonia.

The thus measured work functions, which are presented in Table 1, can be considered to be an estimate below the value symbolized by W in Figs. 1 and 2. The symbol W is the work function corresponding to the equilibrium configuration of the solvent (q_0). A substantial decrease in the work function can be observed when the deviation of this configuration from the equilibrium value is small (see Fig. 2 on the side of decreasing q), and this leads to a decrease in the experimental photoemission threshold [22].

---

* The value 1.72 eV previously presented in [7] is too high, since the free energy of dissolving of atomic hydrogen was not taken into account in the calculation.

† No correction for the Volta potential was introduced in [13-15] in the determination of A_{el} for water, methanol, and dimethylformamide (DMF). As seen from the V_{ms} values presented in Table 1 (for mercury), this entails a considerable error. Using the data on V_{ms} for water [16] and values calculated by Damaskin from [17, 18] for methanol and DMF, we converted the experimental results of [13-15] to determine A_{el} of these solvents.

On the basis of the data presented in Table 1, one can estimate several values that characterize the energy states of the dry and solvated electron in solution.

Let us first examine the difference between A_{solv} and A_{el}, i.e., the difference between the levels of the "dry" and solvated electrons. For water, it is ~ 0.2 eV. Thus equilibrium between the hydrated and "dry" electrons can be established in this solvent, and the equilibrium concentration of the latter is not vanishingly small.* This may be manifested, for example, in investigations of the reactivity of the solvated electron, etc.

As seen from Table 1, A_{el} varies over broad limits: from 1.3 eV for water to -0.1 eV for DMF. However, it follows from the closeness of the refractive indexes (n) of the investigated solvents that their electronic polarizations should not have differed so markedly. It can be assumed that the marked change in A_{el} on passing from one solvent to another reflects mainly the difference in the surface potential differences (χ).† According to the estimates in [23], χ for water is 0.1-0.2 V, and the negative end of the surface dipole is directed to the outside. One can conclude that the surface potential difference has a positive sign for alcohols and, particularly for DMF, the difference in χ for water and DMF approaches 1 V [close to the value (0.85 V) presented in [24]].

Another interesting problem is associated with the position of the first excited level of the solvated electron [$2p(q_0)$]. If the A_{solv} and $h\nu_0$ values are compared, it is seen that the $2p(q_0)$ level in water lies 0.15 eV higher than the "zero reading" (i.e., the level of the electron in vacuo for an equilibrium configuration of the solvent). On the other hand, in liquid ammonia and HMPT this level in all likelihood is substantially lower than the zero reading.

The total depth of the well, i.e., the energy that must be imparted to the solvated electron in order to transfer to the zone corresponding to the nonequilibrium solvent, is $A_{or} = W - A_{el}$. It can be estimated only for HMPT to be 0.5 eV (however, one must bear in mind that the accuracy of both values for this solvent is low).

The energy of reorganization of the solvent $E_s = W - A_{solv}$ can be estimated only approximately: the chief error is associated with the inaccuracy in the determination of W. For HMPT, $E_s \approx 0.4$ eV.

The other path makes it possible to estimate the lower limit of E_s with greater accuracy. It follows from Fig. 1 that $E_s = A_{or} - A_{solv} + A_{el}$. Since $h\nu_0 \leq A_{or}$, one can write $E_s \geq h\nu_0 - A_{solv} + A_{el}$. For HMPT we obtain $E_s \geq 0.35$ eV, which does not contradict the value found above. For water, $E_s \geq 1.45$ eV, and all three numbers used to calculate E_s are known with an accuracy of no less than 0.1 eV. One's attention is directed to the impressive value of the reorganization energy, which exceeds the energy of one hydrogen bond by a factor of ~ 8.

We thank B. B. Damaskin for providing us with data on the Volta potentials for methanol and DMF and A. V. Vannikov and Yu. Ya. Gurevich for proofreading the manuscript and making useful comments.

LITERATURE CITED

1. A. K. Pikaev, The Solvated Electron in Radiation Chemistry [in Russian], Nauka, Moscow (1969).
2. E. J. Hart and M. Anbar, The Hydrated Electron, Wiley (1970).
3. R. Parsons, Some Problems of Modern Electrochemistry [Russian translation], Izd. Inostr. Lit., Moscow (1958), p. 125.
4. G. Kenney-Wallace and D. C. Walker, J. Chem. Phys., 55, 447 (1971).
5. R. R. Dogonadze and A. M. Kuznetsov, Progress in Science, Electrochemistry [in Russian], VINITI, Moscow (1969), p. 3.
6. Z. A. Rotenberg, Élektrokhimiya, 8, 1198 (1972).
7. J. H. Baxendale, Radiation Res., Suppl., No. 4, 139 (1964).
8. J. Jortner, J. Chem. Phys., 30, 839 (1959).
9. B. Baron, P. Delahay, and R. Lugo, J. Chem. Phys., 53, 1399 (1970).
10. R. V. Ivanova and M. G. Fomicheva, Élektrokhimiya, 8, 1259 (1972).

---

[*] It follows from the $A_{solv} - A_{el}$ value that the ratio of the equilibrium concentrations of the "dry" and hydrated electrons in water can be estimated by a value of the order of 10^{-3}.

[†] Nevertheless, one must bear in mind that in addition to χ, interaction of a nonelectrostatic character of the electrons with molecules of the medium, which may differ appreciably for different solvents, also makes a contribution to A_{el}.

11. T. Biegler and R. Parsons, J. Electroanalyt. Chem., 22, App. 4 (1969).
12. A. N. Frumkin, Élektrokhimiya, 1, 394 (1965).
13. Yu. V. Pleskov and Z. A. Rotenberg, J. Electroanalyt. Chem., 20, 1 (1969).
14. L. I. Korshunov, Ya. M. Zolotovitskii, and V. A. Benderskii, Izv. Akad. Nauk SSSR, Ser. Khim. 802 (1972).
15. Ya. M. Zolotovitskii, V. A. Benderskii, S. A. Babenko, L. I. Korshunov, and T. S. Rudenko, in: The Double Layer and Adsorption on Solid Electrodes [in Russian], Vol. 3, Izd. Tartusk. Univ. (1972), p. 119.
16. J. E. B. Randles, Trans. Faraday Soc., 52, 1573 (1956).
17. B. Case and R. Parsons, Trans. Faraday Soc., 63, 1224 (1967).
18. I. M. Ganzhina, B. B. Damaskin, R. I. Kaganovich, and R. V. Ivanova, Élektrokhimiya, 7, 362 (1971).
19. N. M. Alpatova, E. I. Mal'tsev, A. V. Vannikov, and S. E. Zabusova, Élektrokhimiya, 9, 1034 (1973).
20. P. Delahay, J. Chem. Phys., 55, 4188 (1971).
21. J. Häsing, Ann. Physik, 37, 509 (1940).
22. D. A. Copeland, N. R. Kestner, and J. Jortner, J. Chem. Phys., 53, 1189 (1970).
23. A. N. Frumkin, Z. A. Iofa, and M. A. Gerovich, Zh. Fiz. Khim., 30, 1455 (1956).
24. I. M. Ganzhina, B. B. Damaskin, and R. I. Kaganovich, Élektrokhimiya, 8, 93 (1972).
25. J. M. Brooks and R. R. Dewald, J. Phys. Chem., 72, 2655 (1968).
26. L. M. Dorfman, in: The Solvated Electron, Amer. Chem. Soc., Washington (1965), p. 36.
27. G. K. Teal, Phys. Rev., 71, 138 (1947).
28. Handbook of Chemistry [in Russian], Vol. 1, Khimiya, Leningrad (1971).
29. T. Baddington (editor), Nonaqueous Solvents [Russian translation], Khimiya, Moscow (1971).
30. A. Norman, Usp. Khim., 39, 990 (1970).
31. A. Weissberger, A. Proskauer, J. Riddick, and A. Toops, Organic Solvents, Wiley (1955).