THE ELECTROCHEMISTRY OF SOLVATED ELECTRONS

L. I. Krishtalik and N. M. Alpatova

UDC 541.13

The review deals with the laws of the electrochemical generation of solvated electrons (s.e.) and compares them with the laws of ordinary electrochemical reactions. Also discussed are the properties of s.e. generated electrochemically in media where their stability is relatively high and the emission of electrons from alkali-metal solutions in liquid ammonia and hexamethylphosphoramide.

INTRODUCTION

The electrochemical properties of solutions of solvated electrons were begun to be studied before the turn of the century, but in those years the attention was focussed on electrolytic dissociation in such systems (alkali-metal solutions in liquid ammonia), while electrode processes were practically not studied. Interest in this problem was suddenly revived only in the mid-sixties, which had much to do with the advances of radiation chemistry, where the central role of solvated electrons in numerous chemical transformations had been made apparent. Over recent years a number of reviews on this problem have appeared; their authors frequently adhere to directly contrasting viewpoints [1-4]. It must be noted that the electrochemistry of solvated electrons develops very rapidly, so that the review [3], for instance, which had only been written a year ago, already could become obsolete in many respects.

The electrochemistry of solvated electrons encompasses an extremely wide range of problems; not all of these will be discussed by us. Thus, it will not be necessary here to touch upon the photoemission of electrons from metals into solutions, because the pertinent material has been exposed in detail in a recent monograph [5]. The vast data on the structure and properties of solvated electrons also cannot be presented within the present review, and will only be discussed to the extent to which they will seem necessary for the discussion of electrode reactions.

The electrochemical generation of solvated electrons, i.e., their formation at highly negative, cathodic potentials, was only begun to be studied a few years ago. This process is of interest under several aspects in media where the stability of the solvated electrons is relatively high. The generation is a convenient method of producing electrons in the bulk. In this way one can obtain information about the properties of the electrons in the condensed phase.

The mechanism of the generation process itself is of interest as the mechanism of a singular, and in a certain sense of the simplest, electrochemical reaction.

Moreover, information about the mechanism of the elementary act of electrochemical processes can be obtained when the laws of generation are compared with the laws of ordinary electrochemical reactions. Finally, electrochemically generated solvated electrons can be used to carry out a variety of syntheses involving organic and inorganic materials. Attention in the review is primarily focussed on just these problems. In addition we discuss the emission of electrons into the gas phase from solutions containing solvated electrons,

---

Institute of Electrochemistry, Academy of Sciences of the USSR, Moscow. Translated from Élektrokhimiya, Vol. 12, No. 2, pp. 163-194, February, 1976. Original article submitted February 28, 1975.

because this problem was treated incompletely in the review [3].

THE ELECTROCHEMICAL GENERATION OF SOLVATED ELECTRONS

1. Qualitative Data

Solvated electrons in the condensed phase are obtained by various methods. In the radiation-chemical method, solvated electrons are produced when electrons are torn from molecules, ions, or atoms by the action of high-energy x rays, gamma radiation, or fast-electron flow. Also known is a photochemical method of producing solvated electrons by the action of light upon materials usually serving as electron donors [6, 7].

Solvated electrons also can be obtained via atomic hydrogen [6-9]. Hydrated electrons in yields close to 100% are formed when a mixture containing molecular and atomic hydrogen is passed through aqueous solutions of alkali with pH > 12 or of other compounds, e. g.,

$$H + OH^- \rightarrow e^-_{hydr}.$$

For ammonia, however, only the reaction of gaseous hydrogen with the amide anion [7, 10] is of interest among the reactions which are known, viz.: $(1/2)\ H_2 + NH_2^- \rightarrow NH_3 + e_s^-$ [7]. A similar reaction occurs with other particles, too [10].

The radiation-chemical and photochemical methods, in addition to the solvated electrons, produce radicals and ions which can rapidly react with the e_s^-, and therefore are not suitable for the production of stable systems containing solvated electrons. The reactions of atomic and molecular hydrogen are exceptional in character. Devoid of these disadvantages are those methods of producing solvated electrons as, e. g., the dissolution of alkali metals and electrolysis. Moreover, in the electrochemical generation of solvated electrons one can readily regulate the concentration of the e_s^- or repeat the measurements.

In the dissolution of alkali and alkaline-earth metals in certain solvents, the crystal lattice of the metal is destroyed while solvated cations and electrons are formed.

The solvated electron is a very reactive, reducing particle. Most solvents rapidly react with it chemically. For example, in aqueous solutions the lifetime of the solvated electron $\tau_{1/2} = 0.5$ msec [11]. The most stable systems are those in ammonia, amines, ethers, and hexamethylphosphoramide (HMP). Characteristic blue solutions are formed when alkali metals are dissolved in them. The solubilities of the metals are reported in Table 1; they can be taken as a conditional measure for the solvent's ability to form systems with solvated electrons. The alkali metals are also known to form unstable blue solutions in tetramethylcarbamide (tetramethylurea) [27] and an entire series of other amines, ethers [28] and cyclic polyethers [28-30]; high solubility of K and Cs and stability of the solutions are observed, in particular, in systems containing the polyether cyclohexyl-18-crown-6 [30]. Certain physicochemical properties of the solvents which are of interest to us are compiled in Table 2 [3, 12, 24, 31-35].

One can see by comparing Tables 1 and 2 that there is no simple correlation between the macroscopic properties of the solvents and their ability to dissolve alkali metals. Thus, as one goes from HMP to the corresponding thio derivative, the ability to dissolve alkali metals is lost, even though the replacement of oxygen by sulfur leads to a higher dipole moment of the molecule (4.83 instead of 4.48 Debye units) and to a higher dielectric constant of the liquid. Important in the dissolution of the alkali metals is the solvating power of the solvent, both toward the cation and toward the electron, which depends on the structural specifics of the solvent and its molecules and, in particular, on the charge distribution.

The solutions of electrons in ammonia, amines, ethers, and amides are relatively stable as compared to those in water, but these systems nevertheless are metastable, and in the long run decompose because of chemical interaction between the solvated electrons and the solvent molecules. It is difficult to compare the stability of the solutions, since this is very strongly dependent on the purity of the chemicals and the care taken in the operations. Thus, in the case of ammonia, the reaction $e_s^- + NH_3 \rightarrow NH_2^- + (1/2)\ H_2$ is catalytic, and will be accelerated by platinum black, Fe_3O_4, NaOH, and even products of interaction of the solutions with the water which was adsorbed at the walls of the apparatus. The decomposition rate of very pure sodium solutions in liquid ammonia is less than 1% per day. According to

TABLE 1. Solubilities of the Alkali Metals in Certain Solvents*

Metal	Solvent													
	ammonia		methyl-amine [15]	ethyl-amine [16]	ethylene-diamine, mole/liter [17]	propyl-ene-diamine [18]	tetrahydrofuran		dimethoxyethane		[19]	HMP, mole/liter		thio-HMP
	at −33,5°C, mole/liter [13]	at −35°C, molality [14]					[19]	at −78°C, mole/liter [20]	at −78°C, mole/liter [20]	at −40°C, mole/liter [21]		[22]	[23]	[24]
Li	10,7	15,7	7,4 †	+	0,29	+						>1		
Na	7,3	10,8	+		$2{,}4\cdot10^{-3}$	∓	−				−	>1	0,6	−
K	8,1	11,8	+		$1\cdot10^{-2}$	+		$3\text{–}5\cdot10^{-4}$	$6\text{–}10\cdot10^{-4}$	$1{,}7\cdot10^{-3}$		>1		−
Rb		12,5	+		$1{,}3\cdot10^{-2}$									
Cs		13,0 25 ‡	+		$5{,}4\cdot10^{-2}$									

---

*Plus and minus denote the presence and absence of solubility according to visual observation. Lithium is insoluble in propylamine and in all higher, secondary and tertiary amines [12], while sodium is insoluble in secondary and tertiary amines [12].

†Molality, at −22.8°C (from data of [25]).

‡In mole % at −50°C (from data of [26]).

TABLE 2. Physical Properties of the Solvents

Solvent	t_m, °C	t_b, °C	Dielectric constant		Specific gravity		Viscosity	
			value	at tem., °C	g/cm^3	°C	cP	°C
Ammonia	−77,7	−33,4	22	−34	0,6826	−34	0,2558	−34
Methylamine	−92,5	−6,7	12,7	−22,8	0,699	−11		
					0,714	−22,8	0,353	−22,8
Ethylamine	−81	16,6	5,87	20,0	0,708	−2		
Ethylenediamine	11	116,5	16,8	18				
			14,2	20	0,8977	20	1,54	25
			12,9	25				
Tetrahydrofuran	−65	64−65	7,39	25	0,888	20		
HMP	7,2	232	28,74	25	1,020	25	3,1	25
thio-HMP	29,0	94 (1,5 mm Hg)	39,5	30	1,043	30	5,55	30

literature data, the most stable solutions of alkali metals in HMP have a "lifetime" of a few hours at room temperature [36], and of up to three days at 0°C [23]. The stability of sodium solutions is much higher than that of lithium solutions*. By the action of alkali metals, HMP in the long run splits up forming the dimethylamide and diamidophosphite of the alkali metal [37].

According to [23], the reaction of alkali metal with HMP is autocatalytic, i.e., will be accelerated by the reaction products.

The electrochemical generation of solvated electrons can be carried out in a number of solvents, primarily those where the alkali metals are soluble. The chief quantitative results, however, have been obtained in HMP, the reasons being that the high boiling point, the relatively high value of the dielectric constant, and the high solvating power toward cations in combination with the considerable stability of the solvated electrons give HMP certain advantages over other solvents in the electrochemical measurements. In particular, it is due to the properties of HMP that strong interaction between the solvated electrons and the cations in the bulk of the solution is absent in certain cases, e.g., with the strongly solvated Li^+ ion. This makes it possible to examine the properties of the solvated electrons and the laws of electrode reactions in which they are involved under relatively simple conditions.

The appearance of blue coloration which is similar to that of alkali-metal solutions usually serves as the qualitative criterion for the formation of solvated electrons during cathodic polarization. The largest number of observations of this kind refer to solutions in liquid ammonia. This very solvent was the first and for a long time the only solvent studied which had high stability of the solvated electrons.

In 1897 Cady described the increase in the intensity of blue coloration at the cathode which occurred during electrolysis of alkali-metal solutions in liquid ammonia [38] (see also [39]).

Blue coloration also was often seen to occur during the electrolysis of ammoniacal solutions of salts of sodium [40-44], lithium [44], aluminum [45-47], and magnesium [47-48], as well as tetrasubstituted ammonium, NR_4^+, at low temperatures [49-55]. This pertains to salts with cations which cannot be reduced cathodically or react chemically with solvated electrons between −36 and 80°C. In the case of tetrasubstituted salts one chiefly has to do with cations carrying alkyl substituents. Blue coloration failed to appear in the cases where R was benzyl, cetyl, or H, and also with the alkyl derivatives of phosphonium, arsonium, and stibonium [50, 52, 55, 56].

Data on the electrolysis of alkali metal halide solutions in amines and HMP are reported

---

*It is interesting that, according to the data of [23], the stability of lithium solutions in HMP increases on addition of tetrahydrofuran, and to a smaller degree on addition of $(CH_3OCH_2)_2O$ and diglyme.

TABLE 3. The Electrolysis of Alkali Metal Halide Solutions in HMP, Amines, and Dimethoxyethane

Solvent	Salt	Salt concentration, mole/liter	t, °C	Cathode material	Cathodic current density, A/cm²	Catholyte coloration	Electrodeposition of K or Na at high current yields	Literature
HMP*	LiCl	0,2–0,5	Room	Platinum, copper, vitr. carbon	10^{-5}–10^{-1}	Dark-blue	–	[57–60]
	$NaClO_4$	0,2	5	Platinum	–	Same	–	[36]
	$NaBF_4$		Room	»	–	» »	–	[24]
	NaBr		5–25	Platinum, copper	–	» »	–	[61]
Methylamine	LiCl	0,1	–70	Platinum	$6\cdot10^{-2}$–$1\cdot10^{-1}$	Blue	–	[62, 63]
Ethylenediamine†	LiCl	0,3	Room	»	$2{,}5$–$7\cdot10^{-3}$	»	–	[64, 65]
	KI+ NaI	2,1 0,5	100	Copper	$1\cdot10^{-1}$	No coloration	Na (90% yield)	[33]
	KI	2,1				Same	K	
	NaBr	1,8	150		$1{,}3\cdot10^{-1}$	» »	Na	[12]
Dimethoxyethane	KI, $KClO_4$ KPF_6 RbI, CsI				–	Sky-blue	–	
	NaI LiI				–	No coloration	Alkali metal	[66]

---

*A less intense, blue coloration of the layer next to the cathode also is observed during the electrolysis of lithium chloride solutions in the mixtures HMP—ethyl alcohol, HMP—ethyl alcohol—benzene [60, 67], and HMP—anthracene [68]. When tetraalkylammonium halides or perchlorates are used as the base electrolyte in HMP, the blue coloration fails to appear, and there is no ESR signal [36, 69].

†In tetrabutylammonium iodide solution no coloration is observed [65].

in Table 3. Appearance of blue coloration is particularly characteristic of lithium salt solutions. Generation of solvated electrons possibly also occurs in those lithium salt solutions where the starting potential of the rise in cathodic current is very negative (in solvents such as pentamethylphosphoric diamide, $CH_3[(CH_3)_2N]_2PO$) [70]. In the case of ethylenediamine, the nature of the cathodic process will be changed by variation of the conditions (replacement of the lithium cations by sodium or potassium cations, increases of temperature and current density) [12, 71]. Electrodeposition of the alkali metal will occur instead of electron generation. The electrodeposition can be accompanied by a secondary generation of solvated electrons. Thus, sky-blue color is seen to appear at the surface of the metal crystals during sodium deposition from solutions in ethylenediamine [12].

Some authors have suggested that solvated electrons also exist in the solutions of alkali, and possibly of certain other, metals in melts of their own salts, and that during electrolysis of the melts the formation of such solutions is caused by the cathodic generation of electrons [72-75]. This is a likely suggestion, but so far these systems have not been examined sufficiently, and it is difficult to draw specific conclusions.

On the basis of the material presented above, electrochemical generation of solvated electrons can be conjectured for a whole series of systems. However, application of quantitative physicochemical methods was required for a more authentic identification and for an examination of the properties of the particles being formed. The methods of ESR, optical absorption spectra, and dynamic proton polarization of the solvent have been used for these purposes in the case of HMP, and optical absorption spectra in the case of liquid ammonia.

2. The Properties of Electrochemically Generated Solvated Electrons

An extensive literature deals with the properties of solvated electrons, e.g., [11, 76-79]. There have been detailed studies of solvated electrons in metal—ammonia solutions [13, 80-86] and of the importance of solvated electrons in radiation—chemical processes [76, 87, 88].

We briefly discuss the properties of electrochemically generated solvated electrons in our review, and also report some other data required to interpret the results of electrochemical investigations.

It had been established [69, 89] that an ESR signal appears simultaneously with the passage of current through LiCl and NaBr solutions in HMP and with the appearance of blue or dark blue coloration near the cathode. At 20°C and a salt concentration of 0.2 mole/liter, the spectrum is characterized by a single, narrow line, both in lithium chloride and in sodium bromide solution. This signal had been attributed to the solvated electron. Its g factor was found to coincide with that of the free electron. Solvated electrons can be found in sufficiently large quantity even a few tens of minutes after disconnection of the generating current.

By studying the influence of the state of aggregation on the ESR spectra of electrochemically generated solvated electrons and comparing them with those of stabilized electrons obtained radiation—chemically in frozen lithium chloride and sodium bromide solutions it was possible to conclude that in the case of lithium chloride solutions in HMP, the line of the ESR spectrum of electrochemically generated solvated electrons is so narrow because of the high, almost spherical symmetry of the arrangement of solvent molecules relative to the electron. The data on the ESR spectra also indicate that there is no substantial contact interaction between the solvated electrons and the alkali metal cations (absence of hyperfine structure in the ESR spectra under conditions of weak exchange interaction) [69, 89].

Optical absorption spectra have been studied for the particles generated electrochemically at the cathode in HMP [90] and liquid ammonia [55]. The optical spectra for HMP are presented in Fig. 1. Absorption spectra for solutions of metallic sodium in HMP according to the data of Brooks et al. [91] and spectra obtained during pulse radiolysis of pure HMP and of sodium bromide solution in the same solvent are reported for comparison in the same figure.

Optical absorption spectra of the solvated electron obtained radiation-chemically in pure ammonia [92], during the dissolution of alkali metal [93], and during electrochemical generation in sodium, potassium, cesium, strontium, barium, and tetraalkylammonium halide

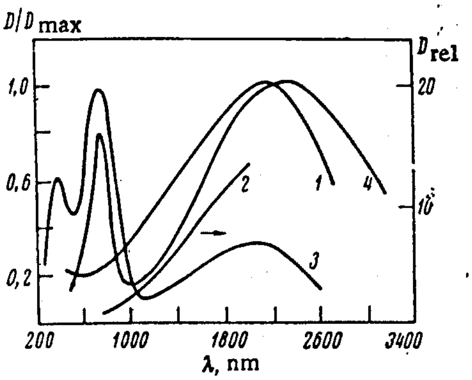

Fig. 1

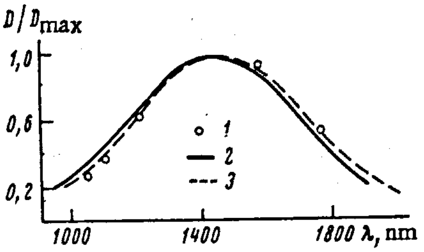

Fig. 2

Fig. 1. Optical absorption spectra in HMP at 20°C: 1) and 3) electrochemical generation, 0.2 mole/liter LiCl (1) and 0.2 mole/liter NaBr [90]; 2) pulse radiolysis, the pure solvent; 4) dissolution of metallic sodium [91].

Fig. 2. Optical absorption spectra in liquid ammonia at –65 to –70°C: 1) pulse radiolysis [92]; 2) electrochemical generation in halide solutions [55, 94]; 3) dissolution of alkali metal [93].

solutions [55, 94] are presented in Fig. 2*. Matching absorption during the radiolysis of pure HMP and pure ammonia serves as the most direct proof that these bands really belong to the solvated electron, and are not due to the presence of alkali metal cations in the liquid. By comparing the absorption curves one can see that solvated electrons in fact are generated during cathodic polarization. The particles being formed during metal dissolution, during pulse radiolysis of the pure solvents and of salt solutions in these solvents, and likewise during electrolysis are identical. A similar situation is found in molten salts, too. The particles which are produced during the cathodic polarization in alkali metal halide melts have an optical absorption spectrum which is similar to that of the particles arising during the dissolution of alkali metals in these media [75, 96].

The method of dynamic polarization of the HMP protons has also been used to study the particles being produced at the cathode [97]. The magnitude and sign of dynamic polarization in lithium chloride and sodium bromide solutions indicate that there is a certain spin density of unpaired electrons present at the locations of hydrogen nuclei. However, no paramagnetic shift of the ESR spectrum of the HMP protons is found in the presence of solvated electrons. This indicates that the interaction between electron and solvent protons is minor; the spin density at the proton is less than 10^{-4} unit. The results of these measurements are in agreement with the data obtained for lithium and sodium solutions in HMP [98, 99].

Taken all together the results reported indicate that indeed solvated electrons are formed during electrochemical generation, rather than anion-radicals, e.g., $\{[(CH_3)_2N]_3PO\}^-$, or alkali metal atoms (contact-type ion pairs). In these cases splitting or significant broadening of the ESR line would have to be expected owing to the interaction of e_s^- with the nuclear magnetic moments of P, Li, etc.

We shall now discuss association effects in systems containing solvated electrons. Electrochemical generation is very convenient to use when examing association, because it allows one to vary the concentration of solvated electrons continuously over a wide range, at any given excess of cations. In systems with HMP, the interaction between the cations of the dissolved salt and the solvated electron causes, first, a small shift in λ_{max} of the electron's absorption band toward shorter waves [90]. It is shown below how λ_{max} of the

---

*A similar optical spectrum had been obtained for the solvated electron by reflection of light from smooth silver, gold, and platinum electrodes during electrochemical generation in a solution of potassium iodide in liquid ammonia [75, 95].

solvated electron depends on total electrolyte concentration in HMP for $c_{M^+} = 10^{-3}$ mole/liter (in [91]) and $c_{M^+} = 2 \times 10^{-2}$ mole/liter (in [90]):

	Li^+	Na^+
λ_{max}, nm:		
data of [91]	2300	2300
data of [90]	2156	2000

The presence of interaction between the solvated electrons and the cations is in agreement with the results of conductivity measurements with sodium solution in HMP [23, 100], which indicate that aggregates of the type of ion pairs are formed.

In the optical spectra of solvated electrons in liquid ammonia (cf. Fig. 2) one absorption band is observed; its properties are weakly dependent on the nature and concentration of the cation [55, 94, 101]. The presence of association follows from conductivity measurements on metal-ammonia systems [102]. Therefore, the absorption band in liquid ammonia and the long-wave band in HMP are caused both by free solvated electrons and by solvated electrons linked electrostatically to cations. Such interaction can show up both in the development of ionic atmospheres made up of ions of the opposite sign and in the formation of non-contact-type ion pairs, triplets, etc. The absence of contact-type interaction can be inferred from the data on the ESR spectra [11, 69, 89]. In the case of the contact pairs which exist, e.g., in ethylamine [103], the narrow, single line is split up into a quartet; such is observed neither in ammonia nor in HMP. The absence of contact-type ion pairs in ammonia and HMP can, apparently, be attributed to the high solvating power of these solvents.

Of particular interest among the aggregates are the so-called bielectrons, e_2^{2-}, i.e., two electrons with paired spins having a common solvation sheath.

No direct spectroscopic proof exists for the existence of complexes containing the bielectron in metal—ammonia solutions [104]. Recently a paper appeared [101] where an argument for the presence of bielectrons in metal—ammonia solutions was obtained by separating the absorption band into two bands, one being attributed to the electron and the other to the bielectron. However, isolating two spectra which are similar in their characteristics (λ_{max} = 1455 and 1580 nm, $E_{1/2}$ = 0.402 and 0.371 eV for the electron and the bielectron, respectively) from a single, smooth band does not seem to be a reliable procedure.

Upon dissolution of alkali metals in amines and ethers, systems are formed which are more complex than the ones obtained with liquid ammonia. The optical spectra of such systems [18, 20, 21, 28, 29, 66, 105-116] may contain up to three absorption bands, and in a number of cases one of these is attributed to a complex containing the bielectron.

In [106], the conclusion that M^- is formed in ethylamine (where M can be K, Rb, Cs) is drawn from analogies between the spectrum examined and that of I^-. For these systems, the band with λ_{max} = 850 nm had been attributed [107] to a complex containing the bielectron. However, in this paper the equilibrium of the complex had been examined not with the solvated electron, which is absorbing in the region of 1300 nm, but with a species giving rise to a band with λ_{max} = 650 nm. The interference has been based on the assumption that this last band belongs to the pair $M^+ ... e^-$. However, there are certain difficulties here. The λ_{max} value of this band, in contrast to the λ_{max} of the band at longer waves, does not depend on the cation, which clearly is in contradiction with its being interpreted as caused by an ion pair. The suggestion had been made [117] that it was caused by traces of sodium ions which had appeared after leaching of the walls of the glass apparatus. However, this question cannot be regarded as solved. It remains obscure which equilibrium the constant determined in [107] should be properly referred to, and whether the species with λ_{max} = 850 nm could be treated as the bielectron.

The existence of bielectrons had been suggested and proven by examining the influence of light on solutions in ethers and amines [66, 113]. Upon illumination with long-wave light corresponding to the absorption band of the bielectron being contemplated, the ESR signal [66] or the optical absorption [113] corresponding to the solvated electrons were found to increase. The disappearance of the latter after illumination by a second-order reaction implies the formation of bielectrons [66, 113].

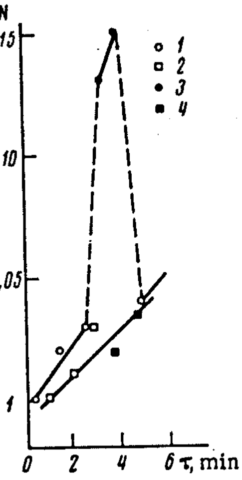

Fig. 3

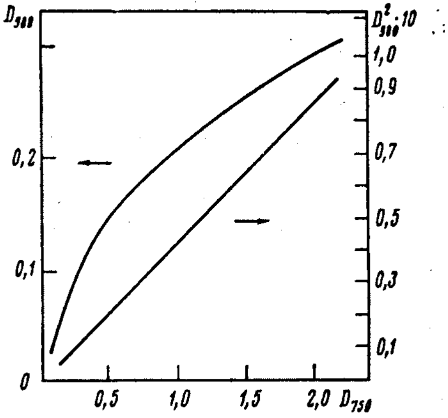

Fig. 4

Fig. 3. The concentration of solvated electrons, N, as function of the time, τ, in the dark (1, 2) and during illumination with 650-1200 nm (3) or 400-650 nm (4), during constant-current electrolysis in 0.2 mole/liter NaBr solution in HMP at 20°C [120].

Fig. 4. The optical density D_{980} as a function of the optical density D_{750} during electrochemical generation in 0.2 mole/liter NaBr solution in HMP at 20°C [121].

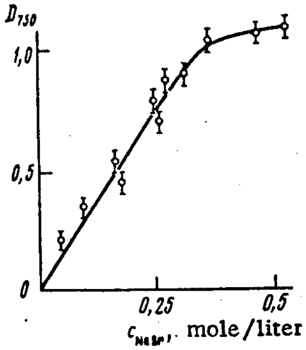

Fig. 5. The optical density D_{750} as a function of sodium ion concentration during electrochemical generation in NaBr solutions in HMP at 20°C, with the optical density D_{980} = 0.2 [122].

The HMP turned out to be a convenient solvent for studying bielectrons. During electrochemical generation in sodium bromide solutions, an absorption band with λ_{max} = 750 nm is observed in addition to the band of the solvated electron [90] (cf. Fig. 1). A similar picture was obtained for sodium solutions [91] and during pulse radiolysis of sodium bromide solutions [118, 119]. The second absorption band is not observed during electrochemical generation in lithium chloride solutions [90] (Fig. 1) or during the dissolution of metallic lithium in HMP. The ESR spectrum obtained during electrochemical generation in sodium bromide solution is identical with that in lithium chloride solution [69, 89]. This indicated that the species causing the band with λ_{max} = 750 nm are not paramagnetic (cf. also [23]).

The nonparamagnetic nature of the corresponding species had also been confirmed by measurements of dynamic polarization and spin—lattice relaxation time of the HMP protons during the cathodic generation of solvated electrons. The effects caused, under identical electrolysis conditions, by the presence of solvated electrons are much stronger in lithium chloride solutions than in sodium bromide solutions. This points to a difference in the true concentrations of solvated electrons, which is caused by fixation of part of the electrons in the sodium bromide solutions into nonparamagnetic aggregates [97].

When solutions of solvated electrons on the basis of sodium bromide are illuminated with light embracing 750 nm, the amplitude of the ESR signal increases in proportion to the concentration of solvated electrons (Fig. 3). Light not including 750 nm does not cause any increase in the concentration of paramagnetic species under these conditions. In lithium chloride solutions there is no increase in the concentration of solvated electrons when light embracing all wave lengths is acting upon them [120]. These results unambiguously indicate that an even number of electrons are contained in the nonparamagnetic species which, by photodissociation, yield solvated electrons.

The equilibrium between the complexes and the solvated electrons was examined with the optical absorption spectra in order to determine the stoichiometry of the complex [121, 122]. The connection between the optical densities at $\lambda = 750$ nm (the complex) and $\lambda = 980$ nm (the solvated electron) at different concentrations of solvated electrons and constant excess concentration of sodium cations is shown in Fig. 4. It can be seen from this figure that there is linearity when D_{750} is plotted against D_{980}^2. This law (which is found with an excess of salt, i.e., with an excess of Na^+) corresponds to the equilibrium $2e_S^- \rightleftarrows e_2^{2-}$, i.e., to the formation of the bielectron. Since during formation of the bielectron one has a drastic change in the optical characteristics and a loss of paramagnetism, one can affirm that the bielectron is some unique species rather than the simple combination of two solvated electrons.

The probability that a complex containing the bielectron will be formed depends on the nature of the cation.

A band corresponding to the bielectron is not present in pure HMP containing solvated electrons obtained by pulse radiolysis. The aggregates existing in solutions containing sodium cations are also absent from systems with Li^+. This indicates that the bielectron only exists in systems where it can be stabilized by interaction with cations. That this interaction becomes weaker as one goes from sodium to lithium probably is due to the larger solvation of the lithium ion as compared to the sodium ion [123]. With increasing solvation there is less interaction of the cations with anions, and in particular with e_2^{2-}. The absence of bielectrons from liquid ammonia possibly is caused by weaker interaction of cations and anions, and in particular of solvated electrons, in this solvent relative to HMP (compare the weak dependence of the e_S spectrum on the nature and concentration of the cation [55, 94, 101]).

It can be seen from Fig. 5 that at sodium bromide concentrations of up to 0.35 mole/liter, the amount of bielectrons is directly proportional to the sodium ion concentration. The deviation from linearity observed at high salt concentrations probably is due to incomplete dissociation of the salt.

On the basis of all the results obtained one can ascribe the formula $Na^+ \ldots e_2^{2-}$ to the complex. The same composition had been proposed for the complex in Gremmo and Randles's recent paper for Na solutions in HMP [23], but the stoichiometry of the complex was not established accurately.

From the data of pulse radiolysis it was possible to determine the extinction coefficients of the particles and to calculate the equilibrium constant $K = (2.8 \pm 1.4) \times 10^4$ liter²·mole⁻² for the reaction $Na^+ + 2e_S^- \rightleftharpoons Na^+ \ldots e_2^{2-}$, where e_S^- is the solvated electron which is free or electrostatically bound without contact to sodium cations [122].

The diffusion coefficient is important for the characterization of the solvated electrons. Diffusion coefficients, Walden products, and ratios between the diffusion coefficient of the solvated electron and that of the sodium cation in the corresponding solvent are reported in Table 4. It follows from this table that the mobility of the solvated electron is substantially higher than that of ordinary ions. For this reason and because of the low values of the activation energy of mobility (1.6 kcal/mole) in the case of HMP a jump mechanism of electronic motion in the liquid can be proposed [130]. It is interesting to note that the Walden product for the solvated electron remains approximately constant in water, ammonia, and HMP.

3. The Laws of Electrochemical Generation of Solvated Electrons. The Reversible "Electron" Electrode

Let us consider the results of kinetic investigations of the generation process.

The first paper in this field was published in 1948 by Laitinen and Nyman [54], who recorded cathodic polarization curves in liquid ammonia at −36°C in 0.005 molar solutions at various electrodes (the potentials were measured relative to that of the mercury pool). The results of their measurements, which have been analyzed in the form of semilogarithmic Tafel

TABLE 4. Diffusion Coefficients, D, of Solvated Electrons in Liquid Ammonia, Water, and HMP

Solvent	t, °C	Method of determining D	D, $10^4 \cdot$ cm$^2 \cdot$ sec^{-1}	$D \cdot \eta \cdot 10^6$	$\frac{D_{s.e.}}{D_{Na^+}}$	Literature
Ammonia	−36	Chronopotentiometric anodic oxidation of s.e.	1.45	–	–	[124]
	−36	Measurement of conductivity and transference number	1,74	4.45	6.7	[125, 126]
	−30	Radiation–chemical; current–relaxation curves	2.14*	–	–	[127]
Water	Room	Radiation–chemical; conductivity measurements	0.48	4,75	3.7	[87, 128]
			0.49	4,90	–	[76]
HMP	»	Radiation–chemical; current–relaxation curves	0,14	4,59	~10	[119, 123, 129]

---

*The combined mobility of solvated electron and ammoniated proton.

TABLE 5. Constants of the Tafel Equations Describing the Cathodic Polarization Curves in Liquid Ammonia at −36°C [54]

Electrode	Base electrolyte	Concentration, mole/liter	$-A$, V	$-b$, mV	α
Dropping mercury	$(C_2H_5)_4NI$	0.005	2.26		
	$(C_3H_7)_4NI$	0.005	2,34	64	0,72
	$(C_4H_9)_4NI$	0.0057	2.36	63	0,73
Platinum	LiI	0.005	2,35	104	0.44
	NaI	0.005	2,34	120	0,38
	$(CH_3)_4NI$	0.0042	2,35	105	0,44
	$(C_4H_9)_4NI$	0,0057	2,34	98	0,47
Stationary mercury	$(C_4H_9)_4NI$	0,0057	2,34	93	0,50
Platinum	Metallic sodium	0,006	2.35	73	0,63

plots $\varphi = A + b \lg I = A - \frac{2.3RT}{\alpha F} \lg I$, are presented in Table 5. It can be seen that these data are of a qualitative rather than quantitative character. There is large scatter in the experimental α values. The use of dilute solutions at low temperatures may have led to distorted results of the polarization measurements, owing to ohmic voltage drops.

A systematic investigation of the electrochemical generation of solvated electrons has become possible with the advent of solvents such as HMP. The latter has a number of advantages over ammonia (cf., the Introduction section). Such research is conducted at the Institute of Electrochemistry of the Academy of Sciences of the USSR since the end of the sixties. Soon after, publications of Japanese [36] and British [57] workers also appeared.

Generation in HMP occurs at very negative potentials, viz., −2.7 to −2.9 V relative to the normal hydrogen electrode in this solvent (−2.9 to −3.1 V relative to the point of zero charge of the mercury electrode in this medium [131]).

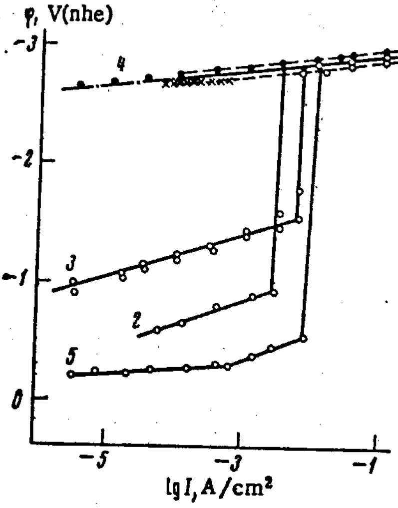

Fig. 6

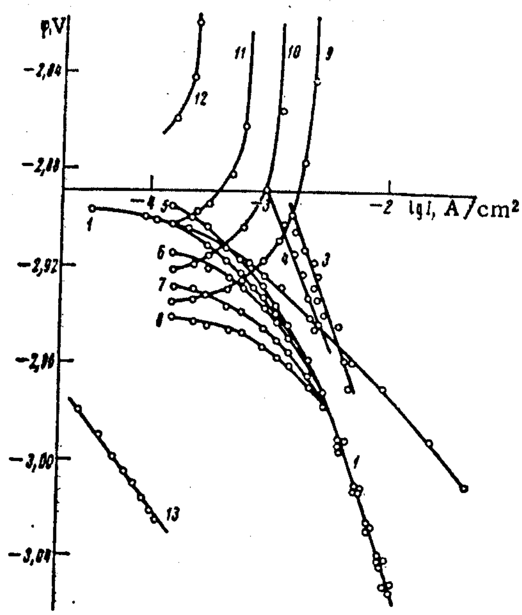

Fig. 7

Fig. 6. The potential φ as function of current density I at 25°C in HMP [58, 133-136] with 0.2 mole/liter LiCl: 1) on copper, platinum; 2) - 5) with additional 0.15 mole/liter HCl on copper (2), 0.17 mole/liter HCl on cadmium (3), 0.20 mole/liter NaBr on cadmium and solvated electrons on platinum (4), and 0.18 mole/liter HCl on platinum (5).

Fig. 7. The cathodic and anodic currents and the exchange currents as functions of potential φ on a copper electrode in 0.32 mole/liter LiCl solution in HMP (5.5°C) in the presence of solvated electrons with a rate of rotation of the stirrer of 1700 rpm: 1) - 12) curves for the active surface: 1) experimental cathodic curve, φ_0 = −2.896 V; 2) cathodic curve calculated via the equation of concentration polarization for the data of curve 1; 3) the values corresponding to curve 1 as corrected by Eq. (1); 4) the corrected exchange currents as function of the equilibrium potentials φ_0; 5) to 12) the cathodic and anodic curves for φ_0 = −2.885 (5, 12), −2.909 (6, 11), −2.924 (7, 10), and −2.939 V (8, 9); 13) the cathodic curve for the passive surface. The potentials were measured relative to an aqueous saturated calomel electrode.

It had been demonstrated that the mechanism of electron generation depends on the surface state of the electrode. Prior cathodic polarization with large currents, storage of the electrode in the solution at open circuit, or the presence of impurities in the bulk of the solution causes passivation of the electrode. This effect can be caused by adsorption layers or phase layers of basic alkali metal compounds or by decomposition products of the solvent on the electrode surface. The basic alkali metal compounds, which are poorly soluble in HMP, can be produced with hydrogen evolution from impurities, e.g., water: $H_2O+e^-+Li^+ \rightarrow 1/2\ H_2+LiOH$ (for more details on passivation cf., [3], also [132]).

It had been shown in our work [58, 133-136] that on the passive surface of a copper electrode in HMP (0.2 mole/liter LiCl at 25°C), the polarization curve can be described over a wide range of currents (about five orders of magnitude) by the Tafel equation with slope 60 mV (Fig. 6, curve 1). A similar dependence, though over a narrower current range, had been obtained at 5.5°C in LiCl solution when solvated electrons were present in the bulk (Fig. 7, curve 12). According to the data of Avaca and Bewick [57], the slope is 83-93 mV for a cathode of vitreous carbon where the surface also appears to be passive (0.5 mole/liter LiCl at 25°C), but these authors mention instability and poor reproducibility of the results.

The shape obtained for the polarization curve can correspond to several mechanisms of cathodic generation of solvated electrons: 1) concentration polarization for the removal of solvated electrons as the reaction product; 2) electrodeposition of the base electrolyte cation followed by dissolution; 3) barrierless electrochemical discharge of solvent molecules; 4) thermal emission; and 5) the barrierless electrochemical dissolution of electrons yielding electrons localized near the electrode.

The hypothesized mechanism of concentration polarization for passive electrodes contradicts the experimental facts. It had been shown in our work [58, 133-137] that during generation in lithium chloride solutions in HMP there is no shift of potential in the positive direction when the stirring rate is increased. Stirring either remains without effect or, when traces of water are present, causes passivation. This is confirmed by Avaca and Bewick's data [57]. These workers used cyclic voltammetry (vitreous carbon, lithium chloride in HMP) and observed that the cathodic current in the initial portion of the anodic sweep is higher than the current of the cathodic sweep, i.e., the accumulation of products of the cathodic reaction has no inhibiting effect on the process.

The influence of stirring on the rate of generation at a passive surface will remain unseen even where concentration polarization is of determining importance, provided that the diffusion takes place in the narrow pores of a film covering the electrode. However, under these conditions the anodic limiting currents of the oxidation of solvated electrons, which are of a diffusional nature (cf., p. 177 this article), also should be independent of stirring intensity. Yet, they increase with increasing stirring rate, while the cathodic currents are independent of stirring.

Let us now consider the mechanism which involves discharge of the base-electrolyte cation. Since HMP is capable of dissolving alkali metals with the formation of solvated electrons, the latter can be produced by two principally different processes: a primary process, i.e., direct escape of the electron from the electrode into the solution, and a secondary process, i.e., the electrolytic deposition of alkali metal followed by its chemical dissolution. We had attempted to investigate the question about the primary nature of generation by comparing the cathodic polarization curves in dilute lithium chloride solutions at copper and amalgamated copper electrodes [58, 134]. At the amalgamated electrode one observes diffusion and migration limited lithium ion discharge currents and amalgam formation. Originally [58, 134] we had regarded the absence of diffusion and migration limited currents at the copper electrode as one of the arguments against the secondary electron generation mechanism. Laitinen and Nyman [54], who had shown that in dilute tetrabutylammonium chloride solutions in liquid ammonia one cannot attain the limiting current of tetrabutylammonium discharge, also took this observation as confirming the hypothesis of primary generation. This conclusion is ambiguous, however, because the mass transport processes in systems with solvated electrons are highly complex, in particular on account of the development of Stefan flow which is generated by the considerable changes in solution density* during an electrode reaction. Therefore, strictly speaking, we do not have sufficient theoretical reasons to expect a limiting cathodic current to appear under our experimental conditions.

The direct experimental proof was accomplished by running the generation in HMP solutions not containing metal ions [139]. A rise in current at potentials which are characteristic for the electron generation in alkali metal salt solutions was observed following the limiting current of proton donor discharge on the cathodic polarization curves recorded in dilute $HClO_4$ and HCl solutions at copper, platinum, and dropping mercury electrodes. From these data one can conclude that the generation process in HMP is primary, i.e., not connected with prior deposition of the alkali metal and its subsequent dissolution.

It was shown in the work of Avaca and Bewick [57] that the potentials of generation of solvated electrons in lithium chloride solution in HMP are more positive than the potential of the equilibrium lithium electrode in saturated LiCl solution. This, too, agrees with the

---

*The volume increase during the introduction of solvated electrons is 65-95 ml/mole for liquid ammonia [7], and about 80 ml/mole for HMP [138].

suggestion of a primary process of electron generation.

One more argument for this position is the independence of the rate of generation on salt cation and electrode material.

In the case of HMP the influence of these factors has been examined systematically [135, 136]. The results of polarization measurements in solutions of different composition at passive copper, platinum, and cadmium cathodes had been presented in Fig. 6 (curve 1 and 4). The rate of generation is seen not to depend on the base-electrolyte cation or solution composition. One can see, in particular, that the potentials in lithium chloride and sodium bromide solutions are practically the same. One can expect that for a mechanism involving alkali metal electrodeposition with formation of a separate phase, the difference in the potentials should be much higher, since the difference between the normal potentials of lithium and sodium as a rule is 0.3 to 0.4 V, and depends little on the solvent [140-142]. The rate of generation also is independent of the cathode material, and is the same for copper, platinum, and cadmium electrodes. This implies the absence of any appreciable influence of adsorption effects, i.e., contradicts the hypothesis that cations are discharged with the formation of adatoms at potentials below the equilibrium potentials of the solid alkali metals.

Mechanisms involving discharge of base-electrolyte cations either with the formation of alkali-metal phase or with the formation of adatoms are refuted by the independence of the rate of generation on the cation and on electrode material.

The independence of the rate of generation of solvated electrons on the electrode metal serves as an experimental confirmation of Frumkin's theoretical position that the rates of electrochemical reactions are not directly dependent on the electronic work function from the metal into vacuum. If electrodes made of different metals have the same electrode potential, then the electronic work functions from these electrodes into the solution will be the same. Independence of the reaction rate on the electronic work function into vacuum had been established by Rotenberg and Pleskov for photoemission into solutions [143], and by Nikolaeva-Fedorovich et al. for the electroreduction of anions [144].

The data of Laitinen and Nyman [54] for liquid ammonia (Table 5) are not in contradiction with the assumption that the rate of generation is independent of the base-electrolyte cation and the cathode material, even though they cannot be used to establish the precise shape of the polarization curve.

This also is true for the data on the so-called "cathodic limits", i.e., the potentials where the current begins to rise during cathodic polarization in HMP [36, 145-149]. These data have been reviewed in [3].

Excepting one particular case, Dubois et al. [145] and Gal et al. [146, 147] attribute the current rise to the beginning discharge of base-electrolyte cations. To us it seems to be more correct to attribute this effect to the generation of solvated electrons. Kanzaki and Aoyagi [36] came to a similar conclusion.

In ethylenediamine solutions the situation is qualitatively similar to that in HMP. Schöber and Gutmann [150, 151] observed a rise in current at −3.05 V against the normal calomel electrode in water during their polarization measurements at mercury in dilute solutions of base electrolyte (10^{-3} mole/liter $LiNO_3$, $(C_2H_5)_4NNO_3$, $LiCl$, $KClO_4$); this rise followed the wave of the cation. The potential of the rise was independent of the cation.

The polarization curve which corresponds to the cathodic process in HMP and which is described by a Tafel equation with the slope of 60 mV can also fit the mechanism of barrierless reduction of solvent molecules. The rate of this process could slightly depend on the nature of the base electrolyte. It would be difficult to assume, however, that the electrode material has no influence on the discharge of the solvent molecules, so that this mechanism appears to be unlikely.

In examining the kinetics of the generation process one can use an electrode which is reversible with respect to the solvated electrons. Values of the transfer coefficient α of the cathodic reaction are determined from the dependence of the equilibrium potential of this electrode on exchange current. An electron electrode in liquid ammonia had been proposed by

Kraus as early as 1914 [152], later by Laitinen and Nyman [54] and by Dye [126]. In HMP, electrodes have been realized which were reversible with respect to solvated electrons generated both electrochemically [61, 153] and by dissolution of metallic sodium [36, 154]. Platinum and copper were used as electrode material [36, 61, 153].

At passive copper and platinum electrodes in lithium chloride solutions in HMP containing solvated electrons, the initial sections of the polarization curves are independent of stirring, and represent straight lines going through the coordinate origin without a break [153]. This implies the establishment of thermodynamic equilibrium at the electrode, and allows one to determine the exchange currents from the slope of the $I-\varphi$ curve. The exchange currents thus determined coincide, within the limits of experimental accuracy, with the values obtained by extrapolating the cathodic polarization curve recorded far from equilibrium [153]. For a one-electron process the connection between equilibrium potential φ_0 and exchange current I_0 is given by the expression $\varphi_0=\mathrm{const}-\frac{RT}{\alpha F}\ln I_0$. The experimental dependence for 5°C is described by the equation φ_0 (in V) = const - (0.060 + 0.004) log I_0, and thus corresponds to $\alpha = 1$, as does the shape of the polarization curve.

Among the mechanisms of primary electron generation which proceeds far from the equilibrium potentials, that of thermionic emission seems to be the most likely. Here the electron escapes into the solution in delocalized form, as a wave. For this process one must expect a slope of 60 mV, since an increase in potential by $\Delta\varphi$ will lower the electronic work function from the metal into the solution by $\Delta\varphi\cdot e$, where e is the electronic charge [155, 156]. A linear dependence of the emission current raised to the power 0.4 upon potential must be expected for cold emission into the solution, just as for photoemission [155, 157, 158]. This type of dependence is not observed. The slope of 60 mV could also correspond to the electrochemical dissolution of electrons according to a barrierless mechanism, but in this case a transition to the ordinary process should be expected at sufficiently high current densities, together with an increase in the slope of the polarization curves to the more usual values around 120 mV.

Certain estimates also provide arguments in favor of the thermionic emission mechanism. The electronic work function of a mercury electrode which is at the potential of zero charge in HMP is 3.6 V, according to photoemission data [159]. One knows that photoemission into solutions initially produces electrons in the delocalized state [5]. An estimate of the work function from the Richardson–Sommerfeld equation for thermionic emission $I = A\cdot T^2\cdot\exp(-W/RT)$ where $A = 120\ \mathrm{A\cdot cm^{-2}\cdot deg^{-2}}$ and W is the work function [160] gives W = 0.58 V for a current of 10^{-3} A/cm² and a temperature of 25°C. Taking into account that a potential of about –2.78 V (nhe) corresponds to the current of 10^{-3} A/cm² [58, 136] and that the potential of zero charge of mercury in HMP is +0.17 V (nhe) [131] we obtain a value of 3.53 V for the work function of the mercury electrode at the potential of zero charge, which practically coincides with the value of 3.6 V determined from photoemission experiments [159].

It must be appreciated that the experimental data on the kinetics of generation of solvated electrons which are described in the literature are contradictory. Thus, it was established in the work of Avaca and Bewick [57] and in our papers as cited above that the process is not diffusion-limited in HMP. After obtaining a cathodic polarization curve which corresponded to the Tafel equation with a slope of 60 mV, Kanzaki and Aoyagi [36, 161] suggest that the process is diffusion-controlled, while the transfer coefficient of the electrochemical step as determined by nonstationary methods is 0.25–0.30*. The character of the process depends on the surface state. The laws of generation on passive surfaces have been discussed above. It was found that brief anodic polarization using high currents will lead to the active surface state. Upon activation the rate of generation of solvated electrons increases by 1.5 to 2 orders of magnitude, and becomes stirring dependent. On this basis one can suggest that the contradictory results obtained by different workers go back to the use of electrodes which had different degrees of passivity.

---

*Laitinen and Nyman [54] also suggested diffusion control of generation in liquid ammonia. However, their data on the slope of the polarization curves do not conform to this suggestion ($\alpha < 1$, cf. Table 5).

The influence of stirring on the rate of generation implies a substantial influence of the back reaction on the process. We shall designate the oxidation of solvated electrons as the anodic reaction. This designation is conditional, because in contrast to ordinary reactions, no particle other than the solvent molecules remains in the solution after the oxidation.

Corrections for the concentration polarization and for the back reaction were introduced into the experimental values of the cathodic current in order to examine the kinetics of the electrochemical step itself.

The corrected values of the cathodic current are given by

$$I=\frac{I_{\text{meas}}}{1-\frac{I_{\text{meas}}+I_{\text{lim}}^{\text{an}}}{I_{\text{lim}}^{\text{an}}}\cdot e^{-\eta}}, \tag{1}$$

where I_{meas} is the experimental value of the cathodic current, $I_{\text{lim}}^{\text{an}}$ is the anodic limiting current of oxidation of solvated electrons at a given value of equilibrium potential, and η is the overvoltage in units of RT/F. Equation (1) is correct for any one-electron process, even if it includes parallel pathways.

At highly active surfaces the rate of the process is entirely diffusion-controlled and strongly stirring dependent. At less active surfaces, marked irreversibility is observed when the stirring is intense. This follows from the discrepancy between the experimental cathodic curve (Fig. 7, curve 1) and the curve calculated for the equilibrium process from the relation $I_{\text{cath}} = I_{\text{lim}}^{\text{an}} (e^{\eta} - 1)$ (curve 2). The polarization curve is described by curve 3 when the correction following from Eq. (1) is introduced into the experimental values of the cathodic current. Curve 3 corresponds to a Tafel equation with slope 122±6 mV. By such a shape of the true cathodic curve it is shown that under these conditions the generation of solvated electrons occurs according to the electrochemical dissolution mechanism. For this reaction the transfer coefficient $\alpha = 0.45 \pm 0.05$.

For an independent determination of α the connection between the equilibrium potential φ_0 and the exchange current was investigated (curve 4 of Fig. 7). The exchange currents $I_{\text{meas}}^{\text{o}}$ determined from the slopes of the initial portions of the polarization curves as plotted in linear coordinates were corrected according to [162] for diffusional modifications according to the relation $1/I_{\text{meas}}^{\text{o}} = 1/I_{\text{tr}}^{\text{o}} + 1/I_{\text{diff}}^{\text{o}}$, where I_{tr}^{o} is the exchange current of the electrochemical step and $I_{\text{diff}}^{\text{o}}$ is the effective exchange current of the diffusion step, which equals the anodic limiting diffusion current of oxidation of electrons at the given φ_0. The α value determined from the plot of φ_0 against $\log I_{\text{tr}}^{\text{o}}$ is 0.55±0.04, and practically coincides with the values determined from the slope of the corrected cathodic curve. The corrected exchange currents and the extrapolated true cathodic currents (curve 3 and 4) have similar values.

The forward and back reaction rates are given by $I_{\text{cath}} = \vec{k}\cdot e^{-\alpha\varphi}$ and $I_{\text{an}} = \overleftarrow{k}\cdot c\cdot e^{(1-\alpha)\varphi}$. At large departures from equilibrium the rate of the cathodic process is independent of the concentration of solvated electrons governing the value of φ_0 (curves 1, 5, and 6-8 of Fig. 7), but the rate of the anodic process depends on it, as expected (curves 9-12 of Fig. 7).

Thus, the generation of solvated electrons in HMP is a complicated phenomenon. The mechanism of generation appears to change (cf. curves 3 and 13 of Fig. 7) when there is a change in the conditions, and especially in the surface state.

The rate of generation of solvated electrons by the electrochemical dissolution mechanism(as the rate of an ordinary electrochemical process) should strongly depend on the degree of surface passivation. Passivation should have a smaller influence on the rate of generation by the thermionic emission mechanism. In fact, the barrier height for the tunneling of electrons into the delocalized state is smaller than that for tunneling into the localized state, because the energy of the latter is lower. Hence formation of a passivating film, which can be described as an increase in barrier width, has a smaller effect on thermal emission. Therefore as one goes from an active to a passive surface, the rate of generation by the electrochemical dissolution mechanism is decreasing drastically, and the cathodic

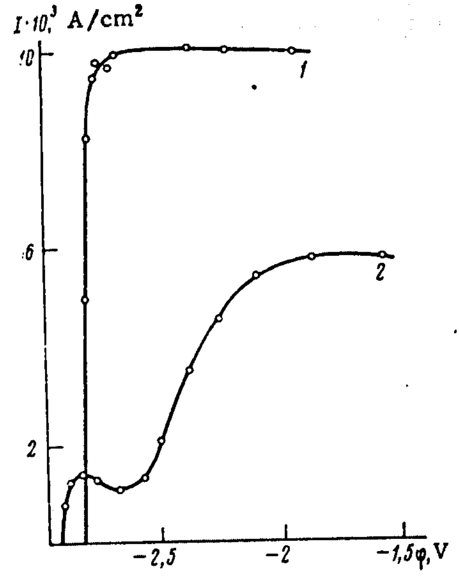

Fig. 8

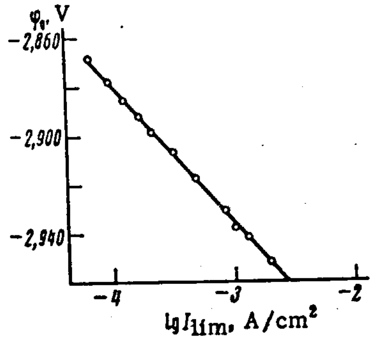

Fig. 9

Fig. 8. The anodic current I as function of potential φ for a copper electrode in HMP (5.5°C) in the presence of solvated electrons, with a rate of rotation of the stirrer of 1750 rpm: 1) in 0.8 mole/liter LiCl solution with φ_0 = 2.917 V, 2) in 0.3 mole/liter NaBr solution with φ_0 = −2.916 V. The potentials are measured relative to an aqueous saturated calomel electrode.

Fig. 9. The limiting anodic current I_{lim} as function of the equilibrium potential φ_0 for a copper electrode in 0.32 mole/liter LiCl solution in HMP (5.5°C) in the presence of solvated electrons, with a rate of rotation of the stirrer of 1700 rpm. The potentials are measured relative to an aqueous saturated calomel electrode [61].

process will chiefly be governed by thermal emission the rate of which is relatively little dependent on the surface state.

Let us now discuss certain other data pertaining to electrodes which are reversible with respect to solvated electrons. The fact that the initial portions of the polarization curves as plotted in linear coordinates pass through zero without a break indicates, in the case of HMP, that thermodynamic equilibrium is established at the electrode, both with passive and with active surfaces. Realization of the Nernst equation should serve as another criterion for the reversibility of the "electron" electrode. Kanzaki and Aoyagi [36, 154] who had checked the compliance with the Nernst equation in $NaClO_4$ solutions containing solvatedelectrons did not take into account that a significant part of the electrons in sodium salt solutions is tied into complexes $Na^+\ldots e_2^{2-}$ containing the bielectron (cf., p. 170 this article).

In lithium chloride solutions the electrons exist as one type of particle, viz., as solvated electrons which are not tied to the cations or, if so, weakly and without contact. The anodic polarization curve for the oxidation of solvated electrons in these solutions shows one wave with a limiting diffusion current [61] (Fig. 8, curve 1) which can serve as a measure for the concentration of solvated electrons. It was shown that at a constant rate of stirring but different concentrations of solvated electrons the values of electrode potential and the limiting diffusion currents are linked by the equation $\varphi_0 = \text{const} - 0.055 \log I_{\text{lim}}$ (Fig. 9), i.e., the electrode potential obeys the Nernst equation.

In sodium bromide solutions the electrons exist as two different species, viz., as solvated electrons and as complexes $Na^+\ldots e_2^{2-}$ (cf., p. 170 this article). Correspondingly, two waves are observed on the anodic curve of electron oxidation (Fig. 8, curve 2). A curve of similar shape had also been obtained by Kanzaki and Aoyagi [154, 163], who regarded the limiting current of the first wave as the kinetic current of dissociation of $Na^+ \ldots e_s^-$ pairs. According to [61], the equilibrium potential and the limiting current of the first wave, which is weakly stirring dependent, are linked by the expression $\varphi_0 = \text{const} - 0.036 \log I$. It had been shown [61] that such a dependence must be found when the first wave is the oxidation current of solvated monoelectrons and the rate of the process is limited by the rate at which the complex containing bielectrons dissociates into monoelectrons. The limiting current of the second wave is a diffusion current; it is governed by the rate of diffusion of both types of species to the electrode: of e_s^- and of the complexes containing e_2^{2-}.

The bielectron thus can be oxidized only at potentials which are markedly more positive than the potential where the monoelectron is oxidized. This species thus is substantially less reactive. The different reactivity of these two forms of solvated electron had been noticed in radiation–chemical experiments [122], but these did not unambiguously answer the question precisely which of the two was the more active form.

Absolute values for the concentration of solvated electrons can be found by determination of the limiting diffusion currents [61]. Thus, at the equilibrium potential of –2.67 V (vs. nhe), the concentration of solvated electrons is 10^{-2} mole/liter (the concentration can be defined with an error of ±0.3 orders of magnitude, owing to uncertainties in the estimate of diffusion coefficients under the conditions of the electrochemical measurements).

The electronic work function from the metal into the delocalized state in solution is about 0.7 eV at the potential of –2.67 V. Physically this quantity is the difference between the internal energies (including the electrical term) of the electron in the metal and in solution (at the bottom of the conduction band). To convert this into the difference in standard electrochemical potentials one must add the chemical potential of the ideal gas which is calculated from the well-known relation $\mu = -kT\ln[2\pi mkT)^{3/2}v/h^3N_0]$ (the electron gas in the metal is degenerate, and its chemical potential can be equated to the partial internal energy without substantial error). For the concentration of 1 mole/liter this correction is calculated as 0.09 eV.

On the other hand, at the potential of –2.67 V the electrode is in equilibrium with a solution of solvated (localized) electrons which have a concentration of 10^{-2} mole/liter, i.e., under these conditions the electrochemical potentials of the electron in the metal and in the localized state in solution are equal. The standard chemical potential of the electron in solution (at the concentration 1 mole/liter) is higher by a value of $-kT \ln 10^{-2} = +0.12$ eV. With these corrections we find that the difference between the standard chemical potentials of the electron in the delocalized and in the localized state is $0.7 + 0.09 - 0.12 = 0.67$ or about 0.7 eV. This means that the equilibrium concentration ratio of delocalized and localized electrons is 10^{-11}. The value of 0.7 eV, even with any possible uncertainty in its definition (which is about ± 0.1 eV), undoubtedly is higher than the activation energy of diffusion of the electrons (about 0.07 eV); this excludes the diffusion mechanism which is by excitation in the conduction band.

COMPARISON BETWEEN THE LAWS OF GENERATION OF SOLVATED ELECTRONS AND THE LAWS OF ORDINARY ELECTROCHEMICAL REACTIONS

Information about the mechanism of the elementary act of electrochemical processes can be obtained by comparing the laws of generation of solvated electrons with the laws of ordinary electrochemical reactions.

A number of workers have suggested that the electrochemical reactions of cathodic reduction and the processes of spontaneous dissolution of metals occur via the intermediate stage of formation of solvated electrons [1, 4, 164-172]. The possibility of such a mechanism and the theoretical and experimental reasoning of these authors were disputed by other workers [2, 95, 156, 173-176]. The best-known argument in favor of the hydrated electron as intermediate species in the hydrogen evolution reaction by discharge of water molecules is Walker's observation [167, 168], who thought that he had been able to demonstrate the appearance of an optical absorption caused by the hydrated electron. Walker's measurements had been done at one wavelength of the probing light. Investigations at various wavelengths [95, 176] have shown that the change in the intensity of reflected light is largest at wavelengths far from the absorption maximum of the solvated electron. Therefore it is caused not by the formation of solvated electrons but by other processes, probably by a change in the electroreflection of the electrode.

Let us discuss the thermodynamic aspect of the problem that solvated electrons be involved in electrochemical processes. The standard equilibrium potential of the electron electrode in aqueous solutions, according to various estimates [11, 76, 177], is between −2.5 and −2.77 V (nhe), that in liquid ammonia is between −1.85 and −1.95 V (nhe) [2, 7]. Processes occurring in these systems at potentials which are much more positive than the equilibrium potential of the electron electrode cannot to any appreciable extent go via a step of formation of solvated electrons. The situation is similar for HMP, where it proved to be possible to compare the two mechanisms directly: the direct discharge of ions and their reaction with solvated electrons. For this purpose the laws of cathodic hydrogen evolution and of electrochemical electron generation were compared [133, 136]. The polarization curves for passive copper, platinum, and cadmium electrodes in LiCl + HCl solutions in HMP are presented in Fig. 6.

The sections of the curves at high current densities, which have a Tafel slope of 60 mV, correspond to the electrochemical generation of electrons. It had been noted above that the rate of generation is independent of cathode material and solution composition. When the current is reduced to a certain value one observes a drastic shift of potential toward positive values, whereupon the blue coloration disappears. Depending on electrode material and experimental conditions the potential shift can be for diffusional or other reasons.

The sections of the curves at low current densities correspond to hydrogen evolution, and are described by the Tafel equation with slopes of 60 and 140 mV for platinum, 120-140 mV for copper, and 150 mV for cadmium. The rate of hydrogen evolution depends on cathode material and acid concentration. The character of the dependence is similar to that observed in aqueous solutions [178].

It can be seen from Fig. 6 that the potentials of electron generation are 1.3 to 2.0 V more cathodic than the potentials of hydrogen evolution. This shows that the process of hydrogen evolution at the different metals (including metals with high hydrogen overvoltage) is a primary process and is not due to the interaction of proton donors with solvated electrons.

These conclusions concerning the primary nature of the cathodic processes in HMP pertain not only to the hydrogen evolution reaction but are more general in character. This is confirmed by data referring to other electrode reactions.

For example, it was established by Avaca and Bewick [68] who applied cyclic voltammetry to solutions of LiCl + anthracene in HMP that the cathodic peak potentials of anthracene reduction are +1.23 V (anion-radical formation, a reversible diffusion wave) and +0.33 V (dianion formation, an irreversible wave), while the starting potential of generation of solvated electrons is +0.16 V (reference electrode was a lithium electrode in saturated lithium chloride solution). A similar separation of the peaks for naphthalene reduction and for generation of solvated electrons was observed by Postl, Schindewolf et al. [75] in liquid ammonia.

Such a relative position of the potentials indicates that the reduction of the organic material is of a primary nature.

It can be seen from Fig. 6 that the potentials of hydrogen are 1.3 to 2.0 V more positive than the potentials of generation of solvated electrons. Energy changes of the electrons and hydrogen ions are possible, of course, as one goes to solutions of higher pH or to other solvents, but it is unlikely that these changes could span a potential interval of more than 1 V.

In the case of aqueous solutions, hydrogen evolution from alkaline solutions (discharge of H_2O molecules) at metals with high hydrogen overvoltage usually takes place at potentials of up to −1.8 to −2.0 V (nhe), which makes it unlikely that solvated electrons are involved.

Hydrogen evolution from liquid ammonia on high-overvoltage metals (e.g., lead), even though it does appear to occur at higher overvoltages than in water (approximate values of

TABLE 6. The Reduction of Organic Substances during Electrolysis in HMP

Electrolyte	Proton donors	Donor concentration	Current density, A/cm²	Organic substance	Reduction product	Reduction %	Current yield, %	Literature
LiCl	C_2H_2OH	67 mole %	$9\cdot10^{-2}$	$(CH_3)_2C{=}C(CH_3)_2$	$(CH_3)_2CHCH(CH_3)_2$		30	[67]
LiBr	—	—	—	$(C_6H_5)_2C{=}CH_2$	$[(C_6H_5)_2C(CH_2)_2C(C_6H_5)_2]^{2-}$		—	[179]
NaI	—	—	—	$(C_6H_5)_2C{=}C(C_6H_5)_2$	$[(C_6H_5)_2C{-}C(C_6H_5)_2]^{2-}$		—	
	—	—	—	$(C_6H_5)_3CCl$	$(C_6H_5)C^-$		—	
LiCl	C_2H_5OH	4 mole %	$5{,}9\cdot10^{-2}$	4-tert-Butylcyclohexanone	4-tert-Butylcyclohexanol trans cis	95 5	87	[180]
	C_2H_5OH	10 mole %		3,3,5-Trimethylcyclohexanone	3,3,5-Trimethylcyclohexanol cis trans	9 91	50	
LiCl	C_2H_2OH	67 mole %	$9{,}1\cdot10^{-2}$	Benzene	Cyclohexane Cyclohexadiene Cyclohexene	67 23 10	95	[59, 60, 67]
$LiClO_4$				Benzene	Cyclohexene Cyclohexadiene			
$NaClO_4$	H_2O	0,1 mole/liter	—	Toluene	1-Methyl-1,4-cyclohexadiene Isomeric cyclohexenes			[181]
LiCl	C_2H_5OH	67 mole %	$9{,}1\cdot10^{-2}$	Naphthalene	Dihydronaphthalene Tetralin Hexalin Octalin Decalin	7 22 20 11 40	96	[67]
LiCl	C_2H_2OH *	67 mole %		Tetralin	Decalin Hexalin Octalin	85 10 5	54	[59, 60]
			$2\cdot10^{-3}$	Anthracene	Dihydroanthracene	100	65	
		1 mole/liter	$5\cdot10^{-3}$ † $1{,}3\cdot10^{-1}$		Di-, tetra-, hexa-, octahydroanthracene ‡			[68, 182]

LiCl	CH_3COOH				Tetrahydroanthracene	70		
			$1{,}5\cdot10^{-1}$	Dihydroanthracene	Hexahydroanthracene	30		
					Ethanol	90		
	CH_3COOH	1,5 mole/liter	$1{,}3\cdot10^{-1}$	Acetamide	Ethylamine**	10	46	[183]
	C_2H_5OH	5–50vol.%			Cyclooctane			[184]
LiCl	C_3H_7OH	10–50vol.%	$1\cdot10^{-2}$	1,5-Cyclooctadiene	Cyclooctene††			
$LiClO_4$	H_2O	$<5\cdot10^{-2}$ mole/liter	−3,7 V††	Benzyltrimethylammonium perchlorate	Toluene	50		[132]
					Dibenzene***	50		
Without electrolyte					Toluene			
					Dibenzyl			
					Orthomethylbenzyldimethylamine***			

---

*Practically no reduction in the absence of proton donor.

†No generation of solvated electrons at these current densities.

‡The last compound as traces. The proportion of highly reduced form (hexahydroanthracene) increases with the ratio between the concentration of solvated electrons and that of anthracene [68]. All anthracene is converted to hexahydroanthracene when a sufficient amount of charge is passed [182].

**The proportion of amine increases with decreasing temperature, decreasing current density, and increasing acidity.

††The proportion of cyclooctene increases (up to 90%) when replacing the ethanol by propanol, decreasing the proton donor concentration, and increasing the current density.

‡‡Electrolysis under potentiostatic conditions, the potential relative to the Ag/Ag^+ (10^{-2} mole/liter) electrode.

***In the presence of lithium salt the ratio of reduction products is independent of cathode material, while in the absence of lithium cations the composition of the electrolysis products depends on the cathode material.

overvoltage are 1.1-1.2 V at current densities of 10^{-4} to 10^{-3} A/cm^2 in 0.1 mole/liter NH_4Cl [140]), still is at potentials which are lower than the reversible potential of the electron electrode.

There are a number of particular cases, however, where the reduction takes place via interaction of the material with solvated electrons which are generated electrochemically. This is true, in particular, for the reduction of organic substances in those media where the stability of the solvated electrons is sufficiently high.

Data on the preparative reduction of organic compounds in HMP are reported in Table 6. Different cases may be observed during the reduction of organic compounds in HMP. Most common is the situation where direct reduction of the organic substance at the electrode takes place at low current densities. As in the case of hydrogen evolution, kinetic or diffusional rate limitations of this process set in with increasing current density.

Inhibition of the direct reduction process causes the cathodic potentials to increase up to the potentials of electron generation. Thereafter the organic substance is reduced by two parallel pathways: electrochemically and chemically via the reaction with solvated electrons; at high current densities the share of direct reduction at the electrode may be very low. In any particular case the rate of this process can practically be close to zero, as, e.g., in the case of benzene.

Benkeser and co-workers [62, 63] and Sternberg and co-workers [64, 65] examined the electrochemical reduction of a number of aromatic hydrocarbons in solutions of lithium chloride and other salts in methylamine and ethylenediamine. The reaction can be carried to the corresponding tetrahydro derivative. In a number of cases, such as, e.g., in the reduction of benzene, the process appears to go via electrochemically generated solvated electrons. The same is true for the cathodic reduction of olefins, amides, and ketones in lithium chloride solution in methylamine [185, 186]. The suggestion was made that benzene is reduced by solvated electrons during cathodic polarization of a mercury electrode in tetrabutylammonium bromide solution in a mixture of water and diglyme [187].

The use of electrochemically generated solvated electrons for the reduction of organic compounds has been discussed in Lund's review [188].

It will be of interest to discuss some special features of reductions with the aid of electrochemically generated solvated electrons. Because of these features, this process can be regarded as a promising method of preparative electrolysis.

With solvated electrons one can reduce compounds which are difficult to reduce, for instance benzene. The reducing action of solvated electrons seems to be very selective. Water present in HMP up to a concentration of 0.1 mole/liter will not react with electrochemically generated solvated electrons in lithium or sodium perchlorate solutions in HMP, and only at a concentration of 0.5 mole/liter will it be reduced to hydrogen [181]. The indirect reduction by solvated electrons in HMP as a rule yields higher degrees of reduction than are obtained by the direct cathodic reduction of the organic substance (cf. the reduction of anthracene, Table 6).

It will be of interest to compare the reduction by solvated electrons in HMP with other methods of cathodic reduction. We shall do this with a ketone as the example. The results of preparative reduction of 4-tertbutylcyclohexanone are presented in Table 7. This ketone is reduced to an alcohol which exists in the form of two stereoisomers. Electrochemical reduction of the ketone seems to take place in all cases other than the first, because the generation of solvated electrons in these media is unlikely. This is also indicated by the values of potential. It can be seen from Table 7 that the reduction takes place with the highest stereoselectivity and with high current yield just in HMP, where electron generation is the most likely cathodic process.

The rate of processes involving electrochemically generated solvated electrons may significantly surpass that of direct cathodic reduction of the organic substance.

Diffusional limitations in the supply of organic substance to the electrode surface can develop during direct reduction. Such limitations are less important during the electrochemical generation of solvated electrons. The large diffusion coefficient of the solvated

TABLE 7. The Reduction of 4-Tertbutylcyclohexanone in Different Media [180]

Solvent	Electrolyte	Cathode material	φ_{cath} (nce)	Current density, A/cm²	Yield, %		Isomers, %	
					chemical	current	trans	cis
HMP–C_2H_5OH, 4 mole-%	LiCl	Pt		$5{,}9\cdot10^{-2}$	87	87	95	5
CH_3OH	BU_4NCH_3COO	Pb	–2,4	$(4{,}5–7{,}8)\cdot10^{-2}$	82	66	88	12
CH_3OH	CH_3COONa	Pb	–2,07– –2,27	$8{,}2\cdot10^{-2}$	81	14	85	15
CH_3OH	CH_3COOH CH_3COONa	Pb	–1,86– –1,87	$8{,}2\cdot10^{-2}$	87	11	44	56
CH_3OH-H_2O	H_2SO_4	Pb	–1,6– 1,65	$1{,}2\cdot10^{-1}$	0	0		

electron in HMP should guarantee the fast removal of the electrons from the cathode. The current densities of generation may surpass the diffusion-limited currents of the organic substance by a factor of 2500 and more [182].

The reducing properties of solutions containing electrochemically generated electrons are close to those of alkali metal solutions in the corresponding solvent. However, the electrochemical generation provides for a more accurately measured feed of electrons and for operational safety.

In water and in liquid ammonia, the equilibrium potentials for the alkali and certain alkaline-earth metals are more negative than that of the electron electrode [141, 142]. This indicates that the participation of solvated electrons in certain processes taking place in aqueous solutions at very negative potentials, possibly in parallel with other mechanisms, cannot be excluded. These processes include, in particular, the dissolution of the most electronegative metals, e.g., the alkali metals. In 1934 already Wolthorn and Fernelius [189] reported that a blue coloration can be noticed briefly at the surface of metallic potassium reacting with cold water. It appears that this coloration is caused by hydrated electrons entrained in the KOH film covering the metal [76]. Jortner and Stein's data [190] on the appearance of the optical absorption spectrum during the reaction of potassium and sodium sprayed onto ice at –10°C could not be confirmed [76]. However, Bennett, Mile, and Thomas [191] report that when this reaction is conducted at –196°C, a dark-blue product is formed which gives the single, narrow line in the ESR spectra which is typical for electrons stabilized in the solid phase.

ELECTRON EMISSION FROM ALKALI-METAL SOLUTIONS IN LIQUID AMMONIA AND HEXAMETHYLPHOSPHORAMIDE

Because of the high stability of solutions of solvated electrons in liquid ammonia and HMP it became possible to use these solutions as convenient materials for an examination of electron emission from the liquid into the gas phase.

Electron photoemission from solutions of electrons in a polar solvent had first been observed for alkali-metal solutions in liquid ammonia [192-194]. The photoemission from solutions of solvated electrons has much in common with the photoemission from the solutions (including aqueous solutions) of any electron donor, e.g., ferrocyanide (see [195, 196]). In all cases we are dealing with an electron in some potential well which is caused by the interaction with the solvent or, in the case of any donor species, with the corresponding ion or molecule. The depth of this well is not constant but depends on fluctuations of the medium interacting with the electron (see, e.g., [159, 197]). By absorbing a quantum of light of sufficient energy the electron is knocked out of the trap and passes into the delocalized state. The probability of this transition is a function of the quantum energy. The delocalized electron, which is the analog of an electron in the conduction band in semiconductors, only interacts with the practically inertia-free part of the medium's polarizability, i.e., with the electron polarizability. Moving about in the medium this quasi-free electron can either be entrained by a new trap (both by a trap which is similar to the one which it had abandoned and by another type of trap) or reach the solution/gas boundary. The average distance covered by the electron in a given medium before it is captured depends on its kinetic energy, i.e., on the difference between the energy of absorbed light and the energy of transition of the electron from the bound state into the continuum (the ionization energy). Depending on its energy an electron arriving at the solution/gas boundary will either be reflected by the energy barrier at this boundary or pass through it.

Thus, photoemission of electrons from solutions is a highly complex set of phenomena. Its quantitative aspects are governed by the properties of the electron traps, of the medium, and of the phase boundary. It will be clear, however, that a threshold must exist which is determined by the minimum quantum energy required for photoionization of a bound electron. It is further known that the ionization probability of any bound state must decrease at high quantum energies. Therefore a maximum appears on the plot of photocurrent against frequency of the light.

The most complete quantitative data on photoemission from solutions of solvated electrons were obtained by Delahay et al. [198] for alkali-metal solutions in HMP. These workers found two maxima of the photocurrent as function of the light quantum energy. The first maximum is attributed to photoionization of the solvated electron, the second maximum (at higher energies) is attributed to the ionization of an electron which is bound in the more stable complex with the Na^+ ion (probably $Na^+...e_2^{2-}$). The photoemission spectrum thus turns out to be similar to the absorption spectrum of these solutions. This interpretation is supported by the observation that the second maximum diminishes more rapidly than the first one as the solution is diluted, which is what one must expect for the dissociation of intricate complexes.

By extrapolating the plot of photocurrent against quantum energy to zero current one can find the threshold energy, i.e., the minimum energy required to extract the electron from the well and transfer it into the gas phase. The methods of extrapolation will depend on the theoretical model used in data analysis.

Delahay [199] (see also [200]) regards the motion of an electron knocked by light from the trap toward the surface of the liquid as a process of chaotic wandering, and discounts the possibility that electrons are reflected at the phase boundary. Brodskii and Tsarevskii [201] start from a more justified physical model where the electron's motion is regarded as wave propagation, and where the probability of the electron being reflected from the surface barrier is taken into account. For energy values near the threshold energy, the theory leads to a linear dependence of the photoemission current raised to two-fifths power on the light quantum energy, which is in good agreement with experimental data.

The extrapolation carried out by Delahay and coauthors gives threshold energies of 1.34 [199] to 1.4 eV [198] for the escape of an electron from the bound state in HMP into the gas phase*. The extrapolation according to Brodskii and Tsarevskii gives the lower value of 0.9 eV [201]. For the solvated electron in liquid ammonia the corresponding figures are 1.85 eV [199] (based on the data of [194]) and 1.53 eV [201].

The difference between the results obtained in [198, 199] and [201] may be due not only to the different ideas of electronic motion adopted in these theories but also to the fact that these workers have considered different regions of electronic energies. Delahay et al. consider high kinetic energies, and believe that the value determined by them corresponds to the work function of an electron in the ground state. Brodskii and Tsarevskii analyze the region of energies near the threshold energy, so that their result may refer to a thermally excited initial state of the solvated electron which is somewhat higher in energy and noticeably lower in ionization energy.

The work function determined from photoemission experiments is not the equilibrium work

---

*Gremmo and Randles [138] extrapolate the approximately linear section of the photocurrent-quantum energy plot, and thus obtain for the threshold energy a value of 1.05 eV. Analysis of Delahay et al.'s data [198] by the same method gives a value of 1.2 eV. It is not quite clear why there is this discrepancy between the experimental data of [138] and [198], but to some extent this is due to the fact that Gremmo and Randles did not reduce their data to a constant value of photon flux.

of transfer of an electron from the ground state in solution into the gas phase. By virtue of the Franck-Condon principle, the solvent during photoionization cannot reorganize, and after extraction of the electron remains in the nonequilibrium state created by orientation of the molecules in the electric field of the electron which before had existed in that place [159]*.

In principle an equilibrium value for the work function could be obtained from data on thermal electron emission. The thermal emission of electrons from a solution in a polar dielectric had first been found by Baron, Delahay, and Lugo [100] in the instance of Na solution in HMP. It was unambiguously demonstrated that the particle being emitted from the solution into the gas phase is an electron. From the temperature dependence of the emission current an energy of activation (or effective work function) of 1.0 eV could be determined. According to the data of [138], the activation energy decreases with solution concentration from 0.95 eV at 0.05 mole/liter (these values practically match those of [100]) to 0.74 eV at 10^{-3} mole/liter. It must be noted, however, that this quantity cannot be regarded as the true work function. It is affected, first, by the temperature dependence of the dissociation equilibrium of the strong complexes between solvated electrons and the Na^+ ion. Secondly, the temperature variation of the surface potential which is due to temperature-dependent adsorption of solution components can contribute importantly to this quantity. That such adsorption is highly probable can be seen from the very unexpected result obtained in the work cited: The thermal emission current diminishes as the sodium concentration increases. Gremmo and Randles showed afterwards [138] that at low alkali-metal concentrations a very sharp maximum appears on the plot of photocurrent against metal concentration (at a Na concentration of 0.9×10^{-3} mole/liter; the same in Li solutions). The most reasonable explanation of this effect is by strong adsorption of cations or (and) electrons, which alters the surface potential in such a way that the escape of electrons is made more difficult, and that this more than compensates the increase in electron concentration [198, 138].

High surface activity of alkali metal in HMP is likely on the basis of the qualitative observation that the blue coloration is spreading rapidly over the surface of the liquid when it comes in contact with a piece of alkali metal [138].

Gremmo and Randles [138], who regarded a strong specific adsorption of electrons as the cause of double-layer formation at the solution surface and, therefore, as the cause of inhibition of emission, at the same time pointed out that this analysis is contradictory. They believe that the surface electrons forming the outer side of the double layer can quit the solution without experiencing the inhibiting effect of the surface potential. To us this contradiction is an apparent one. The point is that the thermal equilibrium in the solution is not upset during thermal emission. The electrons at the surface and in the bulk of the solution are in equilibrium with each other, so that the result cannot depend on the particular location of the electrons which we consider. The electrons on the outer side of the double layer in fact do not experience the inhibiting effect of the double layer, but their energy is higher than that in the bulk of the solution by the amount $F \cdot \Delta\varphi$, and therefore their concentration is lower by a factor of $\exp(F \cdot \Delta\varphi/RT)$. The surface potential shift is estimated to be 0.1 V when the Na concentration changes from 0.004 to 0.18 mole/liter [198], and 0.24 V when the concentration changes from 10^{-3} to 0.4 mole/liter [138].

The influence of Na concentration on photoemission is less pronounced. This probably is due to the fact that at low concentrations of solvated electrons, the photoemission current is strongly reduced owing to the small amount of electrons present in the layer which can be penetrated by the delocalized electron before it is captured [138]. There is no doubt, however, that the photoemission current increases much less than in direct proportion with the concentration. This at least qualitatively agrees with the idea that the surface potential which inhibits the emission is increasing at the same time.

It is the peculiarity of experiments on emission into the gas phase that one must account for two effects altering the magnitude of the photocurrent: 1) back scattering of electrons, and 2) the Schottky effect [160]. Back scattering is the return of electrons

---

*The mechanism of photoexcitation to a high level in the bound state (for solutions in NH_3 the vacant 3s orbital of nitrogen is suggested to be involved) followed by its self-ionization is possible [100] in addition to photoionization of the solvated electron and direct formation of a delocalized particle.

from the gas phase into the liquid as a result of collision with gas molecules. This effect of course is intensified when the gas pressure (p) increases, and is reduced with an increase in the electric field (E) between the solution and the anode which tends to draw the electrons away from the surface of the liquid. The influence of this factor can be excluded by extrapolating the experimental data to $E/p = \infty$. The Schottky effect is caused by a decrease in the energy barrier at the phase boundary when an external electric field is applied. It depends exponentially on the field, but is independent of gas pressure, so that it can be distinguished experimentally from the back scattering effect. In the experiments of [100] and [198], the effect of back scattering was important, while the Schottky effect yielded a noticeable correction only in the experiments on thermal emission [100].

It can be seen from the material presented above that the features of photo and thermal emission of electrons from solutions have not yet received a sufficiently complete quantitative interpretation, but as a matter of fact these interesting effects have just begun to be studied, so that from this direction one can expect to obtain new and important information about the properties of solvated electrons.

LITERATURE CITED

1. L. I. Antropov, Progress in Science, Electrochemistry, 6, 5 (1971).
2. B. E. Conway, in: Modern Aspects of Electrochemistry (ed. by B. E. Conway and J. O'M. Bockris), Vol. 7, Plenum, New York (1972), p. 83.
3. N. M. Alpatova, Yu. M. Kessler, L. I. Krishtalik, E. V. Ovsyannikova, and M. G. Fomicheva, Progress in Science, Electrochemistry, 10, 45 (1975).
4. I. A. Kenney and D. C. Walker, in: Electroanalytical Chemistry (ed. by A. J. Bard), Vol. 5, Marcel Dekker, New York (1971), p. 1.
5. A. M. Brodskii, Yu. Ya. Gurevich, Yu. V. Pleskov, and Z. A. Rotenberg, Modern Photoelectrochemistry. Photoemission Phenomena [in Russian], Nauka, Moscow (1974).
6. S. R. Logan, J. Chem. Educ., 44, 344 (1967).
7. U. Schindewolf, Chemie unserer Zeit, 4, 37 (1970).
8. J. Rabani, in: Solvated Electron, Advan. Chem. Ser., 50, 242 (1965).
9. M. Anbar and E. J. Hart, J. Phys. Chem., 71, 4163 (1967).
10. J. Belloni and E. Saito, Nucl. Sci. Abstracts, 28, 150 (1973).
11. J. H. Baxendale (D. G. Baksendeil), Zh. Vses. Khim. Obshchest. im. D. I. Mendeleeva, 11, 168 (1966) [translated article].
12. N. P. Fedot'ev and R. N. Kinkul'skaya, in: Proc. First All-Union Conf. Nonaqueous Solutions [in Russian], Izd. Akad. Nauk UkrSSR, Kiev (1935), p. 114.
13. T. P. Das, Advan. Chem. Phys., 4, 303 (1962).
14. P. R. Marshall, J. Chem. Eng. Data, 7, 399 (1962).
15. K. D. Vos and J. L. Dye, J. Chem. Phys., 38, 2033 (1963).
16. W. H. Howland and L. F. Epstein, J. Amer. Chem. Soc., 76, 292 (1954).
17. R. R. Dewald and J. L. Dye, J. Phys. Chem., 68, 128 (1964).
18. G. W. A. Fowler, W. R. McGregor, and M. C. R. Symons, J. Chem. Soc., 3329 (1957).
19. R. Catterall, in: Solutions métal-ammoniac, Propriétés physico-chimiques. Colloque Weyl, Univ. Catholique, Lille (Juin 1963) (ed. by G. Lepoutre and M. J. Sienko), Benjamin, New York (1964), p. 41.
20. F. S. Dainton, D. M. Wiles, and A. N. Wright, J. Chem. Soc., 4283 (1960).
21. F. A. Cafasso and B. R. Sundheim, J. Chem. Phys., 31, 809 (1959).
22. G. Fraenkel, S. H. Ellis, and D. T. Dix, J. Amer. Chem. Soc., 87, 1406 (1965).
23. R. Gremmo and J. E. B. Randles, J. Chem. Soc., Faraday Trans. I, 70, 1480 (1974).
24. J. W. Diggle and D. Bonsányi, J. Phys. Chem., 78, 1018 (1974).
25. E. C. Evers, A. E. Young II, and A. J. Panson, J. Amer. Chem. Soc., 79, 5118 (1957).
26. R. L. Schroeder and J. C. Thompson, Bull. Amer. Phys. Soc., 11, 252 (1966).
27. A. Lüttringhaus and H. W. Dirksen, Angew. Chem. Int. Ed., 3, 260 (1964).
28. J. L. Down, J. Lewis, B. Moore, and G. Wilkinson, J. Chem. Soc., 3767 (1959).
29. I. M. Panayotov, I. V. Berlinova, and N. P. Matev, Dokl. Bolg. Akad. Nauk, 24, 1321 (1971).
30. J. Dye, M. DeBaster, and V. A. Nicely, J. Amer. Chem. Soc., 92, 5226 (1970).
31. R. A. Robinson and R. H. Stokes, Electrolyte Solutions (2nd edition) [Russian translation] (1963).
32. Dictionary of Organic Compounds [Russian translation], Izd. Inostr. Lit., Moscow (1949).

33. G. L. Putman and K. A. Kobe, Trans. Electrochem. Soc., 74, 609 (1938).
34. A. Weissberger (editor), Techniques of Organic Chemistry, Vol. 7, Organic Solvents (2nd edition),Wiley-Interscience, New York (1955).
35. The Chemist's Handbook [in Russian], Vol. 1, Goskhimizdat, Moscow (1962).
36. Y. Kanzaki and S. Aoyagi (Aoyagui), J. Electroanal. Chem., 36, 297 (1972).
37. H. Normant, Uspekhi Khimii, 39, 990 (1970) [translated article].
38. H. P. Cady, J. Phys. Chem., 1, 707 (1897).
39. C. A. Kraus, J. Amer. Chem. Soc., 30, 1323 (1908).
40. B. E. Gordon and V. L. Broude, Zh. Fiz. Khim., 24, 409 (1950) [translated article].
41. E. I. Akhumov and B. B. Vasil'ev, Zh. Obshch. Khim., 5, 334 (1935).
42. E. I. Akhumov and N. A. Goncharov, Zh. Obshch. Khim., 6, 534 (1936).
43. E. I. Akhumov. Proc. Second All-Union Conf. Theoret. Applied Electrochem. [in Russian], Izd. Akad. Nauk UkrSSR, Kiev (1949).
44. E. Masdupuy, Ann. Chimie (Paris), 2, 527 (1957).
45. A. W. Davidson, J. Kleinberg, W. E. Bennett, and A. D. McElroy, J. Amer. Chem. Soc., 71, 377 (1949).
46. A. D. McElroy, J. Kleinberg, and A. W. Davidson, J. Amer. Chem. Soc., 72, 5178 (1950).
47. R. K. Quinn and J. J. Lagowski, Inorg. Chem., 9, 414 (1970).
48. J. K. Thompson and J. Kleinberg, J. Amer. Chem. Soc., 73, 1243 (1951).
49. W. Palmaer, Z. Elektrochem., 8, 729 (1902).
50. H. H. Schlubach, Ber. Deut. Chem. Ges., 53B, 1689 (1920).
51. H. H. Schlubach and F. Ballauf, Ber. Deut. Chem. Ges., 54B, 2811 (1921).
52. H. H. Schlubach and H. Miedel, Ber. Deut. Chem. Ges., 56B, 1892 (1923).
53. C. A. Kraus, J. Amer. Chem. Soc., 35, 1732 (1913).
54. H. A. Laitinen and C. J. Nyman, J. Amer. Chem. Soc., 70, 3002 (1948).
55. R. K. Quinn and J. J. Lagowski, J. Phys. Chem., 72, 1374 (1968).
56. O. Ruff, Chem. Ber., 34, 2604 (1901).
57. L. A. Avaca and A. Bewick, J. Electroanal. Chem., 41, 395 (1973).
58. N. M. Alpatova, L. I. Krishtalik, and M. G. Fomicheva, Élektrokhimiya, 8, 535 (1972).
59. H. W. Sternberg, R. E. Markby, I. Wender, and D. M. Mohilner, Amer. Chem. Soc., Div. Fuels Chem., Preprints, 11, 188 (1967).
60. L. A. Avaca and A. Bewick, J. Electroanal. Chem., 41, 405 (1973).
61. E. V. Ovsyannikova, L. I. Krishtalik, and N. M. Alpatova, Élektrokhimiya, 12, 900 (1976).
62. R. A. Benkeser and E. M. Kaiser, J. Amer. Chem. Soc., 85, 2858 (1963).
63. R. A. Benkeser, E. M. Kaiser, and R. F. Lambert, J. Amer. Chem. Soc., 86, 5272 (1964).
64. H. W. Sternberg, R. E. Markby, I. Wender, and D. M. Mohilner, J. Electrochem. Soc., 113, 1060 (1966).
65. H. W. Sternberg, R. E. Markby, and I. Wender, J. Electrochem. Soc., 110, 425 (1963).
66. S. H. Glarum and J. H. Marshall, J. Chem. Phys., 52, 5555 (1970).
67. H. W. Sternberg, R. E. Markby, I. Wender, and D. M. Mohilner, J. Amer. Chem. Soc., 91, 4191 (1969).
68. L. A. Avaca and A. Bewick, J. Chem. Soc., Perkin Trans.II, 1709 (1972).
69. N. M. Alpatova and A. D. Grishina, Élektrokhimiya, 7, 853 (1971).
70. D. Lelievre and V. Plichon, Compt. Rend., C, 275, 1499 (1972).
71. D. A. Pospekhov, Zh. Prikl. Khim., 27, 552 (1954).
72. Ya. I. Ol'shanskii, Dokl. Akad. Nauk SSSR, 61, 701 (1950).
73. Ya. I. Ol'shanskii, in: Experimental Technique and Research Methods at High Temperatures [in Russian], Izd. Akad. Nauk SSSR (1959), p. 402.
74. M. V. Smirnov, V. Ya. Kudyakov, and N. A. Loginov, Abstracts of Papers, Fifth All-Union Conf. Electrochem. [in Russian], Vol. 1, Izd. VINITI, Moscow (1974), p. 93.
75. D. Postl, U. Schindewolf, W. Schmitt, and P. Wünschel, Ber. Bunsenges. Phys. Chem., 77, 1007 (1973).
76. E. J. Hart and M. Anbar, The Hydrated Electron, Wiley-Interscience, New York (1970).
77. U. Schindewolf, Angew. Chem., 80, 165 (1968).
78. J. K. Thomas, Radiat. Res. Rev., 1, 183 (1968).
79. J. Teply and I. Janovsky, Chem. Listy, 67, 449 (1973).
80. Solvated Electron. Advan. Chem. Ser., 50 (1965).
81. Solutions métal-ammoniac, Propriétés physico-chimiques, Colloque Weyl, Lille (Juin 1963), G. Lepoutre and M. J. Sienko, editors, Benjamin, New York (1964).
82. Metal-Ammonia Solutions, Proc. Colloque Weyl No. 11, Ithaca (1969), J. J. Lagowski and M. J. Sienko, editors, Butterworths, London (1970).

83. W. L. Jolly, Progress Inorg. Chem., 1, 240 (1959).
84. M. C. R. Symons, Quart. Rev., 13, 99 (1959).
85. M. H. Cohen and J. C. Thompson, Advan. Phys., 17, 857 (1968).
86. H. Kelm, Umschau, 70, 701 (1970).
87. A. K. Pikaev, The Solvated Electron in Radiation Chemistry [in Russian], Nauka, Moscow (1969).
88. E. J. Hart, Science, 146, 19 (1964).
89. N. M. Alpatova, A. D. Grishina, and M. G. Fomicheva, Ēlektrokhimiya, 8, 258 (1972).
90. N. M. Alpatova, E. I. Mal'tsev, A. V. Vannikov, and S. E. Zabusova, Ēlektrokhimiya, 9, 1034 (1973).
91. J. M. Brooks and R. R. Dewald, J. Phys. Chem., 72, 2655 (1968).
92. G. I. Khaikin, V. A. Zhigunov, and P. I. Dolin, Khimiya Vysokikh Ēnergii, 5, 54 (1971).
93. R. C. Doughit and J. L. Dye, J. Amer. Chem. Soc., 82, 4482 (1960).
94. R. K. Quinn and J. J. Lagowski, J. Phys. Chem., 73, 2326 (1969).
95. D. Postl and U. Schindewolf, Ber. Bunsenges. Phys. Chem., 75, 662 (1971).
96. E. A. Ukshe and N. G. Bukun, Uspekhi Khimii, 30, 243 (1961).
97. Yu. P. Pavlov, M. G. Fomicheva, A. I. Mishustin, and N. M. Alpatova, Ēlektrokhimiya, 9, 541 (1973).
98. G. Berthet, J. Dupuis, and J. P. Imbaud, in: Magnetic Resonance and Related Phenomena, Proc. Congr. AMPERE, 16th, 1970, I. Ursu, editor, Bucharest, Publ. House Acad. Soc. (1971), p. 972.
99. J. Dupuis and J. P. Imbaud, Compt. Rend., B, 270, 517 (1970).
100. B. Baron, P. Delahay, and R. Lugo, J. Chem. Phys., 53, 1399 (1970).
101. G. Rubinstein, T. R. Tuttle, and S. Golden, J. Phys. Chem., 77, 2872 (1973).
102. E. Arnold and A. Patterson, J. Chem. Phys., 41, 3098 (1964).
103. R. Catterall, L. P. Stodulski, and M. C. R. Symons, J. Chem. Soc., 437 (1968).
104. J. L. Dye, Mei Tak Lok, F. J. Tehan, R. B. Coolen, N. Papadakis, J. M. Cesaro, and M. G. de Backer, Ber. Bunsenges. Phys. Chem., 75, 659 (1971).
105. K. Bar-Eli and T. R. Tuttle, J. Chem. Phys., 40, 2508 (1964).
106. S. Matalon, S. Golden, and M. Otoolenghi, J. Phys. Chem., 73, 3098 (1969).
107. M. Ottolenghi, K. Bar-Eli, H. Linschitz, and T. R. Tuttle, J. Chem. Phys., 40, 3729 (1964).
108. R. Catterall, M. C. R. Symons, and J. M. Tipping, J. Chem. Soc., 1529 (1966).
109. R. Catterall and M. C. R. Symons, J. Chem. Soc., 6656 (1965).
110. M. Ottolenghi and H. Linschitz, in: Solvated Electron, Advan. Chem. Ser., 50, 149 (1965).
111. H. Blades and J. W. Hodgins, Can. J. Chem., 33, 411 (1955).
112. R. R. Dewald and J. L. Dye, J. Phys. Chem., 68, 121 (1964).
113. D. Hupper and K. H. Bar-Eli, J. Phys. Chem., 74, 3285 (1970).
114. R. Catterall, J. Slater, and M. C. R. Symons, J. Phys. Chem., 52, 1003 (1970).
115. J. Eloranta and H. Linschitz, J. Chem. Phys., 38, 2214 (1963).
116. I. M. Panayotov, Ch. B. Tsvetanov, and R. St. Velichkova (Velitschkova), Monatsh. Chem., 103, 1119 (1972).
117. I. Hurley, T. R. Tuttle, Jr., and S. Golden, J. Chem. Phys., 48, 2818 (1968).
118. E. I. Mal'tsev and A. V. Vannikov, Dokl. Akad. Nauk SSSR, 200, 379 (1971).
119. E. I. Mal'tsev, A. V. Vannikov, and N. A. Bakh (Bach), Radiation Effects, 11, 79 (1971).
120. N. M. Alpatova and A. D. Grishina, Ēlektrokhimiya, 9, 1375 (1973).
121. A. V. Vannikova, N. M. Alpatova, E. I. Mal'tsev, and L. I. Krishtalik, Ēlektrokhimiya, 10, 830 (1974).
122. A. V. Vannikov and N. M. Alpatova, Ēlektrokhimiya, 11, 996 (1975).
123. S. N. Bhadani, Indian J. Chem., 10, 88 (1972).
124. R. P. Gordon and B. R. Sundheim, J. Phys. Chem., 68, 3347 (1964).
125. J. L. Dye, R. F. Sankuer, and G. E. Smith, J. Amer. Chem. Soc., 82, 4797 (1960).
126. J. L. Dye, in: Solutions métal-ammoniac, Propriétés physico-chimiques, Colloque Weyl, Lille (Juin 1963), G. Lepoutre and M. J. Sienko, editors, Benjamin, New York (1964), p. 137.
127. G. I. Khaikin, V. A. Zhigunov, and P. I. Dolin, Dokl. Akad. Nauk SSSR, 202, 140 (1972).
128. S. Glasstone, An Introduction to Electrochemistry [Russian translation], Izd. Inostr. Lit., Moscow (1951).
129. C. Atlani, J.-C. Justice, M. Quintin, and J. E. Dubois, J. Chim. Phys. Physicochim. Biol., 66, 180 (1969).
130. E. I. Mal'tsev and A. V. Vannikov, Radiation Effects, 20, 197 (1973).

131. R. V. Ivanova and M. G. Fomicheva, Élektrokhimiya, 8, 1259 (1972).
132. J. E. Dubois, A. Monvernay, and P. C. Lacaze, J. Chim. Phys. Physicochim. Biol., 70, 39 (1973).
133. L. I. Krishtalik, N. M. Alpatova, and M. G. Fomicheva, Élektrokhimiya, 7, 1393 (1971).
134. L. I. Krishtalik, N. M. Alpatova, and M. G. Fomicheva, Croat. Chem. Acta, 44, 1 (1972).
135. L. I. Krishtalik, M. G. Fomicheva, and N. M. Alpatova, Élektrokhimiya, 8, 629 (1972).
136/137. N. M. Alpatova, M. G. Fomicheva, E. V. Ovsyannikova, and L. I. Krishtalik, Élektrokhimiya, 9, 1234 (1973).
138. N. Gremmo and J. E. B. Randles, J. Chem. Soc., Faraday Trans. I, 70, 1488 (1974).
139. S. E. Zabusova, M. G. Fomicheva, L. I. Krishtalik, and N. M. Alpatova, Élektrokhimiya, 11, 1888 (1975).
140. V. A. Pleskov, Uspekhi Khimii, 16, 254 (1947); Zh. Fiz. Khim., 13, 1449 (1939).
141. W. L. Jolly, J. Chem. Educ., 33, 512 (1956).
142. H. Strehlow, in: The Chemistry of Nonaqueous Solvents (ed. by J. J. Lagowski), Vol. 1 Academic Press, New York (1966).
143. Z. A. Rotenberg and Yu. V. Pleskov, Élektrokhimiya, 4, 826 (1968).
144. A. N. Frumkin, O. A. Petrii, and N. V. Nikolaeva-Fedorovich, Dokl. Akad. Nauk SSSR, 147, 878 (1962).
145. J. E. Dubois, P. C. Lacaze, and A. M. de Fiquelmont, Compt. Rend., C, 262, 181, 249 (1966).
146. J. Y. Gal and T. Yvernault, Bull. Soc. Chim. Fr., 2770 (1971).
147. J. Y. Gal and T. Yvernault, Compt. Rend., C, 272, 42 (1971).
148. K. Izutsu, S. Sakura, and T. Fujinaga, Bull. Chem. Soc. Japan, 45, 445 (1972).
149. J. E. Dubois, A. Monvernay, and P. C. Lacaze, Electrochim. Acta, 15, 315 (1970).
150. G. Schöber and V. Gutmann, Z. Elektrochem., 63, 274 (1959).
151. G. Schöber and V. Gutmann, Monatsh. Chem., 89, 401 (1958).
152. C. A. Kraus, J. Amer. Chem. Soc., 36, 864 (1914).
153. N. M. Alpatova, L. I. Krishtalik, E. V. Ovsyannikova, and S. E. Zabusova, Élektrokhimiya, 9, 884 (1973).
154. Y. Kanzaki and S. Aoyagi (Aoyagui), Japan-USSR Seminar of Electrochemistry, Extended Abstracts, Tokyo, October 7-10, 1974, The Electrochemical Society of Japan, p. 155.
155. A. M. Brodskii (Brodsky), Yu. Ya. Gurevich, and V. G. Levich, Phys. Status Solidi, 40, 139 (1970).
156. A. M. Brodskii and A. N. Frumkin, Élektrokhimiya, 6, 658 (1970).
157. Yu. Ya. Gurevich, A. M. Brodskii, and V. G. Levich, Élektrokhimiya, 3, 1302 (1967).
158. A. M. Brodskii and Yu. Ya. Gurevich, Itogi Nauki, Élektrochimiya Progress in Science, Electrochemistry], 1968, Izd. VINITI, Moscow (1970), p. 7.
159. R. R. Dogonadze, L. I. Krishtalik, and Yu. V. Pleskov, Élektrokhimiya, 10, 507 (1974).
160. L. I. Dobretsov and M. V. Gomoyunova, Emission Electronics [in Russian], Nauka, Moscow (1966).
161. Y. Kanzaki and S. Aoyagi (Aoyagui), J. Electroanal. Chem., 51, 19 (1974).
162. R. G. Érenburg, Élektrokhimiya, 10, 457 (1974).
163. Y. Kanzaki and S. Aoyagi (Aoyagui), J. Electroanal. Chem., 47, 109 (1973).
164. G. Hughes and R. J. Roach, Chem. Commun., 600 (1965).
165. H. E. Bartlett, R. A. Basson, P. M. Champion, P. Crowther, and H. Isaacs, J. S. Afr. Chem. Inst., 23, 57 (1970); Chem. Abstr., 72, 137138g (1970).
166. G. J. Hills and D. R. Kinnibrugh, J. Electrochem. Soc., 113, 1111 (1966).
167. D. C. Walker, Can. J. Chem., 44, 2226 (1966).
168. D. C. Walker, Can. J. Chem., 45, 807 (1967).
169. D. C. Walker, Anal. Chem., 39, 896 (1967).
170. T. Pyle and C. Roberts, J. Electrochem. Soc., 115, 247 (1968).
171. J. Kalecinski, Bull. Acad. Polon. Sci., Ser. Sci. Chim., 18, 263 (1970).
172. J. Jansta, F. P. Dousek, and J. Říha, J. Electroanal. Chem., 44, 263 (1973).
173. R. Parsons, J. Electrochem. Soc., 113, 1118 (1966).
174. L. I. Krishtalik, J. Electrochem. Soc., 113, 1117 (1966).
175. B. E. Conway and D. J. MacKinnon, J. Phys. Chem., 74, 3663 (1970).
176. A. Bewick, B. E. Conway, and A. M. Tuxford, J. Electroanal. Chem., 42, App. 11 (1973).
177. Z. A. Rotenberg, Élektrokhimiya, 8, 1198 (1972).
178. L. I. Krishtalik, Advan. Electrochem. Electrochem. Eng., 7, 283 (1970).
179. L. D. McKeever and R. Waack, J. Organomet. Chem., 17, 142 (1969).
180. J. P. Coleman, R. J. Kobylecky, and J. H. P. Utley, Chem. Commun., 104 (1971).

181. J. E. Dubois and G. Dodin, Tetrahedron Lett., 2325 (1969).
182. L. A. Avaca and A. Bewick, J. Appl. Electrochem., 2, 349 (1972).
183. L. A. Avaca and A. Bewick, J. Chem. Soc., Perkin Trans. II, 1712 (1972).
184. T. Asahara, M. Seno, T. Ibuki, and H. Yoshigawara, J. Japan Oil Chem. Soc., 22, 27 (1973).
185. R. A. Benkeser, H. Watanabe, S. J. Mels, and M. A. Sobol, J. Org. Chem., 35, 1210 (1970).
186. S. J. Mels, Diss. Abstr. Int., B, 30, 4053 (1970).
187. T. Misono, T. Osa, T. Yamagishi, and T. Kodama, J. Electrochem. Soc., 115, 266 (1968).
188. H. Lund, in: Organic Electrochemistry. An Introduction and a Guide (ed. by M. M. Baizer), Marcel Dekker, New York (1973), p. 839.
189. H. J. Wolthorn and W. C. Fernelius, J. Amer. Chem. Soc., 56, 1551 (1934).
190. J. Jortner and G. Stein, Nature, 175, 893 (1955).
191. J. E. Bennett, B. Mile, and A. Thomas, Nature, 201, 919 (1964).
192. G. M. Schmeig, The Study of the Spectrophotoelectric Response of Solutions of Sodium and Liquid Ammonia, Ph.D. Dissertation, Univ. of Chicago, Chicago, Ill. (1939) (cited from [100]).
193. J. Hösing, Ann. Physik, 37, 509 (1940).
194. G. K. Teal, Phys. Rev., 71, 138 (1947).
195. B. Baron, P. Chartier, P. Delahay, and R. Lugo, J. Chem. Phys., 51, 2562 (1969).
196. P. Delahay, P. Chartier, and L. Nemec, J. Chem. Phys., 53, 3126 (1970).
197. J. Jortner and S. A. Rice, in: Solvated Electron, Advan. Chem. Ser., 50, 7 (1965).
198. B. Baron, P. Delahay, and R. Lugo, J. Chem. Phys., 55, 4180 (1971).
199. P. Delahay, J. Chem. Phys., 55, 4188 (1971).
200. L. Nemec, J. Chem. Phys., 59, 6092 (1973).
201. A. M. Brodskii and A. V. Tsarevskii, Ēlektrokhimiya, 10, 1635 (1974).