

# Liquid junction potentials between aqueous and nonaqueous medium with different electrolytes

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The results of this study refer to the value of the liquid junction potential between aqueous and nonaqueous solution of different electrolytes which has been determined on the basis of one of the extrathermodynamic assumptions (redox method) and to the factors influencing this value. It has appeared that the "ionic" component of this liquid junction potential is relatively rather low and does not practically depend on the present nonaqueous solvent. Irrespective of this fact, the "solvent" component of the liquid junction potential, which is given by interactions between solvents at the boundary, represents the substantial part of the liquid junction potential and the more different are the donor properties of the contacting solvents, the higher is its value.

Результаты приведенные в работе показывают величину жидкостного потенциала, образованного между водным и неводным растворами разных электролитов и определенное на основании одной из внетермодинамических предпосылок (метод окисления-восстановления) и также факторы, влияющие на величину этого потенциала. Обнаружено, что «ионная» составляющая жидкостного потенциала относительно низкая и практически не зависит от присутствующего неводного растворителя. Напротив этого, «растворительная составляющая жидкостного потенциала, обусловленная взаимодействием растворителей в межфазном промежутке, является существенной частью жидкостного потенциала и ее значение тем выше, чем более различаются донорные свойства контактированных растворителей.

The increasing interest to use the nonaqueous solvents for investigations of the ion—solvent interactions by electrochemical methods meets with the problem of a liquid junction potential formed between aqueous and nonaqueous medium provided some of the aqueous electrodes is reference electrode. This potential gets into the values measured from which it should be either eliminated or reduced to a minimum possible value. Although many investigations were carried out with different solvents, relatively little attention has been paid to liquid junction potentials.

The aim of this study is to point out the magnitude of the liquid junction potential formed between an aqueous and nonaqueous solution of different electrolytes and the factors influencing its value.

### Experimental

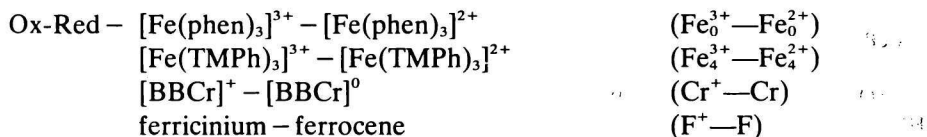
Bis(biphenyl)chromium(I) iodide (BBCrI) [1] and ferrocene [2] were prepared according to the procedures described in literature. Tris(1,10-phenanthroline)iron(II) perchlorate  $[\text{Fe}(\text{phen})_3](\text{ClO}_4)_2$  and tris(3,4,7,8-tetramethyl-1,10-phenanthroline)iron(II) perchlorate  $[\text{Fe}(\text{TMPH})_3](\text{ClO}_4)_2$  were prepared by mixing equivalent amounts of the Mohr's salt and phenanthroline or its methyl derivative in aqueous solution. Perchlorates were obtained by precipitating of these solutions with  $\text{NaClO}_4$  and recrystallizing from the acetonitrile-water mixture. Tetrabutylammonium perchlorate (TBAP) was prepared by neutralization of  $\text{Bu}_4\text{NOH}$  with perchloric acid and recrystallization from the ethanol-water (4:1) mixture.

The solvents used, *i.e.* nitromethane (NM), acetonitrile (AN), propanediol-1,2-carbonate (PDC), acetone (AC), methanol (MeOH),  $N,N'$ -dimethylformamide (DMF),  $N,N'$ -dimethylacetamide (DMA), dimethyl sulfoxide (DMSO), and hexamethylphosphoric triamide (HMPT) were dried and purified according to standard procedures [3].  $N,N'$ -Dimethylthioformamide (DMTF) was prepared from DMF and  $\text{P}_4\text{S}_{10}$  [4] and subsequently purified [5].  $N$ -Methyl-2-pyrrolidone (NMeP), commercially available, was purified according to literature [6] and afterwards dried on molecular sieve and subjected to threefold vacuum distillation.

The electrochemical measurements were performed on a polarographic analyzer, PAR 174 A, with a three-electrode arrangement. Platinum wire was used as a working and auxiliary electrode while an aqueous saturated silver/silver chloride electrode served for reference electrode. The reference electrode was separated from the measured solution by special diaphragms of porous glass which prevented the measured solution from contamination with water [7]. All measurements were carried out with 0.1 M concentration of the supporting electrolyte TBAP at 25°C. The concentration of depolarizer varied within the range  $5 \times 10^{-4}$ — $5 \times 10^{-3}$  M.

$E_1$ V	Results	$E_2$ V	$E_{12}$ V
2100.0		250.0	1.7
1100.0		220.0	1
1100.0		410.0	2

The measurements of the half-wave potential, *i.e.* electromotive force of the cell



S — one of the nonaqueous solvents

revealed that the measured half-wave potentials of the systems  $\text{Fe}_0^{3+}-\text{Fe}_0^{2+}$ ,  $\text{Fe}_4^{3+}-\text{Fe}_4^{2+}$ ,  $\text{Cr}^+-\text{Cr}$ , and  $\text{F}^+-\text{F}$  against the saturated silver/silver chloride electrode varied with character of the used solvent  $S$  in a rather wide range. Equal

*Table 1*  
Values of half-wave potentials of some redox systems measured against the saturated aqueous Ag/AgCl electrode

Solvent	$E_{1/2}$ , V			
	$\text{Fe}_0^{3+}-\text{Fe}_0^{2+}$	$\text{Fe}_4^{3+}-\text{Fe}_4^{2+}$	$\text{F}^+-\text{F}$	$\text{Cr}^+-\text{Cr}$
NM	1.062	0.816	0.370	-0.748
DMTF	0	0	0	-0.722
AN	1.116	0.895	0.447	-0.666
PDC	1.154	0.928	0.473	-0.638
AC	1.202	ls	0.546	-0.580
MeOH	0	i	0.478	-0.642
DMF	0	0.986	0.559	-0.570
NMeP	1.219	1.013	0.568	-0.557
DMA	0	1.014	0.582	-0.550
DMSO	0	0.998	0.553	-0.567
HMPT	0	i	0.658	-0.480

0 —  $E_{1/2}$  was not in electrochemically utilizable region of solvent,

ls — low solubility,

i — insoluble.

*Table 2*

Experimental "overall" values of the liquid junction potentials  $E_j$ , the calculated "ionic" components of the liquid junction potentials  $E_{j,i}$ , and donor properties DN of the solvents [9]

Solvent	$E_j$ V	$E_{j,i}$ V	DN
NM	0.032	0.0015	2.7
DMTF	0.058	—	11.5 <sup>a</sup>
AN	0.114	0.0011	14.1
PDC	0.142	0.0024	15.1
AC	0.200	0.0010	17.0
MeOH	0.138	0.0014	19.0
DMF	0.210	0.0016	26.6
NMeP	0.223	—	27.3
DMA	0.230	0.0018	27.8
DMSO	0.213	0.0022	29.8
HMPT	0.300	0.0025	38.8

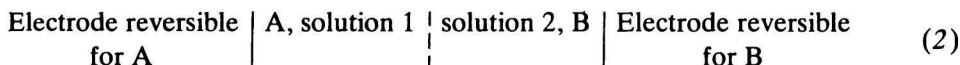
a) See Ref. [13].

tendency in the change of the measured half-wave potentials was observed with all redox systems, *i.e.* a shift to more positive values with increasing donor properties of the solvents (Table 1).

Provided there are no specific interactions between the investigated redox systems and solvents, the observed changes in the half-wave potentials  $E_{1/2}$  (Table 1) must be due only to varying liquid junction potentials between the aqueous and nonaqueous solution. Considering that the investigated redox systems do not specifically interact with the solvents used and assuming that the value of the half-wave potential of the  $\text{Cr}^+ - \text{Cr}$  system against the aqueous saturated  $\text{Ag}/\text{AgCl}$  electrode is  $-0.78$  V in all solvents [8], the values of the liquid junction potentials  $E_j$  at the boundary of the aqueous and nonaqueous medium have been calculated (Table 2).

### Discussion

The electromotive force  $E$  of the general cell of the type



where the solutions differ only by electrolytes is given [10] by the equation

$$E = E_B - E_A + E_j \quad (3)$$

$E_B$  and  $E_A$  are the potentials of individual electrodes separated from each other by a boundary at which the liquid junction potential  $E_j$  has arisen.

Provided the solvents of solutions (1) and (2) in cell (2) are different, there must exist an additional contribution to liquid junction potential due to a change in the Gibbs energy produced by interactions of the solvent molecules diffusing through the boundary. The electromotive force  $E$  of such a cell must be given by the following equation

$$E = E_B - E_A + E_{j,i} + E_{j,s} \quad (4)$$

where  $E_{j,i}$  is the above-mentioned liquid junction potential due to the diffusion of the ions through the boundary and  $E_{j,s}$  stands for the contribution to liquid junction potential due to the transport of the solvent molecules through the boundary (transition layer). However, the flow of the ions is dependent on the flow of the solvent molecules owing to which a precise division of the liquid junction potential into the "ionic" component  $E_{j,i}$  and the "solvent" component  $E_{j,s}$  is, in principle, not possible.

Assuming  $E_{j,s}$  is predominantly due to the change in the Gibbs energy owing to interactions among the solvent molecules which are transferred by moving ions, we may write the following equation for this change if the charge of 1F passes through the cell

$$\Delta G_s = \int_1^2 \Delta G' dz \quad (5)$$

$\Delta G'$  is the change in the Gibbs energy connected with reaction of the molecules of contacting solvents



and  $z$  is the number of interactions (in moles) on a given place of the boundary accompanying the charge transfer of 1F ( $z$  is a function of transport numbers and solvation numbers of the ions transporting solvents). This change in the Gibbs energy  $\Delta G_s$  is related to the "solvent" component of the liquid junction potential  $E_{j,s}$  by the following equation

$$\Delta G_s = -FE_{j,s} \quad (7)$$

according to which it holds for  $E_{j,s}$

$$E_{j,s} = -\frac{1}{F} \int_1^2 \Delta G' dz \quad (8)$$

Applying eqn (4) to cell (1), the subsequent expression is valid for the measured half-wave potential  $E_{1/2}$

$$E_{1/2} = E_{\text{ox-red}} - E_{\text{Ag/AgCl}} + E_{j,i} + E_{j,s} \quad (9)$$

The liquid junction potential in the investigated cells was formed between the saturated aqueous solution of KCl (4.16 M) and 0.1 M solution of TBAP in nonaqueous solvent  $S$ . The "ionic" component of this liquid junction potential was calculated by means of the Henderson equation. This equation allows to calculate the liquid junction potential at the boundary of two different electrolyte solutions. If one of the solutions is the saturated aqueous solution of KCl and the experiment is performed at 25°C, the Henderson equation assumes the form [11]

$$E_{j,i} = 0.059 \frac{U_1 - V_1 + 11.6}{U'_1 + V'_1 - 623} \log \frac{U'_1 + V'_1}{623} \quad (10)$$

where  $U = c_+ \lambda_+^0$ ,  $V = c_- \lambda_-^0$ ,  $U' = c_+ \lambda_+^0(z_+)$ ,  $V' = c_- \lambda_-^0(z_-)$ .  $\lambda^0$  is the limiting molar conductivity, ( $z$ ) is the absolute value of charge (charge number), and  $c$  is concentration. Table 2 contains the values of  $E_{j,i}$  calculated from eqn (10) by means of the limiting molar conductivity [12] as well as the experimental values of the liquid junction potential  $E_j$  representing the sum of the "ionic" component and

“solvent” component. The results obtained show that the values of  $E_{j,i}$  are relatively low in comparison with the experimental values of the liquid junction potential  $E_j$  and are negligibly affected by the kind of solvent.

As mentioned above, the additional term to the liquid junction potential  $E_{j,s}$  must be taken into consideration for the liquid junction potentials between solutions of different solvents. It expresses the change in the Gibbs energy corresponding to interactions of the transported solvent molecules. An exchange of solvent  $S$  in investigated cell (1) shall have a negligible influence on the first three terms of eqn (9) because

a) the value of  $E_{j,i}$  found by calculation is very small in comparison with the total value of the liquid junction potential  $E_j$  and does not remarkably change with replacement of the solvent,

b) the redox potential of the system studied is independent of solvent on the basis of the above assumption,

c) the value of electrode potential of the silver/silver chloride electrode is constant.

It means that all observed changes in the measured half-wave potential  $E_{1/2}$  should be prevalingly caused by a change in the “solvent” component of the liquid junction potential  $E_{j,s}$ . In order to express  $E_{j,s}$  by eqn (8), we must know  $\Delta G'$  corresponding to interactions between the solvents as well as solvation numbers of the ions occurring at the boundary ( $K^+$ ,  $Cl^-$ ,  $TBA^+$ , and  $ClO_4^-$ ). Supposing the solvation numbers of the ions are equal in all solvents, *i.e.* the number of interactions at each boundary is constant,  $E_{j,s}$  assumes the form

$$E_{j,s} = -\frac{\Delta z}{F} \Delta G' \quad (11)$$

If these conditions are valid, a simple linear relationship between the total liquid junction potential  $E_j$  and  $\Delta G'$  ought to exist. As it is very difficult to obtain a sufficient amount of information concerning  $\Delta G'$  and the interactions between solvents at the boundary may be regarded as acid-base interactions of the Lewis type, *i.e.* donor-acceptor interactions, the relationship between  $E_j$  and the donor property of solvent DN, which should, to a certain degree, express the extent of the pertinent interaction, was investigated. DN is an enthalpic quantity expressing the donor properties of individual solvents with respect to  $SbCl_5$  while  $E_{j,s}$  is related to free enthalpic quantity (Gibbs energy). The linear relationship between these two quantities could be observed only if the entropic contributions  $T\Delta S$  were relatively very low or linearly dependent on the enthalpic quantity. In spite of considerable simplifications (*e.g.* constant solvation numbers) and the fact that one of the interacting solvents is always water for which the entropy change may not be a simple function of enthalpy, the data obtained show a good correlation of the considered quantities.

The results given in Table 2 have shown that the idea of the "solvent" component of the liquid junction potential  $E_{j,s}$  is justified and conveniently characterizes the contribution to the liquid junction potential between solutions of different solvents, in particular, water—nonaqueous solvent. This value can be relatively high so that the values of the "total" liquid junction potentials are much higher than in cases if the solutions in cells differ only in electrolytes.

The "ionic" component of the liquid junction potential  $E_{j,i}$  in the investigated systems is relatively small in comparison with the component given by properties of the solvents  $E_{j,s}$  which represents the major portion of the liquid junction potential between solutions of different solvents. The more different were the donor-acceptor properties of contacting solvents (the stronger were their interactions), the higher values of  $E_j$  were observed. This observation is in agreement with theory and experiment.

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