Lecture Notes in Chemistry

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Electrochemistry on Liquid/Liquid Interfaces

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List of symbols

a	activity
A	area
AC	alternating current
b	backward, bulk (in subscript)
Bu	butyl
c	concentration
C	capacitance
D	diffusion coefficient
DC	direct current
E	potential, energy
Et	ethyl
f	forward, frequency
F	Faraday constant
G	Gibbs energy of transfer
i	ion, current
I	current, imaginary (in subscript)
IR	voltage loss during current flow
ITIES	interface between two immiscible electrolyte solutions
j	current density, flux
k	rate constant
K	equilibrium constant
L	inductance
L/L	liquid/liquid
m	convolution integral
Me	methyl
n	nonaqueous, number of exchanged electrons
nb	nitrobenzene
o	oil (nonaqueous)
P	preexponential factor, phenyl
Pe	pentyl
Pr	propyl
PTC	phase transfer catalysis
PZC	potential of zero charge
r	radius
R	resistance, real (in subscript), gas constant
t	time
tr	transfer
T	absolute temperature
TBA	tetrabutylammonium
TEA	tetraethylammonium
TMA	(also TMeA) tetramethylammonium
TPAs	tetraphenylarsonium
TPB	tetraphenylborate
U	potential
V	potential
w	water, aqueous phase
z	charge on transporting ion
Z	impedance
α	charge transfer coefficient
β	$1 - \alpha$
Δ	difference
ε	permitivity
μ	chemical potential
$\tilde{\mu}$	electrochemical potential
τ	transition time, time constant
ϕ	Galvani (inner) potential, electrostatic potential, phase angle
ω	circular frequency

I. INTRODUCTION

A charge transfer across the interface between two immiscible liquid media has an important role both in nature and in man-designed applications. Ion transfer across the biological membranes, behavior of ion-selective electrodes with liquid membranes and similar sensors, extraction processes, phase transfer catalysis and applications in electroanalytical chemistry can serve as examples.

Present interest in the interface between two immiscible electrolytes (liquid - liquid or L/L interface) was originated by Koryta's idea (Koryta, Vanýsek and Březina 1976) that the interface between immiscible liquids could serve as a simple model for one half of a biological membrane in the contact with the surrounding electrolyte. It was also Koryta who started using the acronym ITIES (Interface between Two Immiscible Electrolyte Solutions) which generally encompasses all the phenomena discussed in this book. Physiological and electrochemical investigations have certainly well established tradition. In his classic experiments with frog thighs Luigi Galvani discovered in 1791 relationship between electricity and nerves and muscles. As outlined by Koryta and Štulík (1983) in the introduction to their book, the study of electrophysiological phenomena did not progress much for several decades and only a few experiments were performed. For instance M. Faraday (Williams, 1965) studied the electricity produced by an electric fish and Du Bois-Reymond (1848) suggested that the surface of biological formations have properties similar to the electrode of a galvanic cell. However, the properties of biological membrane could not be explained before the first concept of electrochemistry was postulated. Gibbs (1928) derived in 1875 thermodynamic relationship for membrane equilibrium. The theory of electrolyte solutions was formulated even later, by Arrhenius in 1887. An important progress was marked by the works of Nernst (1888 and 1889) and Planck (1890a-b) on transport in electrolyte solutions. Nernst and Riesenfeld (1902) were also first to describe an experiment on L/L interface. Figure 1 shows the cell drawing from this historical paper.

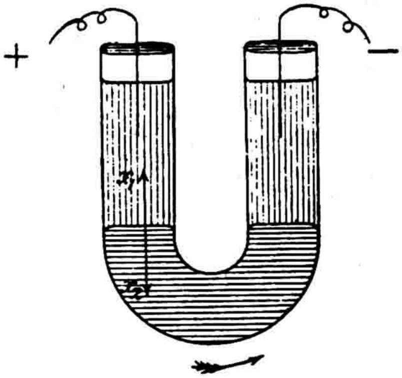

Fig. 1.

Fig. 1 Original drawing of an electrochemical experiment on liquid - liquid (phenol - water) interface from the work of Nernst and Riesenfeld (1902).

The authors solved the boundary problem of diffusion-migration when constant current was passing through the system, i.e. the system maintained a steady concentration gradient. This report was followed by two papers by Riesenfeld (1902a-b). A solution related to previously mentioned papers limited to cases of supporting electrolytes was derived by Sand (1901). His results were used for determining the transference numbers in nonaqueous phases (Nernst and Riesenfeld 1902, Riesenfeld 1902a). It is of course quite likely that people were fascinated by the immiscible interface and perhaps even its electrical properties much earlier. Krouchkol for instance published a paper on electrocapillarity of liquid/liquid interface in 1886.

Membrane electrochemistry in a stricter sense began by the work of Ostwald (1890). At the turn of the century a membrane theory was proposed for the electrical properties of cells and tissues by Overton (1902) and Bernstein (1902), whose principles remain valid to the present day.

For years the investigation of the liquid/liquid interface was limited to the study of equilibria or steady state electrical potential differences between water and a nonaqueous phase in the presence of different electrolytes (Baur and Kronman 1917, Beutner 1913a-b, 1918, Cremer 1906, Haber and Klemensiewicz 1909, Riesenfeld 1902b and Riesenfeld and Reinhold 1909). Kandidow (1911 and 1913) studied electrocapillary phenomena of the interface water/ether in the presence of uranyl nitrate. Bell (1982) gave the first treatment of a redox reaction rate at a liquid-liquid interface. Exact thermodynamic descriptions of chemical and electrochemical equilibrium properties were done by Bonhoeffer, Kahlweit and Strehlow (1953, 1954) on the system quinoline/water and in still more detail by Karpfen and Randles (1953), Kahlweit and Strehlow (1954) and Sollner and Shean (1964).

It was not until the mid fifties when new experiments on L/L interface started. At that time Dupeyrat and Guastalla (1956) studied the effect of passing the electric current across the water/nitrobenzene interface on the interfacial potential difference. Guastalla (1956, 1957) also began his studies on electroadsorption. He observed in the system of cetyltrimethylammonium bromide in water and nitrobenzene a change of interfacial tension when current was passing through the interface. Similar systems were also studied by Blank and Feig (1963), Dupeyrat (1964a-b), Dupeyrat and Michel (1967, 1969) and Watanabe et al. (1967). Blank (1966) analyzed the results and showed that the effect of electroadsorption is caused by accumulation and depletion of the surface-active species at the interface. These studies also led to the discovery of mechanical interfacial movement. This phenomena, which was studied by a few investigators, will be described in the chapter on current flow.

Boguslavskii and Gugeshashvili (1972) measured Volta potential of the water - isoamylalcohol interface in the presence of potassium chloride and potassium picrate. In another paper they provided a practical solution for elimination of junction potentials in the water - nitrobenzene - water system by introduction of a special salt bridge (Gugeshashvili, Lozhkin and Boguslavskii 1974). Gavach (1973) and Gavach and Savajols (1974) measured equilibrium potentials between water and nitrobenzene as a response to various ions present in both phases.

The first attempt to measure polarization curves of the interface between two immiscible electrolytes was made by Gavach, Mlodnicka and Guastalla (1968). The system was stirred and therefore a steady state value was obtained. Guastalla (1970) measured the current flowing across the L/L interface as a response to an applied triangular voltage scan. Since he did not use a potentiostatic control, the obtained curves, which would otherwise have been cyclic voltammograms, were seriously distorted. However, his main contribution in this paper was the introduction of a hydrophilic salt for an aqueous phase (KCl) and a hydrophobic salt (tetradecyltrimethylammonium picrate) for the nonaqueous phase. Some of the earliest chronopotentiograms were obtained by Gavach and coworkers (Gavach, Seta and Henry 1974; Gavach 1969; Gavach and d'Epenoux 1974; Gavach and Henry 1972, 1974).

Equilibrium states at the L/L interface and the Galvani potential difference are discussed in works of Hung (1980, 1983) and Koczorowski (1981). Equilibrium electrochemical principles have been applied uniformly to the interfacial systems in critical and comparative ways (Buck 1978a-c, 1979, 1981a-b) and Buck and Hackleman (1977). Standard Gibbs energies of transfer of individual ions between water and nitrobenzene for different ions obtained from partition measurements were given by Rais (1971). These data were later summarized in an IUPAC publication (Marcus 1983) and the most up-to-date compilation is in Table 1.

Properties of L/L interfacial double layers were studied in several earlier works (Kahlweit and Strehlow 1954; Guastalla 1973; Gavach, Henry and Sandeaux 1974; Gavach, Seta and d'Epenoux 1977; Schuhman and Seta 1979, 1980; Gros, Gromb and Gavach 1978; Seta, d'Epenoux and Gavach 1979; Boguslavskii et al. 1976, 1977; d'Epenoux et al. 1979 and Dupeyrat and Nakache 1977). A more recent series of papers on the double layer was begun by the communication of Samec, Mareček and Homolka (1981) using impedance measurements of the interfacial capacitance of water/nitrobenzene boundary. Interfacial tension at the L/L interface between reversibly distributed electrolyte solutions of nitrobenzene and water has been studied using a drop pressure method by Reid, Melroy and Buck (1983). The differential interfacial capacitance of the blocked nitrobenzene/water interface was also measured by Reid, Vanýsek and Buck (1984a). The ohmic potential drop and the interfacial capacitance has been recently evaluated by Mareček and Samec (1983a, 1985), using the galvanostatic pulse method.

The interface between two immiscible electrolytes is, with a proper experimental setup, an analog of the interface metal electrode/electrolyte solution (Koryta, Vanýsek and Březina 1977; Koryta et al. 1978, 1980; Koryta 1980, 1981; Koryta and Vanýsek 1981). Therefore it can be studied by the methods analogous to those used with metallic electrodes.

Transport of ions across an immiscible electrolyte/electrolyte interface, however, differs in several ways from electrolyte/metal interfacial process (Melroy 1982).

A) Diffusion-migration via Nernst-Planck equation rather than Fick's first law must be considered.

B) Interfacial transport of ions of opposite signs must be considered because of salt partition equilibria.

C) Partition equilibrium is a non-linear ionic process that can lead to insoluble equations.

The most extensively used experimental techniques are chronopotentiometry, polarography with electrolyte dropping electrode, cyclic voltammetry and impedance measurements. The extensive list of referencies can be found in the respective chapters dealing with these techniques. Other approaches to liquid - liquid area are surfacing as more researches are getting involved. For instance Albery, Choudheri and Fisk (1984) suggested a wall jet electrode approach. Girault and Schiffrin (1984c) used a streaming jet electrode for measurement of L/L potential of zero charge. Practical contribution to the study of photosensitizers which are important for possible use for the decomposition of water was done by Samec et al. (1983). They investigated transfer of tris-(2,2'-bipyridine)ruthenium(II), methylviologen and heptylviologen between water and nitrobenzene, 1,2-dichloroethane and dichloromethane. Kakutani, Osakai and Senda (1983) employed potential-step chronopotentiometry and Osakai, Kakutani and Senda (1984) tried AC polarography for the study of water - nitrobenzene interface. The electrical response of an interface to a mechanical perturbation was investigated by Koczorowski and Kotowski (1978), Koczorowski, Kalinska and Figaszewski (1982) and Kotowski, Kalinska and Koczorowski (1982).

The transfer across the phase boundary between organic and aqueous phase can be also employed in electrosynthesis. Conversion of ferrocene dissolved in dichloromethane can serve as an example (Feess and Wendt 1981). The process involved is not simply the electrochemical reaction of substrate in the organic phase on the surface of an electrode. The transfer of ions between the droplet of organic solvent on the electrode and the surrounding aqueous phase plays also a significant role during the electrosynthesis. A short chapter in this book is devoted to the Phase Transfer Catalysis, a procedure of organic chemistry which has much in common with liquid - liquid electrochemical processes.

Electrochemical studies on ITIES are attracting more and more attention. Several years ago it was possible to name the few research groups involved in electrochemistry of ITIES without danger of omitting someone. Today, with the more advanced knowledge about the topic, more scientists are finding it important to try at least a few ideas of their own on the liquid - liquid interface and interest is coming from more biology aimed groups. But the most important clusters of liquid - liquid interface electrochemical research can still be named. At this point some of the last works of A. N. Frumkin should also be mentioned (Boguslavskii, Frumkin and Gugeshashvili 1974; Frumkin, Boguslavskii and Manvelyan 1976). Presently the Moscow group produces ocassional papers on ITIES (Manvelyan, Neugodova and Boguslavskii 1976a-b; Manvelyan and Boguslavskii 1976a-b; Kornyshev and Volkov 1984; Kharkats and Volkov 1985). The following are research groups having more involvement in the ITIES electrochemistry: Buck (Chapel Hill, NC), Freiser (Tucson, AZ), Gavach (Montpellier, France), Hundhammer (Merseburg, DDR), Kihara (Tokai, Japan), Kozcorowski and Figaszewski (Figaszewski, Koczorowski and Geblewicz 1982) (Warszaw, Poland), Koryta (Prague, CS), Samec (Prague, CS), Senda (Senda and Kakutani 1980) (Kyoto, Japan), Schiffrin (Southampton, England), Solomon (Addis Abbaba, Ethiopia) and Vanýsek (DeKalb, IL).

The motivation for study of liquid - liquid interfaces is both of theoretical and practical interest. The useful range may be very broad and is probably going to attract even more interest. The applications suggested by Vanýsek and Buck (1984) are:

(A) Modelling of biochemical processes especially in biological membrane models.

(B) Elucidation of processes in ion-selective electrodes with liquid membranes.

(C) Applications in electroanalytical chemistry.

(D) Design of sensors.

(E) Analysis of processes taking place during phase transfer catalysis (PTC).

(F) Analysis of processes in emulsified, ion transporting systems.

(G) Extraction governed by electric current.

(H) Design of new systems in material science.

The following chapters are summaries of progress on liquid - liquid electrochemistry research published before May 1985. It would be presumptuous to state that the book includes all the literature on ITIES to that day. The attempt was to include all relevant material which has been known to the author at that time. Although it is the most comprehensive compilation so far, the reader should also refer to other sources. Other reviews on L/L interface phenomena were published by Koryta and Vanýsek (1981), Samec et al. (1980), Koryta (1979, 1983, 1984) and Vanýsek and Buck (1984a-b). New publications can appear in various journals, but mostly those with electrochemical, surface science or analytical bearing. The journal which most often publishes results of research on L/L interface is the Journal of Electroanalytical Chemistry and Interfacial Electrochemistry. The recommended nomenclature to be used in description of liquid - liquid interfaces has been published by Trasatti and Parsons (1983).

II. THEORY

Equilibrium conditions

First we shall deal with the interface at equilibrium conditions. Figure 2 shows schematically a liquid-liquid interface at equilibrium as compared with similar situation at the boundary electrolyte - electrode.

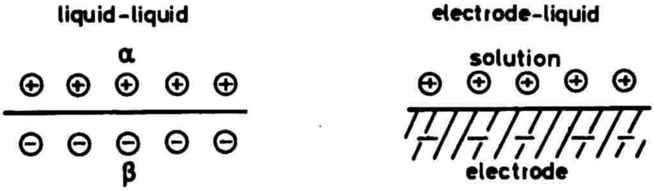

Fig. 2 Interface at equilibrium. [After Koryta and Vanýsek 1981]

In the liquid-liquid equilibrium it is assumed that both phases are in contact and their electrochemical potentials are equal. Equilibrium conditions introduce relationship between activity, chemical potential and inner potential between two immiscible phases. The relation for the difference in phase potentials is analogous to the Nernst equation.

The equilibrium condition for partitioning of a solute between two immiscible solvents which are in contact is based on equating the electrochemical potential, $\tilde{\mu}$, in both phases in contact.

$$\tilde{\mu} = \mu + zF\phi = \mu^o + RT \ln a + zF\phi \tag{1}$$

If a nonionic solute is dissolved in two immiscible liquids, which are brought into a contact, from the requirement of equal chemical potential of that solute in both phases one obtains a relationship

$$\frac{a_1}{a_2} = \exp \frac{1}{RT} (\mu_2^o - \mu_1^o) \tag{2}$$

where the difference in standard chemical potentials is equal to the standard Gibbs energy of transfer, ΔG^o_{tr} . The relationship can be quickly related to the partition coefficient of that solute. Following the same procedure for charged solute (ion) a partition coefficient for a single ion can be obtained.

$$\frac{a_1}{a_2} = \exp \frac{1}{RT} (\mu_2^o - \mu_1^o + zF(\phi_2 - \phi_1)) \tag{3}$$

where ϕ_1 and ϕ_2 are the electric potentials of the respective phases.

This property can be related to a standard Gibbs energy of transfer for individual ion from one specified phase to another specified phase. These values make possible to compare tendency of different ions to partition between the two solvents. Thus a concept of hydrophobicity and hydrophilicity of an ion can be introduced.

A real system, however, cannot be treated in this simplest way. The condition of electroneutrality requires a presence of counterions. As a result, the distribution of one kind of ions will not, in general, correspond to the partition coefficient of that single ion, but will be instead determined by all the ions in the solution. The simplest realistic situation is then the case of a single salt (two ions) equilibrated between two phases (Bronner 1985). For the electrochemical potentials stands

$$\tilde{\mu}_1(+) = \tilde{\mu}_2(+) \quad \text{and} \quad \tilde{\mu}_1(-) = \tilde{\mu}_2(-) \tag{4}$$

For a uni-univalent salt it holds for a cation (symbol (+))

$$\phi_2 - \phi_1 = \frac{RT}{F} \ln \frac{a_1(+)}{a_2(+)} + \frac{\mu_1^o(+) - \mu_2^o(+)}{F} \tag{5}$$

and for the anion (symbol (-))

$$\phi_2 - \phi_1 = - \frac{RT}{F} \ln \frac{a_1(-)}{a_2\,(-)} - \frac{\mu_1^o(-) - \mu_2^o(-)}{F} \tag{6}$$

From the last two equations one arrives at an expression for a distribution coefficient:

$$\frac{a_1(+)a_1(-)}{a_2(+)a_2(-)} = \exp \frac{1}{RT} (\mu_2^o(+) - \mu_1^o(+) + \mu_2^o(-) - \mu_1^o(-)) \tag{7}$$

As the concentrations of cations and anions in the same phase are equal, allowing that the activity coefficients are the same for both ions, it holds for either ion:

$$\frac{a_1(\pm)}{a_2(\pm)} = \exp \frac{1}{2RT} (\mu_2^o(+) - \mu_1^o(+) + \mu_2^o(-) - \mu_1^o(-)) \tag{8}$$

By applying the above concepts and respecting conservation of matter and requirement of neutrality of charge, it is possible to solve partition of systems involving more than one salt.

The Nernst Potential

The difference of inner potentials of two phases can be calculated from the ion distribution between the two phases. For any ion distributed between two phases the result is

$$\begin{aligned} \phi_2 - \phi_1 &= \frac{1}{zF} (\mu_1^o - \mu_2^o + RT \ln \frac{a_1}{a_2}) = \\ &= \phi_2^o - \phi_1^o + \frac{RT}{zF} \ln \frac{a_1}{a_2} \end{aligned} \tag{9}$$

The difference in standard electric potentials between two phases can be further written as

$$\Delta_1^2\phi = \phi_2^o - \phi_1^o = \frac{\mu_1^o - \mu_2^o}{zF} = \frac{-\Delta G_{tr}^{o,1\to 2}}{zF} \tag{10}$$

where $\Delta G_{tr}^{o,\,1\to 2}$ is the standard single ion Gibbs energy of transfer from phase 1 to phase 2.

The standard Gibbs energy of transfer is equal to the difference of standard Gibbs solvation energies in the two phases. These standard values are given for infinitely dilute solutions and are usually referred to pure solvents. Since the equilibrium concept presumes the solvents in contact, a mutual saturation has to be expected. Therefore, before any calculation from table data, it is necessary to verify whether the values given are for pure solvents or for mutually saturated solvents.

As Bronner (1985) notes, the equilibrium interfacial potential for multiple salts systems is generally not concentration independent, but can be varied across a limited range by the choice of relative salt concentrations. Additionally, the interfacial potential can be also controlled by applying an external voltage to the polarized interface of two immiscible solutions.

Single Ion Gibbs Energy of Transfer

Transfer of a charge across the interface electrode/solution is possible if the potential of the electrode is higher than is the equilibrium potential of the anodic reaction or if it is lower than the equilibrium potential of the cathodic process. A necessary condition for a quantitative evaluation of experimental results of electrokinetics is to perform the electrolysis in the presence of base electrolytes. The base electrolyte, used at sufficient concentration, makes the solution conductive enough that the transport of the studied species is not governed by migration due to applied electric field.

The base electrolyte contains ions whose electrode reactions occur at such high (anodic process) or low (cathodic process) potentials, that a sufficiently broad potential range (potential window) will be formed, at which, in the absence of other electroactive species, no electrochemical process will occur. It is said that at the potential window the electrode has properties of an ideally polarizable electrode. It means that its potential is determined by the charge on the electrode and does not depend on the composition of the solution.

Properties similar to those described above for the metal electrode can be found for the interface between solutions of two immiscible electrolytes. The role of electrode reaction is in this case played by the transfer of ions across the interface and the role of the electrode is taken by the interface itself.

Although real quantities, the potential difference

$$\Delta_n^w\phi = \phi(w) - \phi(n) \tag{11}$$

where $\phi(w)$ and $\phi(n)$ are inner potentials of aqueous and nonaqueous phase which will be attained on the interface, as well as standard Gibbs energy of transfer of ion from one phase to another (ΔG^{o}_{tr}), are not amenable to direct measurements. This is not, however, a technological or design limitation, but inherent restriction arising from thermodynamics. Thus, for single ions, partition coefficients, Gibbs energies of transfer, Galvani potential differences and other related thermodynamic quantities have to be determined with the aid of an extrathermodynamic assumption.

Quite often it is asumed that both the cation and the anion of tetraphenylarsonium tetraphenylborate have equal Gibbs energies of transfer between any arbitrary solvent (Parker 1969, 1976). Therefore it holds

$$\Delta G^{o,n\to w}_{tr,TPAs^+} = \Delta G^{o,n\to w}_{tr,TPB^-} = \Delta G^{o,n\to w}_{tr,TPAsTPB} \qquad (12)$$

Based on this assumption a standard electric potential difference $\Delta^{w}_{n}\phi^{o}$ for an individual ion can be defined as

$$\Delta^{w}_{n}\phi^{o} = - \Delta G^{o,n\to w}_{tr,i} / z_i F \qquad (13)$$

where z_i is charge of the ion.

In the equilibrium between two phases involving one ion i an equilibrium Nernst-Donnan potential difference will be attained:

$$\Delta^{w}_{n}\phi = \Delta^{w}_{n}\phi^{o}_{i} + \frac{RT}{z_i F} \ln \frac{a_i(n)}{a_i(w)} \qquad (14)$$

Transfer of a cation from aqueous to organic phase occures at a more positive potential than is the equilibrium potential, for transfer of an anion this potential has to be more negative. For transfer from organic to aqueous phase an opposite rule applies.

The standard potential difference has the same function as the standard electrode potential has in systems metal electrode/electrolyte solution.

The values of standard Gibbs energies of transfer for different individual ions obtained from partition measurements were first given by Rais (1971). These and other data were later summarized in a IUPAC publication (Marcus 1983), and the updated list is given in Table 1.

The Parker's (1969, 1976) assumption appears reasonable if one compares tetraphenylarsonium and tetraphenylborate ions (Fig. 3).

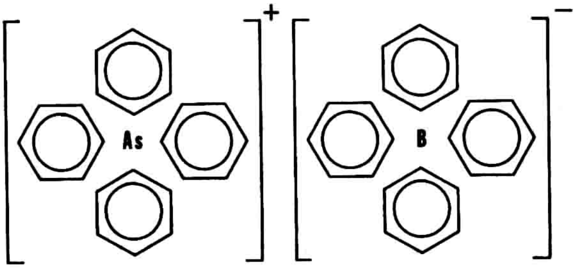

Fig. 3 Tetraphenylarsonium and tetraphenylborate ions.

Table 1a. Standard Gibbs energies of transfer from water to nitrobenzene and the standard electrical potential difference, $\phi_w - \phi_n$.

	$\Delta G^{o,w\to n}_{tr}$ kJ.mol^{-1}	$\Delta^w_n\phi^o$ mV	Reference
Li^+	38.2	395	a
Mg^{2+}	69.6	361	b
Na^+	34.2	354	a
Ca^{2+}	67.3	349	c
Sr^{2+}	66.0	342	b
H^+	32.5	337	a
Ba^{2+}	61.7	320	b
NH_4^+	26.8	277	a
K^+	23.4	242	a
Rb^+	19.4	201	a
Cs^+	15.4	159	a
choline$^+$	11.3	117	d
acetylcholine$^+$	4.8	49	d
$TMeA^+$	3.4	35	a
TEA^+	- 5.7	- 59	a
TBA^+	- 24.0	- 248	a
$TPAs^+$	- 35.9	- 372	a
cryst. violet$^+$	- 39.5	- 410	e
dicarbollylcobaltate	- 50.2	520	a
dipicrylaminate	- 39.4	407	a
I_5^-	- 38.8	401	a
TPB^-	- 35.9	372	a
I_3^-	- 23.4	242	a
octoate	- 8.5	89	e
picrate	- 4.6	47	a
dodecylsulfate	4.1	- 43	e
SCN^-	5.8 (16.0	- 61 - 166	e i)
IO_4^-	6.9	- 72	i
ClO_4^-	8.0	- 83	a
BF_4^-	11.0	- 114	i
I^-	18.8	- 195	a
NO_3^-	24.4	- 253	f
Br^-	28.4	- 295	a
Cl^-	31.4	- 324	a
F^-	44.0	- 454	g