MODERN ASPECTS OF ELECTROCHEMISTRY

No. 7

Edited by
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Preface

Despite reductions in the level of research activity in most fields which, for reasons of economic decline, have taken place in the U.S. during the last year or two, world progress in the fundamental aspects has continued actively. An important aspect of such recent work has been the use of nonaqueous solvents in studies on the constitution of the double-layer and electrochemical reactions. Interpretation of the behavior of electrode interfaces in such solvents demands more knowledge of the solvation properties of ions in nonaqueous media. Chapter 1 by Padova on "Ionic Solvation in Nonaqueous and Mixed Solvents" gives an up to date review of the present state of knowledge in this field, together with tabulations of data that are likely to be of quantitative value in further investigations of both homogeneous and heterogeneous electrochemistry in such media.

Electrochemical studies of cathodic processes in nonaqueous solvents have, in recent years, revealed the role of solvated electrons. These are of interest in new approaches to reductive electro-organic synthesis. Similarly, the generation of hydrated electrons in photocathodic processes is of great interest. In Chapter 2, by Conway, the conditions under which solvated electrons can arise in electrode processes are critically examined and the electro-organic reactions that have been investigated are reviewed. The supposed electrogeneration of hydrated electrons in the water solvent and as intermediates in cathodic hydrogen evolution is shown to be unlikely.

Returning to questions concerned with the double-layer itself, a useful critical appraisal of the significance of measurements and measured quantities concerned with adsorption and the structure of electrode solution interphases is given by Bauer, Herman, and Elving in Chapter 3.

The subject of electrocrystallization and metal dissolution has for many years been a topic of central interest both in fundamental and applied electrochemistry. The possibility of controlling phase growth or dissolution by electric potential control is little appreciated outside the subject of electrochemistry yet it enters into many processes of technological interest not least of which, in a "negative" way, is corrosion. Chapter 4 presents a thorough analysis of various aspects of this topic under the title "Transport Controlled Deposition and Dissolution of Metals" by Despic and Popov. Special attention is given to problems of leveling and dendritic growth. The large number of diagrams and photographs will enhance the value of this chapter both to metallurgists and electrochemists.

Finally, a contribution from the important Russian school of electrochemistry (at the Karpov Institute) is given in Chapter 5 by Losev, who examines the "Mechanisms of Stepwise Electrode Processes on Amalgams." Such studies, which to a large extent are specially his own, allow idealized examination of corrosion-type processes under conditions where various steps in complex reaction schemes can be characterized and their role in the kinetics elucidated. Simultaneous anodic and cathodic processes are involved, the latter naturally involving H.

B. E. Conway
J. O'M. Bockris

Breakers Club
Bermuda
January 1971

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1

Ionic Solvation in Nonaqueous and Mixed Solvents

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I. INTRODUCTION

"Since the beginnings of quantitative physical chemistry, the study of electrolyte solutions has occupied a central position and constituted the early basis of electrochemistry."[1] Most investigations have been conducted with water as the solvent and the primary influence of solvation in determining the properties of aqueous solutions of electrolytes has already been stressed.[2]

Early work in *non*aqueous electrochemistry was confined to the extension of theories applied to aqueous solutions. However, in recent years, there has been considerable interest in the behavior of electrolytes in nonaqueous and mixed solvents with a view to investigating changes in the solvation of ions. The testing of electrostatic theories of ion association in media of varying dielectric constant[3] has occupied many researchers, and a steady increase of thermodynamic data as well as theoretical interpretations of the present knowledge on nonaqueous media[4] have appeared in the recent literature. Correspondingly, recent work on electrode processes in nonaqueous media enhances the importance of ionic studies in such solvents.

The structure of solutions of electrolytes may be inferred from the investigation of both reversible and irreversible phenomena. Both approaches will be considered here, although the present discussion will be concerned mainly with thermodynamic behavior in solutions of electrolytes.

It has recently been proposed[5,6] that a differentiation be made between protic and dipolar aprotic solvents. Protic solvents, such as fluoroalcohols, hydrogen fluoride, methanol, formamide, and of course water, are strong hydrogen-bond donors. Dipolar aprotic solvents are highly polar but are no more than very weak hydrogen donors. Common dipolar aprotic solvents are dimethylformamide, dimethylacetamide, dimethylsulfoxide, hexamethylphosphoramide, acetone, nitromethane, nitrobenzene, acetonitrile, benzonitrile, sulfur dioxide, propylene carbonate, sulfolane, and dimethylsulfone. This distinction is made only for solvents of dielectric constant greater than 15 because of extensive aggregation in solvents of lower dielectric constant.

Frank's classification of solutes[7] according to the relative magnitudes of excess mixing functions with water does not quite agree with the above, since ketones are classed together with alcohols. Parker[5] suggested that there are four types of strong solute–solvent interaction that contribute to solvation phenomena: electrostatic (ion–dipole, dipole–dipole), π-complex-forming, hydrogen-bonding, and structure-making or -breaking. Accordingly, in terms of the concept of hard and soft acids and bases,[8] protic solvents are "hard" since they exhibit general hydrogen bonding with small anions, and dipolar aprotic solvents are "soft," as they have a mutual polarizability interaction with large polarizable anions. Structure-making is defined as lengthening the molecular reorientation time, while shortening it is termed structure-breaking[9] or negative solvation. In many cases, the mechanism by which solvation occurs is unknown; however, we shall define solvation, unless otherwise specified, as the total ion–solvent interaction at infinite dilution.

II. THERMODYNAMICS OF SOLVATION

The term solvation will be used in this discussion to describe the total ion–solvent interaction at infinite dilution. The transfer of a pair of gaseous ions into a solvent characterizes the thermodynamic process of ionic solvation, which may be written as follows:

$$\mathrm{C}^+(g) + \mathrm{A}^-(g) \rightarrow \mathrm{C}^+(s) + \mathrm{A}^-(s) \qquad \Delta Y_s^\circ \qquad (1)$$

where C^+A^- is the ion pair and ΔY_s° represents the change in the thermodynamic property considered.

The enthalpy, free energy, and entropy of solvation of an electrolyte are usually determined from a specific thermodynamic cycle. For instance, the enthalpy of solvation ΔH_s° may be obtained by a Born–Haber cycle in which the solution process involves the sublimation and the dissociation of the crystal lattice followed by dissolution of the ions at infinite dilution (to avoid any ion–ion interaction), and

$$\Delta H_{s0} = -U_0 + \Delta H_s^\circ \tag{2}$$

where ΔH_{s0} and U_0 are the enthalpy of solution and the crystal lattice energy, respectively.

The molal volume of the solvated ions V_s was shown[74] to be given by

$$V_s = \phi_v + nV_0 \tag{3}$$

where ϕ_v is the apparent molal volume of the electrolyte, V_0 is the molal volume of the solvent, and n is the solvation number characteristic of the electrolyte. By definition, the molal volume of the solvated ions may be expressed equally well as[109]

$$V_s = V_{\text{in}} + nV_s^\circ \tag{4}$$

where V_{in} is the intrinsic ionic volume of the electrolyte[75] and V_s° is the molal volume of the solvent in the solvation shell.

III. DETERMINATION OF THERMODYNAMICS OF SOLVATION

1. Heats of Solvation

(i) Methods

Methods for the determination of heats of solvation have been reviewed by Conway and Bockris.[10] Recently, however, a new method, based on a mass spectrometric study of ion–solvent interaction in the gas phase, has been put forward.[11]

The mass-spectrometric gas-phase studies are based on measurement of the relative concentrations of the clustered ionic species $A^+ \cdot nS$, $A^+ \cdot (n+1)S$, etc. Consider the ion A^+ produced in the gas phase by some form of ionizing radiation or by thermal means. If the atmosphere surrounding the ion contains the vapor of a polar molecule (solvent S), a number of clustering reactions will occur, e.g.,

$$A^+ + S \rightarrow A^+ \cdot S \qquad (0, 1)$$

$$A^+ \cdot S + S \rightarrow A^+ \cdot 2S \qquad (1, 2)$$

$$A^+ \cdot (n-1)S + S \rightarrow A^+ \cdot nS \qquad (n-1, n)$$

At equilibrium,

$$\Delta G^\circ_{0,n} = \Delta G^\circ_{0,1} + \Delta G^\circ_{1,2} + \cdots + \Delta G^\circ_{n-1,n} \tag{5}$$

$$\Delta G^\circ_{n-1,n} = -R \ln\left(\frac{P_{A^+ \cdot nS}}{P_{A^+ \cdot (n-1)S + S}}\right) = RT \ln K_{n-1,n} \tag{6}$$

where P_x is the partial pressure of species x. From equation (6), the shell structure will be revealed since the value of $\Delta G_{n-1,n}$ becomes discontinuous whenever a shell is completed. The total free energy of solvation can be obtained from the relation

$$\Delta G_s = \Delta G_{n-1,n} - \Delta G_{\text{evap}}(S) \tag{7}$$

From measurements of this type taken at different temperatures, ΔH and ΔS can be evaluated. This method looks promising, although to date it has only been tried in water, methanol, and ammonia.

(ii) Experimental Results

Heats of solvation obtained from extrapolated heats of dilution at 25°C in various solvents are given in Tables 1–5. In some cases, solvation enthalpies were obtained from transfer data.

(iii) Ionic Enthalpies of Solvation

A modification of the method proposed by Verwey[26] was applied to the determination of ionic contributions to the enthalpy of solvation in formamide.[17] A plot of the solvation enthalpies of, for example, the lithium halides, as functions of the reciprocal crystal radii of the halide ions may be expressed by the straight line

$$\Delta H_s(\text{LiX}) = A_{\text{Li}} + \left(\frac{B}{r_x}\right) \tag{8}$$

The values of the ionic radii are taken from Ahrens'[27] tabulations:

F = 1.33 Å, Cl = 1.81 Å, Br = 1.96 Å, I = 2.20 Å

Table 1
Enthalpies of Solvation ΔH_s° (in kcal mole^{-1}) of Halides in Methanol

Salt	$-\Delta H_S^\circ$	Ref.	Salt	$-\Delta H_S^\circ$	Ref.
LiCl	214.0	78, 81	$LiClO_4$	188.0	78
LiBr	206.1	81	$NaClO_4$	161.1	78
LiI	199.0	81	$Mg(ClO_4)_2$	583.4	78
NaCl	187.9	81	$Ca(ClO_4)_2$	506.7	78
NaBr	180.8	81	$Su(ClO_4)_2$	475.8	78
NaI	173.7	78, 81	$Ba(ClO_4)_2$	443.3	78
KCl	167.80	81	$Pb(ClO_4)_2$	484.6	78
KBr	167.7	81	$LiNO_3$	205.0	80
KI	152.9	81	$NaNO_3$	179.0	80
RbCl	161.6	13, 81	NH_4Br	157.3	80
RbBr	153.7	81	NH_4NO_3	155.5	80
RbI	146.6	81	$AgNO_3$	189.6	80
CsCl	152.9	13, 78, 81			
CsBr	145.0	78			
CsI	137.8	13, 78, 81			
$ZnCl_2$	686.6	79			
$CaCl_2$	559.6	81			
$SrCl_2$	524.4	81			
$BrCl_2$	504.8	81			

Assuming that the contribution of the anion to the enthalpy of solvation vanishes for $1/r_x = 0$, the constant A_{Li} is identified with the experimental ionic solvation enthalpy of the cation. From this value for Li^+ and the molal solvation enthalpy of the salt, the experimental ionic solvation enthalpies of the halides may be deduced.

Table 2
Enthalpies of Solvation $-\Delta H_s^\circ$ (in kcal mole^{-1}) of Perchlorates in Ethanol, Propanol, and Butanol

Salt	Ethanol	Propanol	Butanol	Ref.
$LiClO_4$	187.0	186.6	186.6	404
$Pb(ClO_4)_2$	478.1	476.4	475.5	404
$Mg(ClO_4)_2$	582.3	576.4	575.2	405
$Ca(ClO_4)_2$	500.3	4 6.7	490.1	405
$Sr(ClO_4)_2$	466.9	464.6	463.6	405
$Ba(ClO_4)_2$	435.4	433.1	432.6	405

Table 3
Enthalpies of Solvation (in kcal mole^{-1}) of Salts in Ethanol, Ethylene Glycol, and Formic Acid

Salt	Ethanol	Ref.	Ethylene glycol	Ref.	Formic acid	Ref.
LiCl	−217.0	12	—	—	—	—
NaCl	−185.6	12	—	—	−186.0	13
NaBr	−178.0	12	—	—	—	—
NaI	—	—	—	—	—	—
KCl	−166.7	25	−173.2	15	−170.0	13
KBr	−159.4	25	—	—	—	—
KI	—	—	—	—	—	—
RbCl	—	—	−154.9	15	—	—
CsCl	—	—	—	—	−164.0	13
CsI	—	—	—	—	−157.0	13
$NaClO_4$	−159.4	16	—	—	−140.0	13

The same procedure has been applied to the alkali salts, and in all cases a linear relation was obtained. The slopes of the plots were the same within 0.2% except in the case of Cs^+. No reason could be found for this deviation.

The ionic contributions to solvation enthalpies in formamide and water are listed in Table 6.

In the treatment of data on propylene carbonate solutions, Wu and Friedman[28] tried to apply the following Latimer–Pitzer–Slansky[29] formula for the free energy of solvation of an ion of charge e_i [see Section (iv)] and Pauling crystal radius r_i in a solvent of dielectric constant ε:

$$\Delta G_i = -e_i^2[1 - (1/\varepsilon)]/2(r_i + \delta_i) \tag{9}$$

where δ_i is a parameter depending on the sign of the ion charge and on the solvent. This is a modification of the Born equation for the solvation energy in which the parameter δ_i depends on variations in the dielectric saturation, structure changes, and other effects.[10]

Differentiation of equation (9) gives the corresponding enthalpy of solvation:

$$\Delta H_i = \Delta G_i\left[1 - \frac{T\partial\varepsilon/\partial T}{\varepsilon(\varepsilon - 1)} + \frac{T\partial\delta/\partial T}{r_i + \delta_i}\right] \tag{10}$$

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