modern aspects of electrochemistry

no. 13

Edited by

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MODERN ASPECTS OF ELECTROCHEMISTRY

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Preface

The present volume contains five chapters covering areas of contemporary interest in the fields of electrolyte solutions, the state of solvent molecules at electrode surfaces, charged colloid interfaces, surface chemistry of oxide electrodes and electrochemistry, and bioelectrochemistry of charge transfer complexes.

The first chapter, by Barthel, Wachter, and Gores, covers the topic of conductance of nonaqueous protic and aprotic electrolyte solutions. This field is not only of intrinsic interest in itself, illustrating the important departures of ion-transport behavior in organic solvents from that, more well known, in water, but the information and extensive new data presented in this chapter will be of interest to those working with nonaqueous alkali-metal batteries where the conductivity and ion-association behavior of electrolytes in various solvents other than water is of great importance.

The second chapter is devoted to a very fundamental and ubiquitous aspect of electrochemistry of electrodes: the state of solvent molecules, adsorbed and oriented, at their surfaces. The role of solvent adsorption and orientation in double-layer properties, it will be recalled, remained poorly understood until the early 1960s. This chapter, by Trasatti, gives a thorough account of the present state of knowledge of solvent orientation at electrode interfaces and of the unsuspected (until recent years) role it plays in properties of the double layer and in determining the potential profile at charged metal surfaces in solution.

In Chapter 3, Somasundaran and Goddard give a useful account of electrochemical aspects of adsorption at mineral solids. This field pertains to the important technology of mineral flotation for concentration of ores, many of which (e.g., the sulfides) are semimetallic substances. The adsorption behavior of various surfactants at such materials is therefore closely connected with problems of adsorption at electrodes and with the stability of colloids.

The use of modern techniques of surface science for the study of electrodes has been a rapidly developing area of electrochemistry in recent years. Augustynski and Balsenc give, in Chapter 4, a self-contained account of the principles of Auger and X-ray photoelectron spectroscopy, with applications to the study of oxide films on noble-metal surfaces. Further knowledge of the chemical valence states of elements in such films is desirable for improved understanding of electrocatalysis of reactions such as electrolytic chlorine and oxygen evolution at these metals.

The final chapter, by Gutmann and Farges, is complementary to a previous contribution by these authors to the *Modern Aspects* series (No. 12) and describes the electrochemistry of charge transfer complexes. These are of interest in bioelectrochemistry and more recently in photoelectrochemistry as substances that can be involved in solar energy transfer and utilization.

Ottawa, Canada B. E. Conway
August, 1979 J. O'M. Bockris

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Temperature Dependence of Conductance of Electrolytes in Nonaqueous Solutions

J. Barthel, R. Wachter, and H.-J. Gores

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I. INTRODUCTION

NOTE. All equations in this chapter can be used either with SI or cgs units.[1] For this purpose, appropriate physical constants and conversion factors are summarized in Table 1. Concentration c is used throughout at mol liter^{-1}. This requires a conversion factor 10^n with $n(\mathrm{SI}) = +3$; $n(\mathrm{cgs}) = -3$.

The importance of nonaqueous electrolyte solutions, both in fundamental research and in technology, is manifested by the steady growth of publications in this field in the last decade. Monographs and handbooks[2–11] especially devoted to nonaqueous electrolyte solutions and review articles[12–26] provide a comprehensive survey of investigations and results. A perusal of published data on the temperature dependence of nonaqueous electrolyte solution properties, however, yields few items of information; this kind of research especially has been scarcely applied to transport phenomena in spite of the associated technological interest. One of the technical aspects of these investigations in concentrated electrolyte solutions is the optimization of supporting electrolytes of low-temperature nonaqueous cells and high-energy batteries.[26–30,256,270]

Table 1
Physical Constants and Conversion Factors

Quantity and symbol	Values with estimated uncertainty[a]	
	SI	cgs
Avogadro constant, N_A	6.02252×10^{23} mol^{-1} $\pm0.00028\times10^{23}$ mol^{-1}	
Planck constant, h	6.6256×10^{-34} J s $\pm0.0005\times10^{-34}$ J s	6.6256×10^{-27} erg s $\pm0.0005\times10^{-27}$ erg s
Boltzmann constant, k	1.38054×10^{-23} J K^{-1} $\pm0.00009\times10^{-23}$ J K^{-1}	1.38054×10^{-16} erg K^{-1} $\pm0.00009\times10^{-16}$ erg K^{-1}
Charge of proton, e	1.60210×10^{-19} C $\pm0.00007\times10^{-19}$ C	4.8029×10^{-10} esu $\pm0.0002\times10^{-10}$ esu
Permittivity of vacuum, ε_0	8.854185×10^{-12} J^{-1} C^2 m^{-1} $\pm0.000018\times10^{-12}$ J^{-1} C^2 m^{-1}	$(4\pi)^{-1}$ (exactly)
Conversion factor,[b] Ξ	1 (exactly)	9.98755×10^{11}

[a] From Ref. 1.
[b] From Ref. 8.

The reason for the lack of reliable conductance data, especially in dilute solutions, is obvious. Evaluation of measurements within the framework of present electrolyte theory requires an accuracy in the measurement of data which is difficult to obtain over a sufficiently large temperature range. In order to obtain conductance data which can be evaluated by a complete conductance equation, e.g., Eqs. (1), it is necessary to set each temperature of the temperature program quickly and reproducibly within 10^{-3} K, taking into account a temperature coefficient of conductance up to 0.1 K^{-1} (cf. Section III). Moreover, short as well as long time deviations beyond 10^{-3} K cannot be permitted. Figure 1 shows a thermostat assembly which fulfils these requirements[31,32] within a sufficiently large temperature range (cf. Section II).

According to modern electrolyte theory, conductance data obtained for dilute solutions can successfully be analyzed with the help of the conductance equation in the form of the following set of equations (cf. Section III):

$$\Lambda = \alpha[\Lambda^\infty - S(\alpha c)^{1/2} + E\alpha c \log \alpha c + J_1 \alpha c + J_2(\alpha c)^{3/2}] \tag{1a}$$

$$K_A = \frac{1-\alpha}{\alpha^2 c} \frac{y_A}{y_\pm'^2} \tag{1b}$$

$$y'_{\pm} = \exp\left(-\frac{\kappa q}{1+\kappa R_y}\right) \tag{1c}$$

$$y_A = 1 \tag{1d}$$

As usual, Λ is the experimentally determined molar conductance of the solution at an electrolyte concentration c and Λ^∞ the molar conductance at infinite dilution ($c \to 0$). The coefficients S, E, J_1, and J_2 depend on the pair-distribution functions of the ions and the boundary conditions on which a special conductance theory is based (cf. Ref. 8). K_A is the equilibrium constant for the formation of ion pairs from the free ions, α is the degree of dissociation, $y'_{\pm}$ the mean activity coefficient on the molar scale of the dissociated part of the electrolyte, and y_A that of the associated part. The Debye parameter κ is given by Eq. (2); the Bjerrum distance q by Eq. (3). R_y is the distance parameter for the activity coefficient (cf. Section III):

$$\kappa^2 = 16\pi q N_A(\alpha c) \times 10^n \tag{2}$$

$$q = \frac{z^2 e^2}{8\pi\varepsilon_0\varepsilon_r kT} \tag{3}$$

Equally well-founded equations are not so far known for conductance data for highly concentrated electrolyte solutions. Bruno and Della Monica[33–35] have extended Angell's model of mass transport in aqueous solutions,[36] which is based on the fused-salt theory,[37] to salts dissolved in media other than water. Extensions of Eqs. (1) with the help of empirical parameters,[38–41] e.g., the viscosity of the solution, become doubtful at high concentrations because of the approximations underlying Eq. (1a) as established for low concentrations and the validity of the ion-pair concept itself at high concentrations.

A noteworthy exact extension of Eq. (1a) for nonassociating electrolytes ($\alpha = 1$) into the region of moderate concentrations ($c \approx 0.25$ mol liter^{-1}) is due to Ebeling, Geisler, Kraeft, and Sändig.[42] They based their conductance equation on a statistical–mechanical treatment[42–45] which takes into account interaction potentials other than those for hard spheres. A recent further improvement of this model yields a conductance equation[46] valid up to still higher concentrations.[46,47] Data of nonaqueous solutions, however, have not been treated up to now.

Compilation of conductance data for highly concentrated solutions can best be achieved in an unambiguous manner by means of empirical functions which do not have a theoretical basis. A comprehensive study in this field then allows rules to be expressed which give a first insight into the effects of the conductance-determining factors and are useful for technological applications.

Our experience with different empirical functions has led to the application of functions which relate the specific conductance* κ of the solution to the maximum $\kappa_{\max}$ of κ and the appropriate concentration μ in the molal scale as adaptation parameters.[48] An equation published by Casteel and Amis,[49]

$$\frac{\kappa}{\kappa_{\max}} = \left(\frac{m}{\mu}\right)^{a} \exp\left[b(m-\mu)^2 - \frac{a}{\mu}(m-\mu)\right] \tag{4}$$

has been shown to provide a good fit of data for many solutions over a wide concentration range around μ and at various temperatures (cf. Section IV). The quantities $\kappa_{\max}$, μ, and the constants a and b of Eq. (4) are adjusted by a least-squares method. Equation (4) fulfills the conditions $\kappa = \kappa_{\max}$ if $m = \mu$, and $\kappa = 0$ if $m = 0$ and $a > 0$.

II. EXPERIMENTAL ASPECTS

1. Temperature Control

Figure 1 shows the thermostat assembly with a three-electrode conductance cell immersed in the controlled temperature bath as used in the author's laboratory. The range of operation of a thermostat is limited at high temperatures by the vapor pressure and at low temperatures by the viscosity of the bath liquid. With silicone oil, Baysilon M5® (Bayer), as the bath fluid a temperature range of −60 to +50°C is covered which allows the temperature dependence of the properties of numerous nonaqueous electrolyte solutions and their solvents to be investigated.

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* In accordance with the recommendations of the IUPAC Commission on Symbols, Technology, and Units[1] the symbol κ is used for specific conductance. Confusion with κ, Eq. (2), is easy to avoid. These two quantities are never used in the same context.

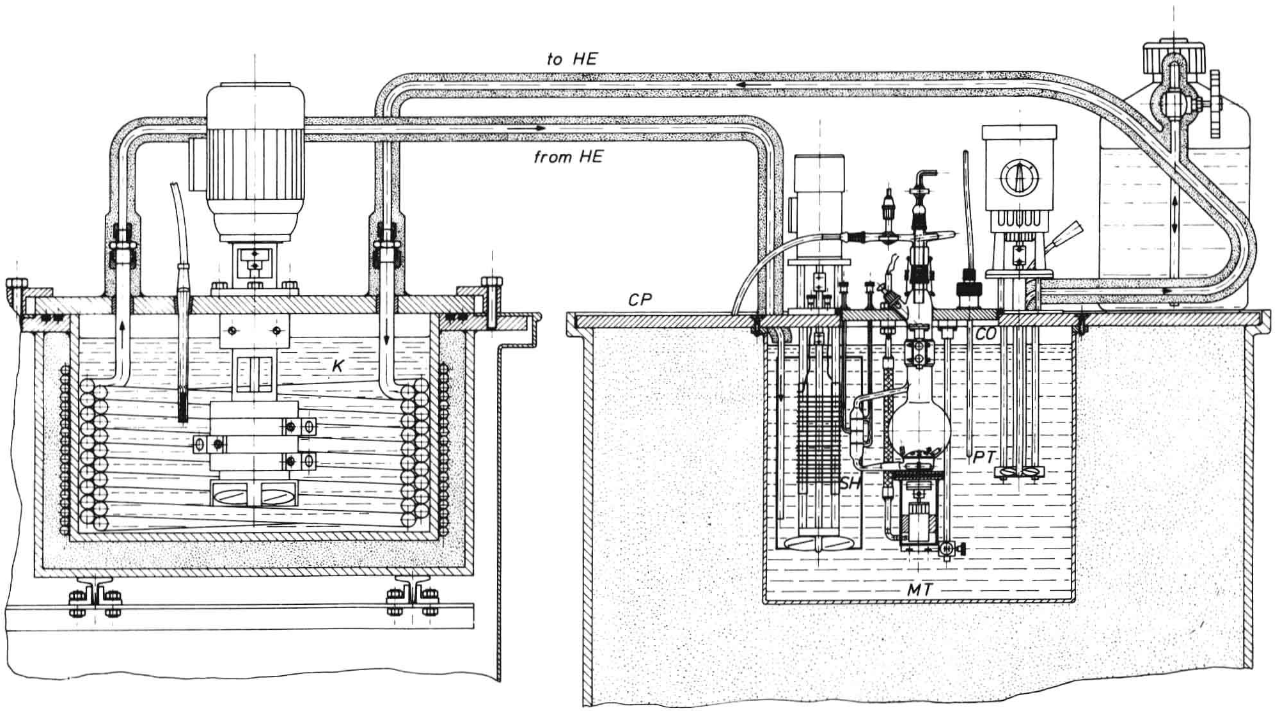


Figure 1. Thermostat assembly with cold bath (K), measurement thermostat (MT), and immersed conductivity cell. For explanation see text.

The measurement thermostat (MT) with a bath of about 60 liters is coupled to a cold bath (K) by means of a heat exchanger (HE). The temperature of the measurement thermostat is controlled by a PID controller joined to an a.c. bridge which contains a platinum resistance thermometer (PT). The error voltage of the bridge is used both for temperature measurement and, via the PID controller, for controlling the heating power of the source of heat (SH). The thermostat is hermetically sealed to prevent atmospheric moisture entering the bath. A circular opening (CO, ϕ 18.5 cm) in the cover plate (CP) permits the immersion or connection of measuring cells (conductance, permittivity, viscosity, density, solubility, etc.) which for their part are supplied with assembly plates guaranteeing hermetical sealing of the opening (CO). For a detailed description, see Refs. 31 and 32.

2. Conductance Measurements

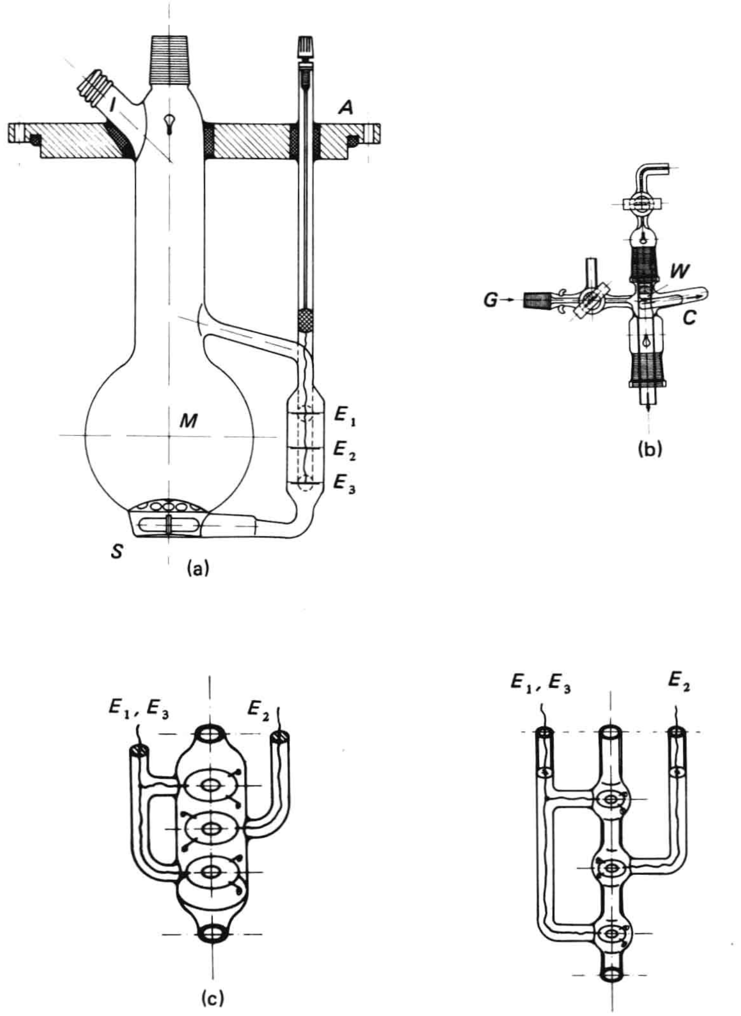
The experimental methods for determining the concentration dependence of conductance are as follows:

(i) preparation of each solution by mixing the solvent and electrolyte compounds by weight (usual method);
(ii) stepwise dilution of a concentrated solution in the measuring cell by adding the pure solvent (cf. Refs. 12 and 50);
(iii) stepwise concentration by successive additions of weighed samples of the electrolyte compound, starting from the pure solvent (cf. Refs. 32, 51, and 52).

Each method requires appropriate measuring cells built according to the requirements of the electrolyte solution and the desired concentration range to be studied.

For the investigation of temperature dependence of conductance and for dilute solutions, method (iii) proves to be the most promising solution of the problem when a method of isologous sections is to be used to establish Λ–c–T diagrams.[8,32,53] Figure 2 shows an appropriate type of conductance cell (cf. also Fig. 1).

For stepwise increase of concentration and isologous sections, the highly purified solvent is introduced into the mixing chamber (M) of the conductance cell (Fig. 2a) through the inlet (I) under protective gas [see Fig. 2b: cap of the conductance cell with gas inlet (G)]. The conductance of the solvent is measured at the various different temperatures of the program. Only then is the first electrolyte concentration prepared by



(a)

(b)

(c)

(d)

Figure 2. Three-electrode measuring cell and mixing chamber with assembly lid (A, Fig. a) for immersion in the temperature bath (cf. Fig. 1). Cell assembly (a); inlet cap (b); electrode assembly of low (c) and moderate (d) cell constant. For further explanation see text.