SOLVENT TRANSPORT BY IONS IN LIQUID ELECTROLYTES

A. Ya. Gokhshtein

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For each type i of current carriers in an electrolyte we shall introduce the notation: m_i for the mass of an ion (gram ion), w_i for the combined mass of solvent molecules accompanying the given ion (and referred to the gram ion), C_i for the concentration of ions (in gram ions per liter), u_i for the mobility, and n_i for the absolute value of the ion's valency. Suppose that the electrolyte contains P sorts of positive current carriers with the parameters m_{cp}, w_{cp}, c_{cp}, u_{cp}, n_{cp}, and Q sorts of negative current carriers with the parameters m_{aq}, w_{aq}, c_{aq}, u_{aq}, and n_{aq}; $p = 1, 2, \ldots, P$; $q = 1, 2, \ldots, Q$. Complete dissociation of the electrolyte, e.g., at infinite dilution, is secured by the absence of other components from it.

Let us find the connection between the w_i and the other electrolyte parameters. Electrode processes or the shape of the vessel have no influence on this connection, and therefore should not enter the computations. In order to actually eliminate their influence we shall consider the electrolyte as being in a long channel along which an electric field exists which has the same direction at all points, but varies with time with amplitude E_0 and angular frequency ω. The electrolyte motions caused by processes at the electrodes and at the channel walls will not reach the central part of the channel above some frequency (e.g., 1 kHz), while the mechanism of current transport still remains stationary. The acceleration of a current carrier of type i is $\omega\tilde{u}_iE_0$. Such motion implies that from without, the unit of electrolyte volume is subjected to a force of frequency ω and amplitude

$$F_0=\omega E_0\left[\sum_p \tilde{u}_{cp}C_{cp}(m_{cp}+w_{cp})-\sum_q \tilde{u}_{aq}C_{aq}(m_{aq}+w_{aq})\right], \tag{1}$$

where $\tilde{u}_i$ is the mobility of an ion in the laboratory system of coordinates. However, the electrolyte is electrically neutral. Therefore, the resultant of the forces applied to it in the electric field is zero. But other variable external forces (from the part of the electrodes and walls of the vessel) are not present at the frequency ω. Thus, $F_0 = 0$, from which

$$\sum_p \tilde{u}_{cp}C_{cp}(m_{cp}+w_{cp})=\sum_q \tilde{u}_{aq}C_{aq}(m_{aq}+w_{aq}). \tag{2}$$

Far from the walls the center of mass of the electrolyte does not shift relative to the vessel. This implies, for example, that if right after cessation of a current pulse a light object is dropped vertically onto an electrolyte surface in the central part of the channel, this object will not move along the channel (it should be entrained by an electrolyte stream moving by inertia).

Let τ_{cp} and τ_{aq} be the true transport numbers for ions of sorts p and q, where $\tau_{cp} = u_{cp}C_{cp}n_{cp}/A$, $\tau_{aq} = u_{aq}C_{aq}n_{aq}/A$, and A is a known coefficient. With increasing dilution, the rate of motion of the solvent which is required to keep the center of mass immobile will decrease because of the increasing ratio of solvent mass to ion mass. Therefore, at infinite dilution the mobility of an ion relative to the solvent (u_i) will coincide with that relative to the vessel ($\tilde{u}_i$), $\tilde{u}_i = u_i$. In practice this condition can be regarded as fulfilled even in moderately dilute solutions. For example, at a concentration of 0.01 N, the equality $\tilde{u}_i = u_i$ is fulfilled with an accuracy of the order of 0.001. At infinite dilution, Eq. (2) can be transformed to

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$$\sum_{p} \tau_{cp}s_{cp} - \sum_{q} \tau_{aq}s_{aq} = \sum_{q} \tau_{aq}\gamma_{aq} - \sum_{p} \tau_{cp}\gamma_{cp}. \tag{3}$$

where $\gamma_{cp} = m_{cp}/n_{cp}m_0$, $\gamma_{aq} = m_{aq}/n_{aq}m_0$, $s_{cp} = w_{cp}/n_{cp}m_0$, $s_{aq} = w_{aq}/n_{aq}m_0$, and m_0 is the molecular weight of the solvent. The left-hand part of expression (3) is the amount of solvent ξ (in moles) which is transported by one faraday from the anode to the cathode in the laboratory system of coordinates. Thence one obtains a relation for calculating the transport number of the solvent ξ from the transport numbers of anions and cations at infinite dilution:

$$\xi = \sum_{q} \tau_{aq}\gamma_{aq} - \sum_{p} \tau_{cp}\gamma_{cp}. \tag{4}$$

In the case of a one-component electrolyte ($P = Q = 1$, and the indices p and q can be dropped), $\xi = \tau_a\gamma_a - \tau_c\gamma_c$. The ξ numbers calculated from this equation from the data of [1-3] on cationic transport numbers for a number of aqueous solutions at infinite dilution and 25°C are given in Table 1. This solvent transport is accomplished by the ions both hydrodynamically and as part of the solvation sheaths.

Because of the finite size of the vessel and because of viscous friction, such a transport mechanism is only effective during average nonstationary motion of the ions, when their inertia becomes manifest. Other than by a time-variable current, nonuniform ionic motion is also brought about by a stationary current of space-variable density, e.g., when the current passes through a hole in a sufficiently thin diaphragm dividing the cathodic and anodic electrolyte compartments.

Let a current of density $j = j_0 \sin \omega t$ pass through the electrolyte, where t is the time. At any electrolyte concentration, the rate of free motion of the solvent as a whole (the velocity of the solvent's coordinate system relative to the laboratory system) is

$$U_s = (j_0 M/F\rho) \sin \omega t, \tag{5}$$

where

$$M = \frac{\tau_a}{n_a}(m_a - \rho\varphi_a) - \frac{\tau_c}{n_c}(m_c - \rho\varphi_c) \tag{6}$$

is the reduced equivalent mass. Here F is the Faraday, ρ is the density of the solution, φ_a and φ_c are the apparent ionic volumes, i.e., the fractions of anion and cation, respectively, in the apparent molar volume φ_{ac} of the electrolyte (the volume of solvent displaced by one mole of electrolyte during dissolution), and $\varphi_{ac} = n_c\varphi_a + n_a\varphi_c$. Moreover, a force

$$g = \sqrt{\omega\mu}\,(j_0 M/F) \cos(\omega t + {}^3\!/_4\pi) \tag{7}$$

is acting upon unit surface area of the dielectric oriented along the lines of above current; here μ is the kinematic viscosity of the solution. Force g develops independently of any electrophoretic force.

At the electrode surface, the solvent is not free to translate along the current lines, since these pass into the electrode in a direction normal to its surface. This gives rise to an alternating pressure upon the electrode [4]. If the solvent system is held fixed in the laboratory system, then a force

$$f = (\omega j_0 M/F) \cos \omega t \tag{8}$$

will act upon unit volume of the solution.

When metal cations are discharged at the immobile cathode, the growing layer of deposit will move the solution away with a velocity

$$U_e = (j/F)\,[\,(V_m/n_c) - \tau_a(V_{ac}/n_a n_c)\,],$$

where V_m/n_c is the volume of one equivalent of metal, V_{ac} is the partial molar volume of the electrolyte (it is assumed that the change in solution composition near the electrode is insignificant). Heating of the electrode–electrolyte boundary gives rise to an additional solution velocity $U_P = (j/F)V_P$, where

$$V_P = PF\left(\frac{1+\nu}{1-\nu}\,\frac{\varkappa}{\zeta_m\rho_m}\,\frac{1}{1+\sigma} + \frac{\beta}{\zeta\rho}\,\frac{\sigma}{1+\sigma}\right). \tag{9}$$

TABLE 1. The Transport Numbers of Water ξ and of Cations τ_c at Infinite Dilution for Different Electrolytes, at 25°C

Electrolyte	τ_c	ξ	Electrolyte	τ_c	ξ
HCl	0,8209	+0,306	$NaC_2H_3O_2$	0,5507	+0,770
LiCl	0,3364	+1,176	$KC_2H_3O_2$	0,6427	−0,224
NaCl	0,3963	+0,682	H_2SO_4	0,813	+0,453
KCl	0,4906	−0,062	Na_2SO_4	0,386	+1,144
KBr	0,4849	+1,232	K_2SO_4	0,479	−0,349
KJ	0,4892	+2,536	$CaCl_2$	0,4380	+0,619
NH_4Cl	0,4909	+0,538	$BaCl_2$	0,4476	−0,619
KNO_3	0,5072	+0,595	$LaCl_3$	0,477	−0,197
$AgNO_3$	0,4643	−0,936			

Here $\sigma = \sqrt{k\zeta\rho/k_m\zeta_m\rho_m}$; k, ζ, and ρ are the coefficient of thermal conductivity, the specific heat capacity, and the density of the electrode (index m) and of the solution (without index), $\varkappa$ is the linear thermal expansion coefficient of the electrode, β is the coefficient of cubical thermal expansion of the solution, ν is Poisson's ratio for the electrode, and P is the Peltier coefficient.

Let a smooth electrode form the bottom of a rather long cylinder filled with electrolyte and open at the opposite end, where provisions are made for sound absorption. Then the variable pressure at the bottom will be $p_e = p_0 \sin\omega t$,

$$p_0 = \frac{\vartheta j_0}{F}\left[M + \rho\left(\frac{V_m}{n_c} - \tau_a\frac{V_{ac}}{n_a n_c} + V_P\right)\right], \tag{10}$$

where ϑ is the velocity of sound in the solution. For a short cylinder of height $H \ll \lambda/2\pi$, where $\lambda = 2\pi\vartheta/\omega$ is the wavelength of sound, the pressure at the bottom will be $p_e = p_H \cos\omega t$, where

$$p_H = (\omega H/\vartheta)\, p_0. \tag{11}$$

In the right-hand part of (10), all quantities other than φ_a and φ_c which enter M are known. Therefore, Eq. (10) can be used for the determination of φ_a and φ_c inasmuch as φ_{ac} is known. Equation (11) is serving the same purpose at low frequencies. The quantity ρV_P is small, on the order of 0.1 g/eq. At $j_0 = 1$ A/cm^2, the quantity p_0 is on the order of 10 dyne/cm^2. When the electrode is polarizable, V_m in (10) is substituted by V_c, which is the partial volume of cations in the double layer. The quantity V_c is not known beforehand, but can be determined by measuring the pressure.

If a current is passed between identical electrodes arranged at opposite ends of a closed cylinder, than at $H = r\lambda$, where r is a whole number, standing waves will arise in the cylinder. In this case, the point of maximum amplitude of the pressure is at a distance $\lambda/4$ away from the electrode; at the electrode surface itself the pressure amplitude is close to zero.

In the case of multicomponent electrolytes, the reduced mass M can be varied by varying the solution composition. With certain combinations of electrolytes, M can be made zero.

LITERATURE CITED

1. S. Glasstone, Introduction to Electrochemistry, Van Nostrand (1942).
2. T. Erdey-Gruz, Transport Phenomena in Aqueous Solutions, Budapest (1974).
3. H. S. Harned and B. B. Owen, The Physical Chemistry of Electrolytic Solutions, New York (1963).
4. A. Ya. Gokhshtein, Élektrokhimiya, 2, 1061 (1966).