

Electrochemical Cells with Chemical Reactions in the Electrolyte with Bipolar Membrane as Junction

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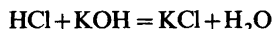
A thermodynamic treatment is developed to describe coupling between charge transfer and chemical reaction in an electrochemical cell employing a bipolar membrane as a liquid junction. A mathematical relationship between the cell emf and the concentration of the components in the electrolyte is derived and its validity is confirmed experimentally. The degree of coupling as well as the internal resistance of the cell is improved by the use of a novel supporting electrolyte.

The specific relation between transport processes and chemical reactions is a central problem in the description of membrane phenomena. Attempts to tackle the problem through the application of irreversible thermodynamic principles, have been made by several workers.^{1,2} Their methods deal with discontinuous description involving models in which the system is treated as a black-box. In such treatment, the chemical affinity of the reaction is considered a separate driving force. These considerations give rise to dependent fluxes and forces which then complicate numerical evaluation of the degree of coupling.

A different thermodynamic treatment of systems with chemical reactions is developed by Førlund and Ratkje.³ Their treatment is characterized by the use of neutral species in accordance with the Gibbs phase rule. This ensures that the Onsager reciprocal relations are fulfilled and that all variables are related to directly measurable quantities. However, their treatment is limited to electrode reactions where complete coupling occurs. Also, it is limited to homogeneous systems where the chemical affinity is considered to be equal to zero, and is not related to a chemical reaction taking place over a range with

changing composition and with affinity different from zero.

Alternative thermodynamic treatment of transport process with chemical reactions in the electrolyte. The electrochemical cell under consideration is schematically shown in Fig. 1. The charge transfer in the cell is due to migration of the ions H^+ , K^+ , OH^- , Cl^- and is accompanied by the reaction,



As the reaction is coupled to charge transfer, it must contribute to the cell emf. The magnitude of the cell emf is determined by the degree of coupling between charge transfer and the chemical reaction.

In the system described by Fig. 1, the electrode components are separate phases in their standard states. Therefore, for the case of no pressure

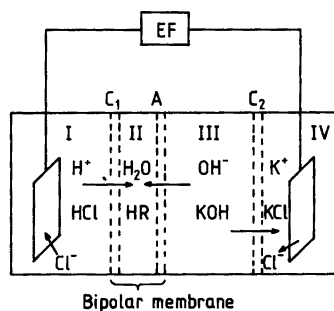


Fig. 1. Transport processes with chemical reactions in the electrolyte. A_1 and C_1 represent the anion and cation exchange membranes, respectively. C_1 and A_1 together with the region between them constitute the bipolar membrane. Electrodes reversible to chloride ions are used.

gradient their difference in chemical potential over the cell is equal to zero. By choosing the membranes to be the reference components for transport and applying the phase rule to the remaining chemical components the number of components necessary to describe changes in the system completely is reduced to three.

The three components are chosen for convenience to be HCl, KCl and H₂O, because we want to make use of the assumption $d\mu_{\text{H}_2\text{O}} \approx 0$ in the calculations. According to Førlund and Røtkje³ the dissipation function per unit volume is given by eqn. (2), where $\nabla\phi$ (given in J/F) is the gradient of

$$\theta = \sum(-\nabla\mu_i J_i) - \nabla\phi I \quad (2)$$

electromotive potential anywhere in the system, measured with electrodes reversible to Cl⁻ ions, μ_i is the chemical potential of component *i*, J_i is the flux of component *i* and *I* is the electric current density. In contrast to conventional approach where the dissipation function per unit volume θ is given by eqn. (3) the chemical affinity of the reaction A is

$$\theta = \sum(-\Delta\mu_i J_i) - \Delta\phi I - A J_r \quad (3)$$

included in the chemical potential term μ_i in (2) and does not appear as a dependent force. J_r is the flux of the chemical reaction and is a scalar.

According to (2) the flux equations become

$$J_{\text{HCl}} = J_1 = -L_{11}\nabla\mu_1 - L_{12}\nabla\mu_2 - L_{13}\nabla\mu_3 - L_{14}\nabla\phi \quad (4)$$

$$J_{\text{KCl}} = J_2 = -L_{21}\nabla\mu_1 - L_{22}\nabla\mu_2 - L_{24}\nabla\phi \quad (5)$$

$$J_{\text{H}_2\text{O}} = J_3 = -L_{31}\nabla\mu_1 - L_{32}\nabla\mu_2 - L_{33}\nabla\mu_3 - L_{34}\nabla\phi \quad (6)$$

$$I = -L_{41}\nabla\mu_1 - L_{42}\nabla\mu_2 - L_{43}\nabla\mu_3 - L_{44}\nabla\phi \quad (7)$$

$$\text{For } I=0, \quad \nabla\phi = t_1\nabla\mu_1 - t_2\nabla\mu_2 - t_3\nabla\mu_3 \quad (8)$$

Considering flows along the *x*-axis only and assuming that local equilibrium is established everywhere in the system (8) becomes eqn. (9), where *F* is the Faraday constant and *E* the cell emf.

$$-\Delta\phi = -EF = \int(t_1 d\mu_1 + t_2 d\mu_2 + t_3 d\mu_3) \quad (9)$$

In eqns. (4)–(8), L_{ij} are the phenomenological coefficients. The transference numbers t_i are those of neutral components defined by eqns. (10)–(12). The measurement of transference numbers is discussed by Førlund.⁴ Eqn. (9) then becomes eqn. (13).

$$t_1 = t_{\text{HCl}} = \left(\frac{J_{\text{HCl}}}{I}\right) \nabla\mu_1 = 0 \quad i=2, 3 \quad (10)$$

$$t_2 = t_{\text{KCl}} = \left(\frac{J_{\text{KCl}}}{I}\right) \nabla\mu_1 = 0 \quad i=1, 3 \quad (11)$$

$$t_3 = t_{\text{H}_2\text{O}} = \left(\frac{J_{\text{H}_2\text{O}}}{I}\right) \nabla\mu_1 = 0 \quad i=1, 2 \quad (12)$$

$$-EF = \int_{\text{over cell}} (t_{\text{HCl}} d\mu_{\text{HCl}} + t_{\text{KCl}} d\mu_{\text{KCl}} + t_{\text{H}_2\text{O}} d\mu_{\text{H}_2\text{O}}) \quad (13)$$

The transference numbers of neutral components are obtained from ionic transference numbers through the stoichiometric relations (14)–(16),

$$n_{\text{KCl}} = n_{\text{K}^+} \quad (14)$$

$$n_{\text{HCl}} = n_{\text{Cl}^-} - n_{\text{K}^+} \quad (15)$$

$$n_{\text{H}_2\text{O}} = n_{\text{OH}^-} \quad (16)$$

where *n* represents number of mol. This way of describing composition is commonly used for molten salt mixtures. Eqns. (14), (15) and (16) give the transference numbers (17)–(19) whereby the relation for ionic transport numbers, eqn. (20), has been introduced.

$$t_{\text{KCl}} = t_{\text{K}^+} \quad (17)$$

$$t_{\text{HCl}} = 1 - t_{\text{Cl}^-} - t_{\text{K}^+} = t_{\text{H}^+} + t_{\text{OH}^-} \quad (18)$$

$$t_{\text{H}_2\text{O}} = -t_{\text{OH}^-} \quad (19)$$

$$\sum_i t_i = 1 \quad (20)$$

Substitution of (17) and (18) into (13) gives eqn. (21).

$$-EF = \int_{\text{I}}^{\text{III}} (t_{\text{H}^+} + t_{\text{OH}^-}) d\mu_{\text{HCl}} + \int_{\text{II}}^{\text{IV}} t_{\text{K}^+} d\mu_{\text{KCl}} + \int_{\text{I}}^{\text{III}} t_{\text{H}_2\text{O}} d\mu_{\text{H}_2\text{O}} \quad (21)$$

Complete coupling between charge transfer and the chemical reaction. If the cation and anion exchange membranes are perfect cation and anion conductors, respectively, and compartment II contains pure water, eqn. (21) reduces to eqn. (22), where the subscripts I, II, III and IV refer to cell compartments. Assuming local equilibrium in compartment III we have eqn. (23).

$$-EF = \mu_{\text{HCl}}^{\text{III}} - \mu_{\text{HCl}}^{\text{I}} + \mu_{\text{KCl}}^{\text{IV}} - \mu_{\text{KCl}}^{\text{III}} - \mu_{\text{H}_2\text{O}}^{\text{III}} + \mu_{\text{H}_2\text{O}}^{\text{II}} \quad (22)$$

$$\mu_{\text{HCl}}^{\text{III}} = \mu_{\text{KCl}}^{\text{III}} + \mu_{\text{H}_2\text{O}}^{\text{III}} - \mu_{\text{KOH}}^{\text{III}} \quad (23)$$

Also it may be assumed that the concentration of water is constant throughout the cell: eqn. (24).

$$\mu_{\text{H}_2\text{O}}^{\text{III}} = \mu_{\text{H}_2\text{O}}^{\text{II}} \quad (24)$$

Introducing (23) and (24) into (22) gives (25)–(26) or (27).

$$-E_i F = \mu_{\text{KCl}}^{\text{IV}} + \mu_{\text{H}_2\text{O}}^{\text{II}} - \mu_{\text{HCl}}^{\text{I}} - \mu_{\text{KOH}}^{\text{III}} \quad (25)$$

$$-E_i F = RT \ln \left(\frac{a_{\text{H}_2\text{O}}^{\text{II}} a_{\text{KCl}}^{\text{IV}}}{a_{\text{HCl}}^{\text{I}} a_{\text{KOH}}^{\text{III}}} \right) \quad (26)$$

$$-E_i F = \Delta G_{\text{reaction}} \quad (27)$$

Therefore, in the case of 100% membrane permselectivity, and pure H₂O in compartment II, complete coupling between charge transfer and the chemical reaction occurs.

Partial coupling between charge transfer and the chemical reaction. Eqn. (26) represents the ideal case which is not observable in real situations. In a real case, electrolytes of concentrations higher than 10⁻⁸ will be present in compartment II and this will have a significant effect on *t*_{HCl}. We assume that the electrolyte present in compartment II is KCl. In (21) the contribution to *EF* due to *t*_{H₂O}*dμ* H₂O may be omitted, since it is assumed that the chemical potential of water is constant throughout the cell. The integral ∫*t*_K+*dμ*_{KCl} over compartment II may be considered to be a small quantity as *dμ*_{KCl} will change sign over compartment II (see Fig. 2) and may therefore be omitted. The significant contribution to *EF* is that given by ∫^{III}(*t*_H+*t*_{OH}-)*dμ*_{HCl} and of main interest is the value of the integral

over compartment II, where loss in coupling occurs. Therefore, eqn. (28).

$$-EF \simeq \int_{\text{over II}} (t_{\text{H}} + t_{\text{OH}} -) d\mu_{\text{HCl}} \quad (28)$$

The water in compartment II would contain KCl or other ionic impurities because the permselectivity of individual membranes is not 100%. Also, there would be adhering K⁺ and Cl⁻ ions in the anionic and cationic membranes, respectively. These ions are derived from the KOH and HCl solutions in which the membranes are equilibrated prior to assembling the cell. In order to avoid uncertainties on the magnitudes of KCl or other impurities within the bipolar junction, a known quantity of KCl is introduced. There would be a continuous removal of KCl from compartment II. At the solution C₁ membrane interphase, there would exist an H⁺-K⁺ ion exchange creating a very low K⁺ concentration and an H⁺-K⁺ interdiffusion in the membrane. Similarly, OH⁻-Cl⁻ exchange and interdiffusion would take place on the other side of compartment II.

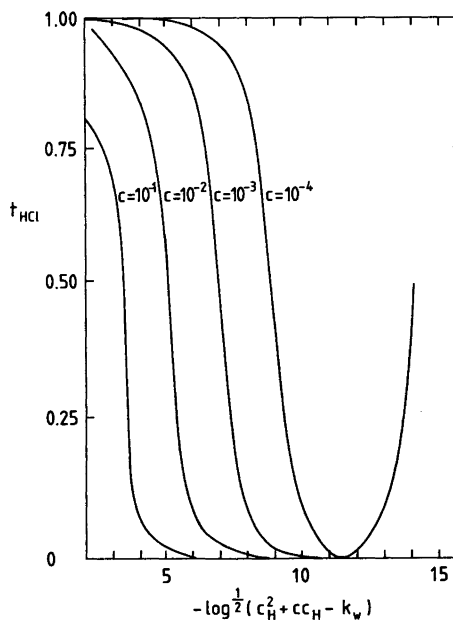


Fig. 2. Variation of *t*_{HCl} as a function of concentration of C_H+ across the bipolar membrane junction for selected concentrations of salt ions at the junction.

According to (18), when the only ions of significant concentration in compartment II are H^+ , OH^- , K^+ and Cl^- , we have eqn. (29), where U_i is the mobility of ionic species i .

$$t_{HCl} = t_{H^+} + t_{OH^-} = \frac{C_{H^+} + \frac{U_{OH^-}}{U_{H^+}} \cdot C_{OH^-}}{C_{H^+} + \frac{U_{OH^-}}{U_{H^+}} C_{OH^-} + \frac{U_{K^+}}{U_{H^+}} C_{K^+} + \frac{U_{Cl^-}}{U_{H^+}} C_{Cl^-}} \quad (29)$$

A rigorous evaluation of concentration profiles and of integral in eqn. (28) involves the solution of complicated integral equations. However, from simplified flux equations for the ions K^+ , H^+ , Cl^- and OH^- assuming ideal mixtures and introducing $U_{K^+} = U_{Cl^-}$ one can show the relation (30) to be

$$\nabla C_{K^+} + \nabla C_{Cl^-} = 0 \quad (30)$$

relevant in the region where the concentrations of K^+ and Cl^- are about equal (paper under preparation). As this region is the most important for evaluation of (28), it may be assumed that (30) is valid over the whole range of integration. Integration of (30) gives for the interphase region where C_{K^+} varies between zero and C_{K^+} , and C_{Cl^-} between C and C_{Cl^-} :

$$C_{K^+} + C_{Cl^-} = C$$

where C is the bulk concentration of KCl introduced in compartment II.

Electroneutrality condition requires that

$$C_{H^+} + C_{K^+} = C_{OH^-} + C_{Cl^-} \quad (31)$$

The condition for local equilibrium of water is according to eqn. (32). With (30), (31) and (32) introduced into (29), the relationships (33) and (34)

$$C_{OH^-} = K_w / C_{H^+} \quad (32)$$

$$t_{HCl} = \frac{C_{H^+}^2 + \frac{U_{OH^-}}{U_{H^+}} K_w}{C_{H^+}^2 + \frac{U_{K^+}}{U_{H^+}} C C_{H^+} + \frac{U_{OH^-}}{U_{H^+}} K_w} \quad (33)$$

$$d\mu_{HCl} = RT \left(\frac{C + 2C_{H^+}}{C_{H^+}^2 + C C_{H^+} - K_w} \right) dC_{H^+} \quad (34)$$

are obtained, where the approximation that $U_{K^+} = U_{Cl^-}$ has been introduced in (33). Introducing (33) and (34) into (28) and assuming that $t_{HCl} = 1$ through either membranes, the resulting expression is eqn. (35).

$$-EF = RT \int_{\text{over II}} \left(\frac{C_{H^+}^2 + \frac{U_{OH^-}}{U_{H^+}} K_w}{C_{H^+}^2 + \frac{U_{K^+}}{U_{H^+}} C C_{H^+} + \frac{U_{OH^-}}{U_{H^+}} K_w} \right) \left(\frac{C + 2C_{H^+}}{C_{H^+}^2 + C C_{H^+} - K_w} \right) dC_{H^+} \quad (35)$$

The effect of a supporting electrolyte on junction conductivity and degree of coupling. When the junction contains pure water i.e. $C = 0$ then from (33), $t_{HCl} = 1$ and (35) reduces to eqn. (36).

$$-EF = RT \ln \left(\frac{K_w}{C_{HCl}^2} \right) \quad (36)$$

The integration limits are $C_{H^+} = C_{HCl} = 0.1$ mol/l and $C_{H^+} = 10^{-7}$ mol/l. In accordance to the system described in Fig. 1 where $C_{HCl}^I = C_{KOH}^{III} = C_{KCl}^{IV}$, eqn. (36) is equal to (26). This is the desired case of complete coupling where the chemical energy derived from the chemical reaction (1) is completely converted to electrical energy.

However, the conductivity of pure water is very low, (58×10^{-7} ohm $^{-1}$ m $^{-1}$).⁵ Consequently, the internal cell resistance of the cell with pure water at the junction is very high. The high resistance renders the cell of no practical importance as an energy storage device.

The conventional methods of increasing cell conductivity involve the use of supporting electrolytes. In the cell described here, introduction of a supporting electrolyte i.e. KCl would destroy coupling as is evident from (35) where the magnitude of Cl is increased. In order to avoid ohmic loss in compartment II the compartment may be made extremely narrow. This method has been tried but proved unsuccessful.⁶ Another approach is to employ a supporting electrolyte which increases the conductivity of water without destroying coupling. Such an electrolyte should be of sufficiently large molecular size to prevent it from diffusing through the channels of the ion exchange membranes and remain trapped in compartment II. It will be shown both theoretically and by experiments that such an

electrolyte can be a derivative of NH_4^+ where up to three of the protons may be substituted by large organic groups. It could also be a base or anion R^- which could accept a proton to form an acid HR or H_2R^+ which would then transfer protons.

By introducing the supporting electrolyte HR in compartment II, the phase rule components for the system become HCl , KCl , H_2O and HR . Neglecting the contribution of water transport, EF is given by eqn. (37). The component HR is trapped within compartment II and if no current is drawn from the cell $d\mu_{\text{HR}}$ is equal to zero. By passing current through the cell gradients of HR will be created in compartment II and a loss (in addition to ohmic loss) will occur given by the integral $\int t_{\text{HR}} d\mu_{\text{HR}}$. It has been shown that this loss is insignificant for moderate current densities.⁶ Under these conditions eqn. (37) reduces to eqn. (38).

$$-EF = \int_{\text{over cell}} \left(t_{\text{HCl}} d\mu_{\text{HCl}} + t_{\text{KCl}} d\mu_{\text{KCl}} + t_{\text{HR}} d\mu_{\text{HR}} \right) \quad (37)$$

$$-EF = \int_{\text{I}}^{\text{III}} t_{\text{HCl}} d\mu_{\text{HCl}} + \int_{\text{III}}^{\text{IV}} t_{\text{KCl}} d\mu_{\text{KCl}} \quad (38)$$

Following similar arguments as for (14)–(20) it can be shown that,

$$t_{\text{KCl}} = t_{\text{K}^+} = 1, \text{ from III to IV}$$

$$t_{\text{HCl}} = t_{\text{H}^+} + t_{\text{OH}^-} + t_{\text{R}^-} = 1, \text{ from I to III}$$

Thus eqn. (38) reduces to (26).

$$-EF = \mu_{\text{HCl}}^{\text{III}} - \mu_{\text{HCl}}^{\text{I}} + \mu_{\text{KCl}}^{\text{IV}} - \mu_{\text{KCl}}^{\text{III}} \quad (26)$$

$$-EF = RT \ln \frac{a_{\text{H}_2\text{O}}^{\text{II}} a_{\text{KCl}}^{\text{IV}}}{a_{\text{HCl}}^{\text{I}} a_{\text{KOH}}^{\text{II}}}$$

The introduction of the supporting electrolyte HR into the junction results in a high degree of coupling and a low electrical resistance.

EXPERIMENTAL

Determination of the cell emf. The electrolytic cell used for emf measurements is schematically presented in Fig. 1. It consists of two glass flasks

interposing two cylindrical plexiglass cells. The plexiglass cells are separated from one another and from the glass flasks by a series array of cation and anion exchange membranes to form four compartments I, II, III and IV, in series. The membranes were commercial cation and anion exchange membranes from Permutit Co.

Compartment I, III and IV contains 0.1 mol/l of HCl , KOH and KCl respectively. Compartment II constitutes the bipolar membrane junction, and contains water or an aqueous solution of one selected supporting electrolyte. The supporting electrolytes include, aqueous solutions of KCl , congo-red indicator, ammonia, benzylamine, naphthylamine, disulfonic acid, naphthylsulfonic acid and a salt of naphthylsulfonic acid and naphthylamine.

The emf of the cell is measured by a direct current differential voltmeter using Ag/AgCl electrodes. The emf changes are recorded using a Servogor potentiometric recorder linked to and synchronized with the differential voltmeter.

The cell assembly is submerged in a thermostated waterbath maintained at $25 \pm 0.1^\circ\text{C}$.

RESULTS AND DISCUSSION

The emf of the cell with KCl at the bipolar membrane junction is given by (35). Contributions to E can be calculated from all local parts in the membranes and in the solutions. Eqn. (35) is also applicable at the surfaces of discontinuity, notably the interfaces between the membranes and the solution.

The emf (E_c) is evaluated from the area under the curve on the plot of t_{HCl} versus μ_{HCl} according to (35). Such a plot is shown in Fig. 2. The transference number of HCl (t_{HCl}) as calculated from (33) decreases rapidly from about 1 at $C_{\text{HCl}} = 10^{-1}$ mol/l to about zero at $C_{\text{HCl}} = 10^{-7}$ mol/l. This is because as H^+ and OH^- ions get depleted by the neutralization reaction to form H_2O , the ions of the salt (K^+ and Cl^-) take over charge transfer.

It is evident from (35) that for a given concentration of the components HCl and KCl , the emf of the cell depends on the magnitude of C , i.e. the concentration of the ionic impurities or salt ions within the neutralization site. As C approaches zero, E approaches a maximum given by the condition of complete coupling according to (26). However, Table 2 shows that when the bipolar membrane junction contains pure water i.e. $C=0$, the experimentally determined emf (E_c) is 0.50 volts

Table 1. Effect of ionic-impurities at the bipolar membrane junction.

	$C/\text{mol}\cdot\text{l}^{-1}$				
	10^{-8}	10^{-4}	10^{-3}	10^{-2}	10^{-1}
E/volt	0.705	0.401	0.288	0.170	0.072
E_0/volt	0.70 ^a	0.370	0.270	0.171	0.065
$\eta = E/E_0$	≈ 100	52	39	24	9

^a Obtained from extrapolation of E vs. $-\log c$ to $c = 10^{-8}$. E_0 is the emf calculated for the case of complete coupling. \bar{E} is the emf obtained from evaluation of eqn. (3).

which corresponds to a degree of coupling equal to only 0.70. The loss in coupling observed experimentally may be mainly due to presence of salt ions at the junction. Salt ions at the junction even when only pure water is used is brought about by the fact that neither the cation nor the anion exchange membrane is 100 percent permselective. The validity of (35) in predicting complete coupling as C approaches zero is demonstrated by extrapolation of the plot of E , versus $\log C_{\text{KCl}}$ to $C_{\text{KCl}} = 10^{-8}$ mol/l as shown in Fig. 3. The results in Table 1 indicate that the discrepancy between theory by eqn. (35) and experiment is about 10 percent. This discrepancy may be attributed to the assumptions inherent in eqn. (35).

The effects on the cell emf when employing supporting electrolytes at the bipolar junction are shown in Table 2. Different supporting electrolytes effect coupling between charge transfer and chemical reaction differently. Best results are obtained when using aminonaphthalene disulfonic

Table 2. The effect of various supporting electrolytes on the degree of coupling.

Supporting electrolyte at the bipolar junction	25 °C pK_a	E/volt	$\eta = E/E_0$
KCl (10^{-2} M)	—	0.171	0.24
Benzylamine (10^{-2} M)	0.33	0.42	0.60
<i>N</i> -phenylmethyl naphthalenesulfonamide (10^{-2} M)	—	0.46	0.65
Naphthalenesulfonic acid (10^{-2} M)	0.57	0.52	0.74
Aminonaphthalene-disulfonic acid (10^{-2} M)	—	0.67	0.95

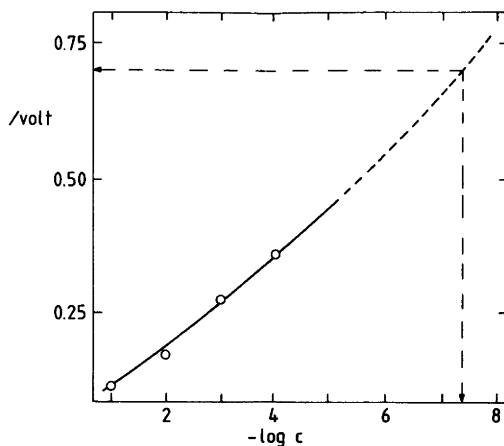


Fig. 3. The effect of ionic impurities at the bipolar membrane junction on the degree of coupling between the chemical reaction and charge transfer.

acid, where the degree of coupling is 0.95. The lower degree of coupling observed when employing KCl, benzylamine, naphthalenesulfonic acid, etc. indicates that the compounds are able to diffuse through the pores of the exchange membranes resulting in loss in coupling.

Aminonaphthalenedisulfonic acid as a supporting electrolyte improves the degree of coupling from

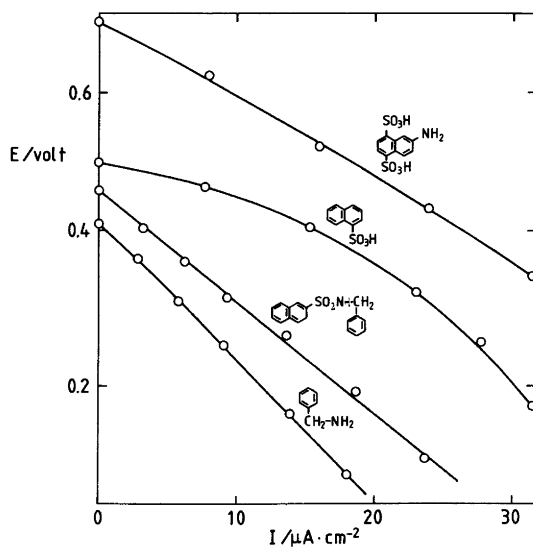


Fig. 4. Observed effect on junction conductivity and on degree of coupling for selected supporting electrolytes.

0.70 for junction with pure water to 0.95. Also, it reduces the internal resistance of the cell from about 400 ohm cm^{-2} for junction with pure water to about 10 ohm cm^{-2} . These results are shown in Fig. 4. One would expect better results when using a supporting electrolyte composed of a compound which dissociates completely in water.

CONCLUSION

The thermodynamic method developed here provides a rigorous thermodynamic treatment to describe coupling between chemical reactions and charge transfer. The treatment is based on using independent fluxes and forces and on the measurable variables only. The number of components is the minimum number as required by Gibbs phase rule. In this way the use of the overall affinity as a force in systems with chemical reactions is avoided.

The treatment provides a general approach in predicting and improving the behaviour of electrochemical systems with chemical reactions for industrial utilization. It may also be useful when dealing with energy conversion in biological systems.

High degree of coupling between charge transfer and chemical reaction and high junction conductivity is obtained by using a big organic anion to carry charge at the bipolar membrane junction.

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