

## Practical Aspects of Electrodifusion

STIG LJUNGGREN

*The Royal Institute of Technology, Division of Physical Chemistry, Stockholm 70, Sweden*

The theoretically derived expression for the electrodiffusion coefficient is examined in order to establish the conditions for a measurable effect to be obtained. The case of electron exchange reactions is treated in detail. The article is only concerned with the magnitude of the electrodiffusion and not with other experimental difficulties such as electrosmosis.

The mathematical treatment of the theory of electrodiffusion has recently been brought to a high degree of perfection.<sup>1-14</sup> In this paper we shall quote only the practical results together with a brief description of the physical situation which leads to the effect in question.

The subject of this article will be some of the practical problems and limitations which present themselves when one attempts to carry out experiments on electrodiffusion. The chief difficulty experienced is that in the majority of cases, the effect is too small to be measured. This, in conjunction with other problems of a more trivial kind, imposes a heavy limitation on the usefulness of the method. It seems, therefore, that apart from the principal aspect the main merit of the method would be its usability for studying special types of systems not easily accessible by other methods but which show a measurable electrodiffusion effect. The possibility of finding such systems possessing a sufficient degree of stability will be discussed.

### THE PHENOMENON OF ELECTRODIFFUSION

A classical diffusion experiment is arranged in the following way. At zero time a solution of the substance, the diffusion of which is to be studied is levelled above a more concentrated solution of the same substance in a cell of constant cross-section, Fig. 1. Then the diffusion of the substance dissolved is registered at intervals by optical or other methods. Let us now assume that we superpose an electric field in the diffusion direction. If the solution contains charged particles (ions) they will migrate in the electric field, and this motion will be superimposed upon the ordinary diffusion. Thus, an alternating electric field will not disturb the diffusion appreciably.

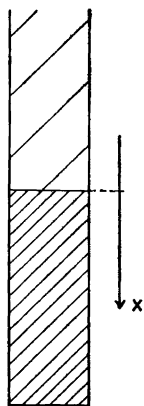


Fig. 1. Arrangement of a diffusion experiment.

Quite a different situation is met with if the ions in the solution take part in a dynamical chemical equilibrium. It may then happen that the superimposed electric field will increase the diffusion coefficient as compared to the ordinary diffusion even if the field is of the alternating type. This increase of the diffusion is called electrodiffusion. It is described by an electrodiffusion coefficient which adds to the ordinary diffusion coefficient.

In order to get an insight into the basic mechanism of electrodiffusion, we shall consider the following situation. Suppose that an atom or molecule A can exist in or enter two ionic forms  $A_1$  and  $A_2$  with different ionic mobilities,  $u_1$  and  $u_2$ . At certain irregular intervals of time, transitions occur between the two forms according to the (simplified) reaction formula



As a simple example of the kind of phenomenon we are dealing with we may take the electron exchange reaction between  $Fe^{2+}$  and  $Fe^{3+}$ . In the electric field, the atom A will migrate alternately with the velocities  $u_1$  and  $u_2$ . If the transitions always occurred regularly at equally spaced time intervals, all atoms A would migrate the same distance during an arbitrary interval of time. Owing, however, to the stochastic character of the times spent in the two states  $A_1$  and  $A_2$ , the distances travelled by the particles A will show a statistical dispersion which reveals itself as an increase of the ordinary diffusion, electrodiffusion.

The mathematics of electrodiffusion has been the subject of a series of papers where the problem has been approached, either by a stochastic argument or by solving the corresponding differential equations. In both cases, identical results are obtained for the electrodiffusion coefficient,

$$D_e = \frac{k_1 k_2 (u_1 - u_2)^2}{2(k_1 + k_2)^3} \sum_{\nu=1}^{\infty} \frac{a_{\nu}^2}{1 + [\nu\omega/(k_1 + k_2)]^2} \quad (2)$$

if the field characteristics is given as the Fourier expansion

$$E(t) = \sum_{\nu=1}^{\infty} a_{\nu} \sin \nu \omega t \quad (3)$$

#### THE MAGNITUDE OF THE EFFECT

We shall now examine the expression for  $D_e$  to find out under what circumstances a measurable effect is to be expected. Since the electrodiffusion has to compete with the ordinary diffusion,  $D_e$  must be of the same order of magnitude as  $D$ . Just as in ordinary diffusion, the primary effect is one of selfdiffusion. Any *simple* mutual diffusion never occurs since a net transport of any ionic species requires the presence of other ions in the solution and the phenomenon then becomes extremely involved\*. The reason for this situation which originates in the electroneutrality condition and the resulting divergenceless character of the electric current has been discussed by the author elsewhere.<sup>6</sup> We shall henceforth concentrate our interest on the selfdiffusion coefficient. Knowing this, more complex situations can then easily be handled.

Returning to the expression for  $D_e$ , we observe that the electrodiffusion always increases with decreasing field frequency. The maximum possible effect is obtained for  $\omega \ll k_i + k_j$ . We then obtain the same value for  $D_e$  as for the direct current case

$$D_e^{\text{DC}} = \frac{E^2(u_i - u_j)^2 k_i k_j}{(k_i + k_j)^3} \quad (4)$$

Here  $E$  is the field strength in the DC case or  $E_{\text{max}}/\sqrt{2}$  in the case of an alternating field. It is now obvious that the magnitude of the effect obtained is determined by the four quantities  $E$ ,  $u_i - u_j$ ,  $k_i$  and  $k_j$ . Of these,  $u_i - u_j$  is a fixed constant characteristic for the system studied, whereas  $k_i$  and  $k_j$  also depend on the concentrations chosen in the solution. Finally, the field strength  $E$  that can be used is limited by the maximum allowable Joule heating and by the isolation resistance of the apparatus used. The Joule heating, in turn, depends on the concentrations and on the presence of other ions in the solution. Owing to these circumstances mentioned, and to other possible complications of a chemical nature, there is no simple and direct rule by which to decide whether a system is suitable for verification of the electrodiffusion effect. Rather, this question will have to be answered from case to case. Furthermore, quite an extensive knowledge of a system is required to render a decision at all possible. It seems, therefore, that this situation would rule out electrodiffusion as a method for studying fast reactions in general.

To facilitate the estimation of the effect we introduce the following abbreviations

$$k = k_i + k_j \quad (5)$$

$$\gamma_i = k_i/k \leq 1 \quad (6)$$

$$\gamma_j = k_j/k \leq 1 \quad (7)$$

---

\* This does not, of course, prevent such cases from being used for the purpose of establishing electrodiffusion.

by the use of which we can write

$$D_e^{\text{DC}} = E^2(u_i - u_j)^2 \gamma_i \gamma_j / k \quad (8)$$

From this we may already conclude that everything else being equal, the effect is favoured by a small  $k$ , *i.e.* by slow kinetics. On the other hand, the kinetics must not be too slow, since a great many transitions are required during one experiment in order that the statistical theory of electrodiffusion should be applicable.

The product  $\gamma_i \gamma_j$  has its maximum value for  $\gamma_i = \gamma_j$ . This gives rise to the important condition that  $k_i$  and  $k_j$  should be of approximately the same magnitude, preferentially equal. The product  $\gamma_i \gamma_j$  may also be expressed in terms of the "equilibrium constant",

$$K_{ij} = k_i / k_j = T_j / T_i = c_j / c_i \quad (9)$$

where  $T_i$  and  $T_j$  denote the average life-times in the two states. We then have

$$\gamma_i \gamma_j = K_{ij} / (K_{ij} + 1)^2 \quad (10)$$

and

$$D_e^{\text{DC}} = E^2(u_i - u_j)^2 K_{ij} / k (K_{ij} + 1)^2 \quad (11)$$

In many cases,  $K_{ij}$  is not a fixed constant but may be altered by varying the concentration of some other ion in the solution. *E.g.* in the system  $I_2/I_3^-$  the concentration ratio  $c_{I_2}/c_{I_3^-}$  is determined by the iodine ion concentration. Of course, in such systems,  $k$  will also depend on the concentrations in the solution, a fact which renders the situation still more complex.

#### THE LIMITING CONDITIONS FOR THE FIELD STRENGTH

The Joule heating per  $\text{cm}^3$  of solution ( $w$ ) can be written

$$w = \kappa E^2 \quad (12)$$

where  $\kappa$  is the specific conductance of the solution. According to electro-phoretic experience, a figure of  $0.2 \text{ watt cm}^{-3}$  would be permissible. If special care is devoted to the cooling of the cell it has been believed possible to exceed this figure considerably. To be on the safe side we shall, however, assume that the Joule heating sets a limit to the field strength according to

$$\kappa E^2 \leq 0.2$$

or

$$E \leq \sqrt{0.2/\kappa} \quad (13)$$

For solutions with a low specific conductance, this limit may reach such high values that the practical limit for the field strength is set by other circumstances such as the capacity of the voltage supply or the insulation resistance of the cell. We can write this condition simply as

$$E \leq E_0 \quad (14)$$

Of the two inequalities (13) and (14) that one is decisive which gives the smallest value for the upper limit of  $E$ .

Thus

$$E = \text{Min} \{ \sqrt{0.2/\kappa}; E_0 \} \quad (15)$$

and

$$E^2 = \text{Min} \{ 0.2/\kappa; E_0^2 \} \quad (16)$$

whence

$$E^2 = 1/\text{Max} \{ \kappa/0.2; 1/E_0^2 \} \quad (17)$$

Introduction into the expression for  $D_e^{\text{DC}}$ , eqn. (11), now gives

$$D_e^{\text{DC}} = (u_i - u_j)^2 K_{ij}/k (K_{ij} + 1)^2 \text{Max} \{ \kappa/0.2; 1/E_0^2 \} \quad (18)$$

For each system, the quantities  $K_{ij}$ ,  $k$ , and  $\kappa$  will depend on the concentrations in a way which is characteristic for that particular system. Since there are so many different types of systems we shall only discuss one of the more common types. Before doing so, we make a few more general observations.

First, we shall give a mathematical form to the condition already mentioned that there should be a sufficient number of transitions during an experiment. Since the "life-times" are related to the rate constants in the following way

$$\begin{aligned} T_i &= 1/k_i \\ T_j &= 1/k_j \end{aligned} \quad (19)$$

we can write our condition as follows

$$T_i + T_j = 1/k_i + 1/k_j \leq T_{\text{max}} \quad (20)$$

Secondly, we make the following observation on eqn. (18). If  $\kappa > 0.2/E_0^2$  we have approximately

$$D_e^{\text{DC}} \approx 0.24 (u_i - u_j)^2 K_{ij}/k (K_{ij} + 1)^2 \kappa \quad (21)$$

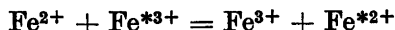
*i.e.* the effect is inversely proportional to  $a$ . If, on the other hand,  $\kappa < 0.2/E_0^2$  we have to the same approximation

$$D_e^{\text{DC}} \approx 1.2 (u_i - u_j)^2 K_{ij} E_0^2 / k (K_{ij} + 1)^2 \quad (22)$$

We see, therefore, that  $\kappa$  should not exceed the value  $0.2/E_0^2$  appreciably. On the other hand, little is gained by reducing the conductivity much below this value. For  $E_0 = 30 \text{ V cm}^{-1}$  we have  $0.2/E_0^2 \approx 2 \times 10^{-4} \text{ ohm}^{-1} \text{cm}^{-1}$ .

#### ELECTRON EXCHANGE REACTIONS

The expression for  $D_e^{\text{DC}}$  in eqn. (18) shows how far we can get without introducing special assumptions about the system. We shall now specialize our formula to the case of electron exchange reactions, a simple example of which is given by the reaction



Such electron exchange reactions constitute a fairly homogeneous group of reactions which makes a unified treatment possible.

We will assume that the experiment is arranged in such a way that the two oxidation states are both found in the same concentration,  $c$ . The exchange being bimolecular in nature, we obtain for the back and forward rate constants

$$k_1 = k_2 = kc \quad (23)$$

The possibility of choosing  $k_1 = k_2$  is the chief advantage of the electron exchange reactions over ordinary redox reactions from the point of view of electrodiffusion.

Owing to the electroneutrality condition, the concentration of the counterions must be proportional to  $c$ , *i.e.* we may express the conductivity of the solution in the following way

$$\kappa = ac \quad (24)$$

where  $a$  is a constant characteristic of the system. Introduction into eqn. (18) then gives

$$D_e^{\text{DC}} = (u_i - u_j)^2 / 8kc \text{Max}\{5ac; 1/E_0^2\} \quad (25)$$

It is seen that in this case  $D_e^{\text{DC}}$  is a decreasing function of  $c$ . We should therefore choose  $c$  as small as possible without violating the condition of eqn. (20) which in this case can be written

$$2/kc \leq T_{\text{max}} \quad (26)$$

or

$$c \geq 2/kT_{\text{max}}$$

We will thus assume that  $c = 2/kT_{\text{max}}$ . Introduction of this value into eqn. (25) and subsequent reduction then yields

$$D_e^{\text{DC}} = (u_i - u_j)^2 T_{\text{max}} / 16 \text{Max}\{10a/kT_{\text{max}}; 1/E_0^2\} \quad (27)$$

The largest possible value of  $D_e^{\text{DC}}$  is reached for such systems where the term  $10a/kT_{\text{max}}$  can be neglected when compared with  $1/E_0^2$ . We then obtain

$$(D_e^{\text{DC}})_{\text{max}} = (u_i - u_j)^2 E_0^2 T_{\text{max}} / 16 \quad (28)$$

If we tentatively assume the following values for the experimental parameters

$$\begin{aligned} E_0 &= 30 \text{ V cm}^{-1} \\ T_{\text{max}} &= 10 \text{ sec} \\ u_i - u_j &= 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ sec}^{-1} \end{aligned}$$

we obtain

$$(D_e^{\text{DC}})_{\text{max}} = 0.56 \times 10^{-5} \text{ cm}^2 \text{sec}^{-1}$$

which is sufficiently large to compete successfully with the ordinary self-diffusion. As already mentioned, there are two conditions if  $(D_e^{\text{DC}})_{\text{max}}$  is to be attained. Firstly, the concentrations must be chosen such that  $c = 2/kT_{\text{max}}$ ,

which requires a fairly complete knowledge of the system before an experiment can be performed. Secondly, it is necessary that

$$10 a/kT_{\max} < 1/E_0^2$$

or

$$k > 10 a E_0^2/T_{\max}$$

With the values for  $E_0$  and  $T_{\max}$  proposed above and with  $a = 1$  l ohm<sup>-1</sup>cm<sup>-1</sup>mole<sup>-1</sup> we have approximately

$$k > 10^3 \text{ l mole}^{-1}\text{sec}^{-1}$$

A further limitation is, of course, that this value of the bimolecular exchange rate constant must be reached without the use of catalysts or buffers that increase the conductivity of the solution. One example of this kind of situation is afforded by the system  $\text{Fe}(\text{CN})_6^{3-} - \text{Fe}(\text{CN})_6^{4-}$  where, according to Wahl, the extrapolated value of  $k$  at zero ionic strength and the temperature 5°C only amounts to 5 l mole<sup>-1</sup>sec<sup>-1</sup>. The reaction is accelerated by the catalytic action of potassium and hydrogen ions. In order to increase  $k$  above 10<sup>3</sup> l mole<sup>-1</sup>sec<sup>-1</sup>, these ions must, however, be added in such quantity that the specific conductance of the solution reaches unacceptable values.

#### REFERENCES

1. Mysels, K. J. *J. Chem. Phys.* **24** (1956) 371.
2. Lamm, O. *Acta Chem. Scand.* **10** (1956) 1132.
3. Giddings, J. C. *J. Chem. Phys.* **26** (1957) 169.
4. Giddings, J. C. *J. Chem. Phys.* **26** (1957) 1755.
5. Bak, T. A. and Kauman, W. G. *J. Chem. Phys.* **28** (1958) 509.
6. Ljunggren, S. *Acta Chem. Scand.* **12** (1958) 1529.
7. Bak, T. A. and Kauman, W. G. *Trans. Faraday Soc.* **55** (1959) 1109.
8. Ljunggren, S. *Trans. Roy. Inst. Technol. Stockholm* **142** (1959).
9. Scholten, P. C. and Mysels, K. J. *Trans. Faraday Soc.* **56** (1960) 994.
10. Thedén, T. *Trans. Roy. Inst. Technol. Stockholm* **165** (1960).
11. Scholten, P. C. and Mysels, K. J. *Trans. Faraday Soc.* **57** (1961) 764.
12. Scholten, P. C. and Mysels, K. J. *J. Chem. Phys.* **35** (1961) 1845.
13. Scholten, P. C. *Diss. Utrecht* (1962).
14. Nagel, B. *Arkiv Matematik* **5** (1964) 363.

Received November 13, 1964.