Thermochimica Acta, 9 (1974) 247–254

EXTERNAL TRANSVERSE MAGNETIC FIELD EFFECT ON ELECTROLYTE DIFFUSION IN $NaCl–H_2O$ SOLUTION

J. LIELMEZS AND H. ALEMAN
Chemical Engineering Department, The University of British Columbia, Vancouver 8, B.C. (Canada)
(Received 14 February 1974)

ABSTRACT

Experiments using modified membrane-cell method show that an externally applied magnetic field influences the integral diffusion coefficient of NaCl (measured at 25°C; 5, 8 and 10 kG magnetic field strength and at ambient pressure) in 0.05, 0.1, 0.2, 0.5 and 1.0 N $NaCl–H_2O$ solution.

These findings verify the previously presented results showing that at the same thermodynamic state conditions, an applied external magnetic field of 5 kG strength alters the integral diffusion coefficient of KCl in 0.01, 0.1, 1.0, 2.0 and 3.0 N $KCl–H_2O$ solutions.

INTRODUCTION

By means of the modified membrane-cell method[1–6], it has been found that an applied external transverse magnetic field of 5, 8 and 10 kG influences the integral diffusion coefficient values of NaCl in 0.05, 0.1, 0.2, 0.5 and 1.0 N $NaCl–H_2O$ solutions at 25°C (Table 1, Fig. 3).

The presented integral diffusion coefficient values (Table 1, Fig. 3) for NaCl were obtained using the standard dilute electrolyte solution diffusion coefficient calculation methods, as derived from Fick's law of diffusion for both, to applied field[1–6] and externally applied magnetic field conditions[6,7]. As in the case of KCl-integral diffusion coefficient calculation[6] under the influence of an external applied magnetic field, it was assumed that the applied transverse magnetic field does not in any way alter the physico-chemical properties (density, viscosity, electric resistance) of water and the used salt[8,9].

The obtained experimental results (Table 1, Fig. 3) verify the recent theoretical Lielmezs and Musbally observation[7] and the experimental finding of Lielmezs et al.[6] that an externally applied magnetic field may influence the diffusion process of electrolytes in solution.

TABLE 1

SUMMARY OF RESULTS[a,b]

$NaCl$–H_2O solution concentration $C_m^{3,4}$, *N*	*Arithmetic mean average*[c] *integral diffusion coefficient,* $\bar{D}^{0}_{25^\circ C}$ *at no field, this work* [$cm^2\ sec^{-1} \times 10^3$]	*Arithmetic mean average*[c] *integral diffusion coefficient,* $\bar{D}^{H}_{25^\circ C}$[d] *with field,* $H = 5$ *kG this work* [$cm^2\ sec^{-1} \times 10^3$]	*Arithmetic mean average*[c] *integral diffusion coefficient,* $\bar{D}^{H}_{25^\circ C}$[d] *with field,* $H = 8$ *kG this work* [$cm^2\ sec^{-1} \times 10^3$]	*Arithmetic mean average*[c] *integral diffusion coefficient,* $\bar{D}^{H}_{25^\circ C}$[d] *with field,* $H = 10$ *kG this work* [$cm^2\ sec^{-1} \times 10^3$]
0.04467	1.5363	—	—	—
0.04479	—	1.5632	—	—
0.07922	—	1.5533	—	—
0.07953	—	—	—	—
0.07960	—	—	—	1.5801
0.08019	1.5218	—	1.5667	—
0.1733	1.5006	—	—	—
0.1767	—	—	—	—
0.4316	1.4722	—	1.5195	—
0.4391	—	1.4860	—	—
0.8461	—	1.4886	—	—
0.8607	1.4800	—	—	—

[a] All results obtained for 25°C temperature. [b] Experimental Stokes[4] data are shown on Fig. 3. [c] Arithmetic mean average value obtained from all experimental runs at the given concentration of NaCl in H_2O. [d] Subscript "H" refers to applied transverse magnetic field condition, this work.

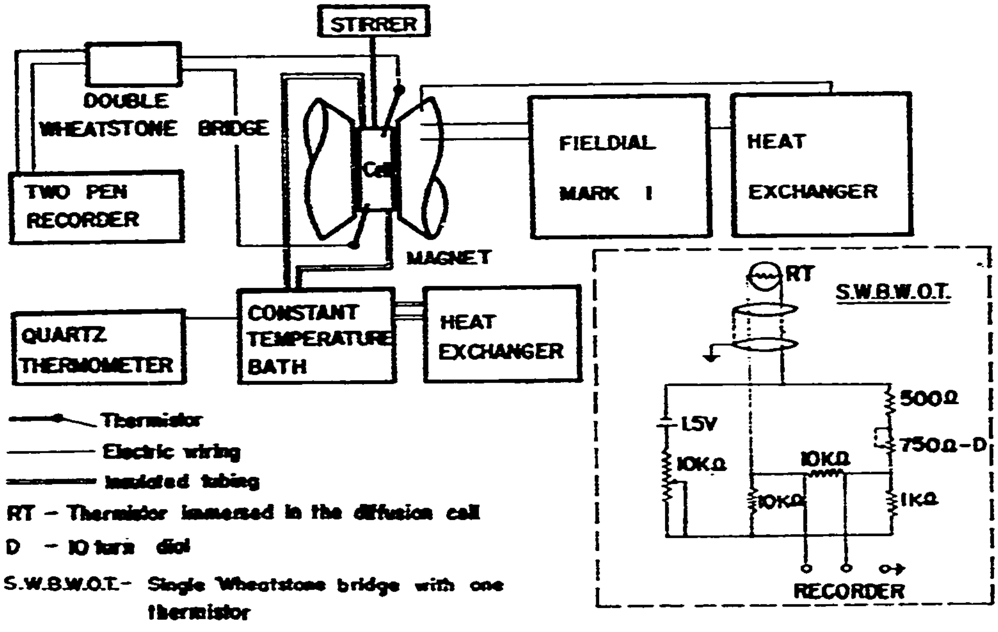

Fig. 1. Diagram of apparatus.

EXPERIMENTAL

The recent paper by Lielmezs et al.[6] describes in detail the apparatus and methods used for the determination of the integral diffusion coefficient of KCl in the KCl–H_2O solution. The same manipulation and techniques were also used in this work. The apparatus consists of two parts: the Varian Ass. 9-in. electromagnet system and the diffusion cell assembly. Figures 1 and 2 recapture the design showing the apparatus diagram (Fig. 1) and the diffusion cell (Fig. 2) equipped with steady-state water jacketing device (thermostatted at 25°C) and specially designed stirring system.

As previously[6] all used chemicals (ACS certified reagent grade) needed for NaCl–H_2O and titration (Mohr method) solution preparation were obtained from Fisher Scientific Co. Again[6] duplicate titration analysis were made and agreed better than to 0.1%. Since none of the runs exceeded 75 h duration, no correction for the change of cell constant[4] during any individual run was deemed to be necessary.

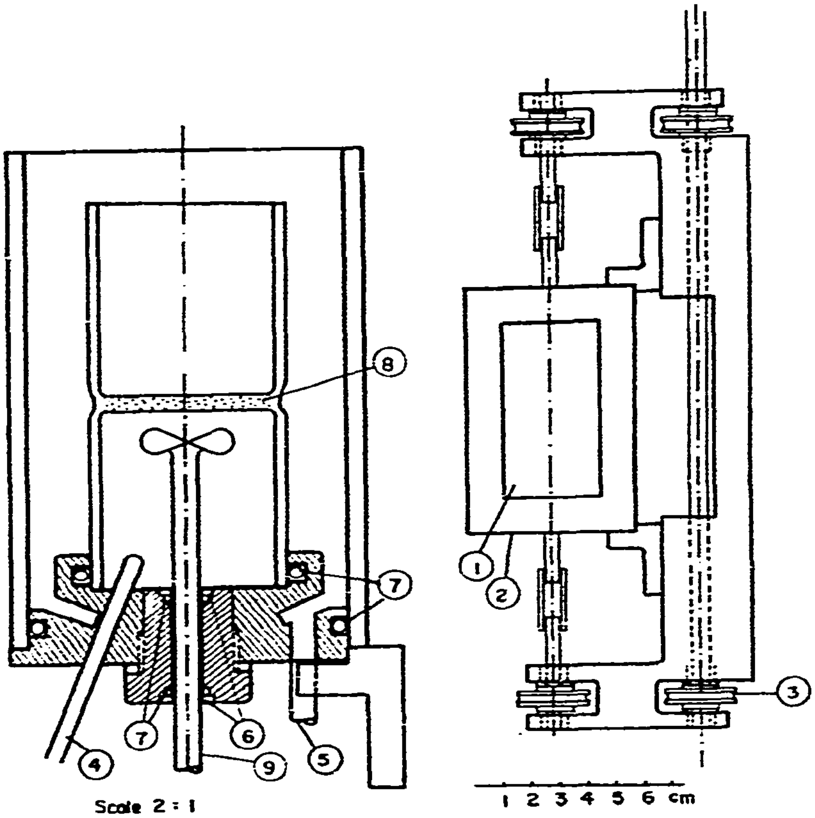

Fig. 2. Details of diffusion cell: (1) = cell (glass); (2) = cell cooling water jacket with cooling water circulated through constant temperature bath; (3) = drive pulley (brass); (4) = thermistor jacket (glass) placed inside the cell; (5) = inlet and outlet for water circulated through constant temperature bath; (6) = plastic retaining ring; (7) = rubber sealing O-ring; (8) = glass membrane; (9) = glass stirrer, rotating with 60 rpm. Stirrer and drive pulley are connected with tygon tubing.

METHOD OF CALCULATION

Following the calculation method of the previous work[6], the diaphragm-cell integral diffusion coefficient[1–5], $\bar{D}$, was obtained from the expression:

$$\bar{D} = \frac{1}{\beta\tau} \ln\left(\frac{C_1 - C_2}{C_3 - C_4}\right) \tag{1}$$

with:

$$C_1 = C_3 + (C_4 - C_2)\left[\frac{V_2 + \frac{1}{2}V_3}{V_1 + \frac{1}{2}V_3}\right]$$

where:

$\bar{D}$ = diaphragm cell integral diffusion coefficient at constant temperature
β = cell constant
τ = time of diffusion (sec)
$C_1 - C_2$ = initial concentration difference between the two cell compartments (Fig. 2)
$C_3 - C_4$ = final concentration difference between the two cell compartments
C_3 = concentration at the end of experiment in the bottom compartment (Fig. 2)
C_4 = concentration at the end of experiment in the top compartment (initially degassed distilled water[6])
V_1 = volume of the top compartment
V_2 = volume of the bottom compartment
V_3 = volume of the porous glass membrane.

On the other hand, to facilitate the calculation, the diaphragm-cell integral diffusion coefficient (eqn 1) can be related to $\bar{D}^0$, the Stokes integral diffusion coefficient[1,3,4,6]:

$$\bar{D} = \left\{\bar{D}^0(C'_m) - \frac{C''_m}{C'_m}\left[\bar{D}^0(C''_m)\right]\right\} \Big/ \left(1 - \frac{C''_m}{C'_m}\right) \tag{2}$$

with:

$$C'_m = \frac{C_1 + C_3}{2} \quad \text{and} \quad C''_m = \frac{C_2 + C_4}{2}$$

Following the calculation method of Stokes[3,4], it was possible to estimate the cell lattice constant value as $\beta = 0.2299$. Assuming that β is independent of the applied external magnetic field it was then possible for both cases, the applied transverse external magnetic field and the no field (neglecting the effect of the existing earth magnetic field) to calculate by means of eqn (1) the diaphragm-cell integral diffusion coefficient $\bar{D}_{25\,°C}$ at 25°C (corrected from the experimental arithmetic mean average run temperature $t_{°C}$ to 25°C by means of linear extrapolation formula*:

$$\bar{D}_{25\,°C} = \bar{D}_{°t} \pm K\Delta T_{°C}; \quad \text{where} \quad K = 0.040$$

Then, for each given concentration an arithmetic mean average diaphragm integral diffusion coefficient, $\bar{D}_{25\,^{\circ}\mathrm{C}}$ was established. Using this average diaphragm-cell integral diffusion coefficient, $\bar{D}_{25\,^{\circ}\mathrm{C}}$, it is possible for each of the given NaCl-concentrations to calculate from eqn (2) the corresponding Stokes integral diffusion coefficient, $\bar{D}_{25\,^{\circ}\mathrm{C}}$.

RESULTS

The results of this study are summarized in Table 1 and Fig. 3. Table 1 presents for all given concentrations of the NaCl–H_2O solution the arithmetic mean average integral diffusion coefficient $\bar{D}^{0}_{25\,^{\circ}\mathrm{C}}$ at no field conditions[**] and the corresponding diffusion coefficient $\bar{D}^{H}_{25\,^{\circ}\mathrm{C}}$, representing the diffusion under the influence of an externally applied magnetic field.

Figure 3 shows a plot of the arithmetic mean average integral diffusion coefficient, $\bar{D}^{0}_{25\,^{\circ}\mathrm{C}}$, at 25°C and at no field; and at field ($H = 5$, 8 and 10 kG) conditions plotted against the NaCl concentration in water.

At no field conditions (except for the presence of the existing weak earth magnetic field) our obtained integral diffusion coefficient values are compared with the available Stokes data[4]. As seen, these two sets of data compare very well indeed. In Fig. 3 we have also compared the NaCl-diffusion data (this work) with the available KCl-integral diffusion coefficient values[6] at no field and at the applied field ($H = 5$ kG) conditions. In our previous work[6], regarding the KCl diffusion in KCl–H_2O solution under the influence of an externally applied magnetic field, we presented evidence that the experimental errors inhereant in the titration process and in temperature fluctuations of the solution during the electrolyte diffusion do not influence the observed integral diffusion coefficient changes. In this work, presenting the NaCl diffusion data in NaCl–H_2O solution we found that titration and temperature measurement uncertainties introduced an error of at most ±0.45% of the integral diffusion coefficient value. It is felt, therefore, that the experimental errors could not influence meaningfully the observed NaCl-integral diffusion coefficient changes in NaCl–H_2O solution (Table 1, Fig. 3). As a matter of fact the presented data (Table 1, Fig. 3) reveal that for 0.05, 0.1, 0.2, 0.5 and 1.0 N NaCl–H_2O solutions, the NaCl-integral diffusion coeficient at fixed temperature ($t^{0} = 25\,^{\circ}\mathrm{C}$) seems to depend directly on the

---

[*] For the linear extrapolation formula: $\bar{D}_{25\,^{\circ}\mathrm{C}} = \bar{D}_{^{\circ}t} \pm K\Delta T_{^{\circ}\mathrm{C}}$, the following nomenclature is used: $\bar{D}_{25\,^{\circ}\mathrm{C}}$ = integral diffusion coefficient at 25°C, and given concentration may be taken from the literature; $\bar{D}_{^{\circ}t}$ = integral diffusion coefficient at the arithmetic mean average run temperature and given concentration; K = integral diffusion coefficient correction factor ($K = 0.040 \pm 0.001$). This K-value ($K = 0.040 \pm 0.001$) was obtained from given literature values for the used NaCl–H_2O solution concentration range[4,10] and the experimental all-run temperature variation from 24.7 to 25.3°C; $\Delta T_{^{\circ}\mathrm{C}}$ = run temperature difference, in °C, referring to the 25°C isotherm.

[**] Superscript "0" denotes the "No" applied magnetic field condition (except for the presence of the surrounding earth magnetic field) while superscript "*H*" represents the presence of an applied transverse external magnetic field in excess over that of the earth magnetic field. Subscript "25°C" means that these diffusion coefficients were calculated for the 25°C isotherm.

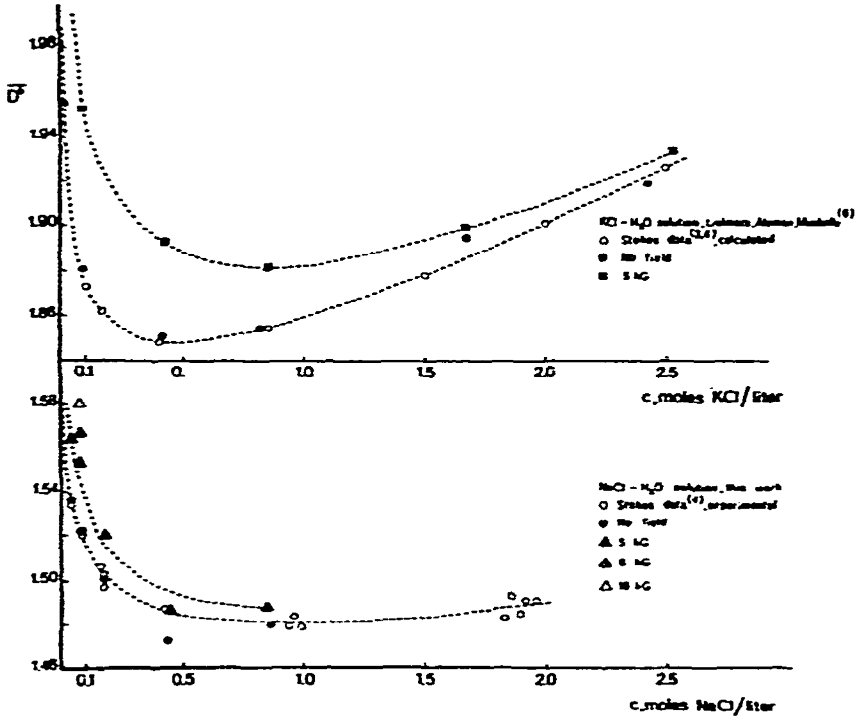

Fig. 3. Arithmetic mean integral diffusion coefficient and concentration plot at 25°C temperature. Compare these plotted data with Table 1.

applied transverse magnetic field strength ($H = 5$, 8 and 10 kG) and inversely on the amount of electrolyte present in the solution. The results show (Table 1, Fig. 3) that the NaCl-integral diffusion coefficient has higher values at low concentrations but appears to approach the magnetic saturation value past the 1.0 N NaCl mark of the solution. This behavior is consistent with the previously observed KCl-integral diffusion coefficient value changes (Fig. 3) at constant applied magnetic field strength ($H = 5$ kG). On the other hand the presented NaCl-integral diffusion coefficient values (Table 1, Fig. 3) indicate that additional to magnetic saturation in concentration at constant applied magnetic field strength, there should also be magnetic field saturation (diffusion coefficient value becomes constant) at fixed electrolyte concentration (for instance refer to integral diffusion coefficient value changes for fixed 0.1 N NaCl–H_2O solution at $H = 5$, 8 and 10 kG).

The exact reason or mechanism for the observed applied external magnetic field influence on the diffusion process of electrolyte solution through inert membrane cannot be decided with any certainty at this time. On one hand we are dealing with the free electrolyte diffusion in solution, but we also have to consider* various solute–

---

[*] It should be recalled that present results (this work and Ref. 6) indicate that an applied external magnetic field increases the electrolyte diffusion coefficient value. Whether the diffusion coefficient values will increase for all electrolyte–water systems, is subject matter of further study.

solvent–membrane surface interactions[3,4,11–21] as well as possible (presently neglected[8,9]) fundamental physical fluid property changes and the applied magnetic field possibly induced secondary flows which may result from magneto-electrophoresis, dielectrophoresis, magneto-mechanical and hydrodynamical and relaxation aspects[21].

It appears that if an idealized mechanism of the ion passage through membrane under the influence of an externally applied magnetic field could be established, then it will also be possible to suggest a molecular-kinetic theory[22] which would predict the diffusion coefficient changes caused by an externally applied magnetic field. In the absence of a plausible mechanism to describe the electrolyte diffusion through membrane under the influence of an applied external magnetic field, or even in the presence of the weak earth magnetic field, the use of the methods of thermodynamics of irreversible processes introduces another, perhaps even more general approach to the solution of this problem. Whether this would be achieved by generalizing (including the complexities of a restricted electrolyte passage through the membrane) the work of Lielmezs and Musbally[7] in which they introduced the Lorentz force as describing the interaction between the free drift velocity of an electrolyte in solution and the applied magnetic field; or again, extending the work of Ene[23] and Vives and Daoud[24] in which they analyze the electrically conducting fluid flow through porous media under the influence of an external magnetic field, remains the subject matter of further study. Nevertheless to properly interpret the proposed theoretical considerations, much more experimental information about the electrolyte diffusion processes through membranes under the influence of an applied external magnetic field over that of the earth field is needed.

ACKNOWLEDGEMENT

We gratefully acknowledge the financial assistance of the National Research Council of Canada.

REFERENCES

1 A. R. Gordon, *Ann. N. Y. Acad. Sci.*, 46 (1945) 285.
2 H. S. Harned and R. L. Nuttall, *J. Amer. Chem. Soc.*, 71 (1949) 1460.
3 R. H. Stokes, *J. Amer. Chem. Soc.*, 72 (1950) 763.
4 R. H. Stokes, *J. Amer. Chem. Soc.*, 72 (1950) 2243.
5 R. L. Robinson, Jr., W. C. Edmister and F. A. L. Dullien, *J. Phys. Chem.*, 69 (1965) 258.
6 J. Lielmezs, H. Aleman and G. M. Musbally, *Z. Phys. Chem.*, *Neue Folge*, (1974) in press.
7 J. Lielmezs and G. M. Musbally, *Electrochim. Acta*, 17 (1972) 1609.
8 J. Kubat and G. Soderlund, *Z. Phys. Chem.*, *Neue Folge*, 62 (1968) 180.
9 V. D. Evdokimov, *Russ. J. Phys. Chem.*, 43 (1969) 1521.
10 T. W. Chapman and J. Newman, *Technical Report*, *UCRL-17767*, Berkeley, Calif., 1968.
11 W. Holzapfel, *Z. Phys. Chem.*, *Neue Folge*, 59 (1968) 166.
12 D. G. Miller and M. J. Pikal, *J. Solution Chem.*, 1 (1972) 111.
13 A. J. Staverman, *J. Electrochem.*, 37 (1972) 233.
14 R. Haase, *Z. Phys. Chem.*, *Neue Folge*, 21 (1959) 244.
15 H. Vink, *Z. Phys. Chem.*, *Neue Folge*, 71 (1970) 51.

16 M. Manes, *J. Colloid Sci.*, 20 (1965) 990.
17 W. Dorst, A. J. Staverman and R. Caramazza, *Rec. Trav. Chim. Pays-Bas*, 83 (1964) 1329.
18 E. A. Mason, R. P. Wendt and E. H. Bresler, *J. Chem. Soc. Faraday Trans.*, 68 (1972) 1938.
19 H. S. Dunsmore, S. K. Jalota and R. Paterson, *J. Chem. Soc., A*, (1969) 1061.
20 J. Hogg and E. J. Williams, *Proc. Roy. Soc. Edinburgh, Sect. A*, 70 (1971/72) 197.
21 R. A. Robinson and R. H. Stokes, *Electrolyte Solutions*, Butterworth, London, 1959.
22 D. Laforque-Kantzer, *Eelectrochim. Acta*, 10 (1965) 585.
23 H. I. Ene, *Proc. Symp. Fundam. Transport Phenomena Porous Media, Haifa, Israel, 1969.*
24 C. Vives and M. B. Daoud, *C.R. Acad. Sci., Paris*, 267 (1968) 958.