Thermochimica Acta, 15 (1976) 63-69 © Elsevier Scientific Publishing Company, Amsterdam – Printed in Belgium

EXTERNAL TRANSVERSE MAGNETIC FIELD EFFECT ON ELECTROLYTE DIFFUSION IN CsCl-H₂O SOLUTION

J. LIELMEZS AND H. ALEMAN

Chemical Engineering Department, The University of British Columbia, Vancouver, B.C. (Canada) (Received 27 August 1975)

ABSTRACT

Experiments using modified fritted glass diaphragm-cell method show that an externally applied magnetic field of 5 kG strength influences the integral diffusion coefficient of CsCl (measured at 25°C and at ambient pressure) in 0.04; 0.08; 0.17, 0.4 and 0.8 N CsCl-H₂O solution.

INTRODUCTION

By means of modified fritted glass diaphragm cell method¹⁻⁹, it has been found that an applied transverse external magnetic field of 5 kG influences the integral diffusion coefficient values of CsCl in 0.04; 0.09; 0.17; 0.4 and 0.8 N CsCl-H₂O solution at 25°C and at the ambient pressure (Table 1, Figs. 1-3).

The presented integral diffusion coefficient values (Table 1, Figs. 1–3) for CsCl were obtained using the standard dilute electrolyte solution diffusion coefficient calculation methods, for both the no applied field¹⁻⁵ and the externally applied magnetic field states⁶⁻¹¹. As in the case of KCl-, NaCl-, HCl- and LiCl-integral diffusion coefficient calculation⁶⁻⁹ when the electrolyte solution is subjected to an applied magnetic field, it was assumed that the applied transverse magnetic field does not in any way influence or alter the physico-chemical properties (density, viscosity and electric resistance) of water* and the used salt¹²⁻¹⁴. The obtained experimental results (Table 1, Figs. 1–3) strengthen the theoretical (Lielmezs and Musbally¹⁰ and Dumarque, Humeau and Penot¹¹) observations and the recent findings of Lielmezs and his coworkers⁶⁻⁹ that an externally applied magnetic field influences the diffusion process of electrolytes in solution.

²Lielmezs, Aleman and Fish¹⁵ have shown that transversally applied magnetic field of 5 kG strength at 25°C increases the distilled water viscosity by 0.056%. In this work, however, this observed viscosity change effect was neglected, first, being too small in magnitude; and secondly, for the given behavior of electrolyte diffusion in solution under the influence of the applied magnetic field; this change effectively can be considered as constant background.

TABLE I

SUMMARY OF RESULTS^a

Arithmetic mean acerage [®] conc. Ĉ ⁱⁱ		Arithmetic mean acerage ^b integral diffusion coefficient $\langle D_{H}^{2} \rangle^{4}$, with $H = 5 \ kg$		Arithmetic mean average ^b integral diffusion coefficient <d*>^c, no field</d*>		Arithmetic mean acerage [®] fractional integral diffusion coefficient	
Č [™] , mol CsCl per liter solution	Standard ^t detiation, σ	$\frac{\langle \bar{D}_{B}^{\circ} \rangle}{cm^{2} s^{-1} \times 10^{5}}$	Standard ¹ deriation, G	$\overline{\langle \vec{D}^{\circ} \rangle}, \\ cm^{2} s^{-1} \times 10^{5}$	Standard ^t deriation, o	$\frac{\langle \vec{D}_{B}^{\bullet} \rangle - \langle \vec{D}^{\bullet} \rangle}{\langle \vec{D}^{\bullet} \rangle} \times 100$	
0.040525	0.001547	1.9295	0.0110	1.9318	0.0096	-0.119	
0.0829	0.0017	1.9054	0.0099	1.9115	0.0063	-0.318	
0.1711	0.0035	1.8857	0.0021	1.8959	0.0084	-0.538	
0.4017		1.8511		1.8574		-0.339	
0.8136	0.0192	1.8588	0.0110	1.8607	0.0109	-0.104	

^a All results listed are at 25 ± 0.06 °C temperature. ^b Arithmetic mean average obtained for all measurements in any test run series (applied field or no applied field) for the given \tilde{C}_{m} of CsCl in H₂O.

^c For definition of \vec{C}_{m} see refs. 1-9. Then $\vec{C}_{m} = \frac{1}{N} \sum_{i}^{N} C_{m_{i}}$; where $i = 1 \dots N$ for the specific test run

series. ^d Subscript "H" refers to the applied transverse magnetic field condition, this work. ^c The no applied field condition means that these measurements were performed in the presence of the ambient

$$\frac{\sum_{i=1}^{N}(X_{i}-\hat{X})^{2}}{\sum_{i=1}^{N}(X_{i}-\hat{X})^{2}}$$

earth magnetic field. ^r Standard deviation, $\sigma = \frac{i}{N-1}$ where X_i is the value of the *i*th measure-

ment; \hat{X} is the arithmetic mean average for N measurements and N is the total number of diffusion cells for the chosen concentration in the given test run series.

EXPERIMENTAL

Lielmezs et al.⁶ describe in detail the apparatus and methods used for the determination of the integral diffusion coefficient of KCl in the KCl-H₂O solution. Similar techniques were also used by Lielmezs and Aleman⁷⁻⁹ in the determination of NaCl-, HCl- and LiCl-integral diffusion coefficient values for NaCl-, HCl- and LiCl-H₂O solutions.

Again, in this work we have used the same apparatus set-up: the Varian Associates 9-in. electromagnet system and the diffusion cell assembly (consult ref. 6). On the other hand, following the HCl- and LiCi-H₂O solution diffusion coefficient measurement methods^{8.9}, for this work we used the dual-diffusion cell measuring system; that is, we at the same time performed two diffusion coefficient measurements: one diffusion cell was placed in the applied magnetic field, while the other was kept at the ambient earth field. Upon completing the measurement, the order of cells (field-no field) was alternated. This arrangement for the same thermodynamic conditions (ambient temperature, pressure and the same initial electrolyte concen-

64

tration in the water) permitted to consider the salt diffusion process as a difference between two possibly similar, simultaneously occurring diffusion processes observed at two separate, distinct external magnetic states: one found at the applied transverse external magnetic field (first diffusion cell); the second subject to the ambient earth magnetic field (second diffusion cell, the no-field condition).

For both of the simultaneously operated diffusion cells (cell I and cell II), the $CsCl-H_2O$ solutions were prepared, the cell compartments filled, the solutions removed at the end of the experiment and final CsCl concentrations determined using methods and techniques as described previously⁶⁻⁹. The diffusion cell compartment and diaphragm pore volumes were determined following previously established procedures⁶⁻⁹. Table 2 presents the determined and used physical constants of both diaphragm diffusion cells.

TABLE 2

PHYSICAL PROPERTIES OF THE DIAPHRAGM CELLS

Cell	V ₁ (cm ³)	$V_2 (cm^3)$	$V_3 (cm^3)$	β	
I	30.11	29.80	0.407	0.2248	
н	26.65	27.20	0.375	0.2325	

RESULTS AND DISCUSSION

The diaphragm cell integral diffusion coefficient¹⁻⁵, \overline{D} , for CsCl electrolyte diffusion in water, was obtained following the previously used calculation methods⁶⁻⁹. The results of this work are summarized in Tables 1. 2 and Figs. 1-3.

Table 1 gives for all considered arithmetic mean average $\bar{C}'_{\rm m} \left(\bar{C}'_{\rm m} = \frac{1}{N} \sum_{i}^{N} C'_{\rm m_{i}}; \right)$

where i = 1...N measurements) concentrations of CsCl-H₂O solution; the arithmetic

mean average diffusion coefficient $\langle \bar{D}_{H}^{\circ} \rangle$ and $\langle \bar{D}^{\circ} \rangle$, with field and with no applied field conditions^{*}, and the corresponding arithmetic mean average fractional integral diffusion coefficient, $(\langle \bar{D}_{H}^{\circ} \rangle - \langle \bar{D}^{\circ} \rangle)/\langle \bar{D}^{\circ} \rangle \times 100$, at 25 °C, values.

Figure 1 shows a comparative plot of the arithmetic means average fractional integral diffusion coefficient at 25 °C plotted against the CsCl concentration, \overline{C}'_{m} , in water. Figure 2 on the other hand represents a comparison, when plotted against the

^{*}In expressions $\langle \tilde{D}_{B}^{\circ} \rangle$, $\langle \tilde{D}^{\circ} \rangle$ and $(\langle \tilde{D}_{B}^{\circ} \rangle - \langle \tilde{D}^{\circ} \rangle)/\langle \tilde{D}^{\circ} \rangle \times 100$; superscript "0" denotes the no applied magnetic field (except for the presence of the earth magnetic field) condition; while subscript "H" represents the transversally applied magnetic field of H = 5 kG state. Hence, the expression $\langle \tilde{D}_{B}^{\circ} \rangle$ could be read: the arithmetic mean average integral diffusion coefficient at applied magnetic field of H = 5 kG, taken with respect to the earth magnetic field at the standard magnetic reference state.



Fig. 1. The arithmetic mean average fractional integral diffusion coefficient and concentration plot at 25 ± 0.06 °C for CsCl-H₂O solution.



Fig. 2. The arithmetic mean average integral diffusion coefficient and concentration plot at 25 ± 0.06 °C for CsCl-H₂O solution. Literature data for CsCl-diffusion coefficient values may be found in refs. 28 and 29. Solid line represents no-field; dashed line represents applied magnetic field conditions.



Fig. 3. Arithmetic mean fractional integral diffusion coefficient and concentration plot for CsCl-H₂O solution at 25 ± 0.06 °C in semilogarithmic coordinates.

concentration \bar{C}'_m , between the two calculated arithmetic mean average integral diffusion coefficients; one obtained the influence of an applied magnetic field; the other, without the presence of an applied magnetic field (i.e., the ambient earth magnetic field) for the CsCl-electrolyte solution in water. Figure 3 represents the data as found in Fig. 1; only now represented in semi-logarithmic fashion. It appears that for smaller concentrations there exists a straight line relation.

In our previous work⁶⁻⁹ we discussed the effect of titration and temperature fluctuations during the run on the calculated integral diffusion coefficient (applied and the no field conditions) in great detail. In this work, as in the previous work⁶⁻⁹ we find that the experimental errors inherent in the titration process and in temperature variations around the 25°C isotherm do not affect meaningfully the observed fractional integral diffusion coefficient values (Table 1, Figs. 1-3).

Since in this work we have used the dual diffusion cell method (compare with refs. 8 and 9), the diffusion process behavior has been observed and evaluated nearly at the same error level using the arithmetic mean average values for the involved parameter, $\langle \bar{D}_{H}^{\circ} \rangle$; $\langle \bar{D}^{\circ} \rangle$ and \bar{C}'_{m} . This has assured us that the observed fractional integral diffusion coefficient values (Table 1, Figs. 1-3) are indeed due to the applied field, the only state parameter which has been kept different for each cell during the dual diffusion cell experiment.

Results (Table 1, Figs. 1-3) show that for 0.04; 0.083; 0.17; 0.4; 0.8 N; CsCl-H₂O solutions the arithmetic mean average integral diffusion coefficient at constant

temperature (in this work 25 ± 0.06 °C) and at constant, externally applied transverse to the sait diffusion path magnetic field of 5 kG; decreases as the salt concentration is increased. This decrease reaches the largest value around a concentration of 0.2 mol CsCl per litre; then steadily becomes smaller as higher CsCl concentrations are approached. Previous work⁶⁻⁸ shows that when the KCl-, NaCl- and HCl-H₂O solutions were subjected to an externally applied magnetic field, the integral diffusion coefficient did increase; although similarly with CsCl behavior, these effects vanish at higher salt concentrations. On the other hand, experiments with LiCl-H₂O solution did show⁹, that similarly to CsCl-electrolyte behavior (this work); the LiCl-electrolyte integral diffusion coefficient value under the influence of an external magnetic field of 5 kG strength, did decrease as the salt concentration in water was increased. For LiCl this decrease reached the largest value around a concentration of 0.8 mol LiCl per litre; then steadily vanished as higher LiCl concentrations in water were approached.

The exact cause for the observed applied external magnetic field influence on the behavior of the diffusion process of electrolyte solution through inert diaphragm (Figs. 1-3) cannot be decided with certainty at this time⁶⁻⁹. Most probably the reason for this electrolyte diffusion process behavior in water may be found in various solute-solvent-diaphragm interaction aspects¹⁶⁻²⁵ and the possible fluid structural and property changes^{16,25-27} associated with the magnetic state change of electrolytewater solution. Indeed, if an idealized mechanism of ion passage through perous obstruction (diaphragm, membrane, plug) under the influence of an applied magnetic field in excess of the ambient earth magnetic field could be established; then it may be possible to propose^{26,27} a molecular or kinetic theory to predict the electrolyte diffusion coefficient changes caused by this field. Lacking such a model, the use of the methods of thermodynamics of irreversible processes may present another even more general approach to this problem. Whether this could be achieved by generalizing the work of Lielmezs and Musbally¹⁰ in which they introduced the Lorentz force as describing the interaction between the drift velocity of an electrolyte in solution and the applied magnetic field; or the more complex work of Dumarque et al.¹¹, is the subject matter of further study.

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, Electrochim. Acta, 17 (1972) 1609.

- 7 J. Lielmezs and H. Aleman, Thermochim. Acta, 9 (1974) 247.
- 8 (a) J. Lielmezs, Tech. Apskats, 74 (1975) 2.
- (b) J. Lielmezs and H. Aleman, Electrochim. Acta, (1975) In press.
- 9 J. Lielmezs and H. Aleman, unpublished data, 1975.
- 10 J. Lielmezs and G. M. Musbally, Electrochim. Acta, 17 (1972) 1609.
- 11 P. Dumarque, P. Humeau and F. Penot, Electrochim. Acta, 18 (1973) 447.
- 12 J. Kubat and G. Sunderlund, Z. Phys. Chem., Neue Folge, 62 (1968) 180.
- 13 V. B. Evdokimov, Russ. J. Phys. Chem., 43 (1969) 1521.
- 14 L. V. Akopyan and V. B. Evdokimov, Russ. J. Phys. Chem., 47 (1973) 1041.
- 15 J. Lielmezs, H. Aleman and L. Fish, Z. Phys. Chem., Neue Folge, (1975) in press.
- 16 J. Richter, Ph.D. Thesis, Rheinisch-Westfaelisch Technische Hochschule, Aachen. Germany, 1967.
- 17 W. Holzapfel, Z. Phys. Chem., Neue Folge, 59 (1968) 166.
- 18 D. G. Miller and M. J. Pikal, J. Solution Chem., 3 (1972) 111.
- 19 A. J. Staverman, J. Electrochem., 37 (1972) 233.
- 20 R. Haase, Z. Phys. Chem. Neue Folge, 21 (1959) 244.
- 21 H. Vink, Z. Phys. Chem., Neue Folge, 71 (1970) 51.
- 22 E. A. Mason, R. P. Wendt and H. Bresler, J. Chem. Soc. Trans., 68 (1972) 1938.
- 23 H. S. Dunsmore, S. K. Jalota and R. Paterson, J. Chem. Soc. A, (1969) 1061.
- 24 R. A. Robinson and R. H. Stokes, *Electrolyte Solutions*, Butterworth, London, 1959.
- 25 W. J. Hamer (Ed.), in The Structure of Electrolyte Solutions, Wiley, New York, 1959.
- 26 D. Laforgue-Kantzer, A. Laforgue and Tran Cong Khank, Electrochim. Acta, 17 (1972) 151.
- 27 D. Laforgue-Kantzer, Electrochim. Acta, 10 (1965) 585.
- 28 T. W. Chapman and J. Newman, Lawrence Radiation Laboratory, University of California Report, UC-4, 1968.
- 29 S. K. Jalota and R. Paterson, J. Chem. Soc. Faraday Trans. 1, 69 (1973) 1510.