MUTUAL DIFFUSION COEFFICIENTS OF AQUEOUS LITHIUM CHLORIDE IN SOLUTIONS AT 25 ºC

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Abstract

Mutual differential diffusion coefficients of lithium chloride in moderately concentrated (0.1 to 1.0 mol dm^{-3}) aqueous solutions were measured at 25 ºC using an improved open-ended conductimetric capillary cell method. A critical examination of the response of the technique to such improvements is done on the basis of the analysis of different experimental parameters as well as from the reproducibility of the diffusion coefficients. The imprecision of the diffusion coefficients, generally < 1 %, is not affected by the improvements. The reported LiCl mutual diffusion coefficients agree with those obtained previously by Gouy interferometry, and Rayleigh interferometry within lower deviations than 2-3 %. Agar's semi-empirical equation for the concentration dependence of electrolyte diffusion coefficients is in good agreement with the experimental data.

Key words: Diffusion / Electrolyte / Aqueous Solutions / Transport Properties

Introduction

Electrolyte diffusion coefficients are necessary for practical and theoretical studies, such as the degradation of polymeric structures [1,2] and the study of the structure of aqueous electrolyte solutions [3,4]. Although some reliable techniques are available [5-8] for the determination of diffusion coefficients in solutions of electrolytes, the development of different techniques [9,10] is useful to test the accuracy of the data [11, 12]. The open-ended capillary cell [13, 14] has been successfully used for the determination of diffusion coefficients, D, of non-associated electrolytes [12,15,16] and for studying the diffusion of electrolytes in polymeric matrices [17].

This paper presents experimental results of mutual differential diffusion coefficients of LiCl (0.1 M to 1.0 M) measured with the open-ended capillary method.

A discussion of the experimental data is based on Agar's equation. This semi-empirical equation has been used to interpret the mutual diffusion coefficients of non-associated symmetrical

(1:1) electrolytes in concentrated aqueous solutions, taking into account different solution features such as the viscosity and the thermodynamic deviations from ideality.

Experimental

The apparatus is essentially the same as that described elsewhere [13,14]. However, to measure diffusion coefficients of aqueous electrolyte solutions up, at least, 2 M of concentration, some developments were carried out. Once the open-ended capillary method is based in measurements with a RLC system [18], the developments consisted basically in increasing the capacitance of one of the variable capacity boxes, adding capacitors according to the concentration of the electrolyte solution.

The cell consists of two vertical tubes, each closed at one end by a platinum electrode and positioned in the same vertical axis. The open ends are approximately 10 mm apart. A third platinum electrode is in the middle of the other two. The capillary tubes are 23.81 mm long. The upper and lower capillaries, initially filled with solutions of concentration 0.75 c and 1.25 c, respectively, are surrounded with solution of concentration c. Convection currents and the temperature are carefully controlled (± 0.01 °C). Solutions of 1.25 c and 0.75 c are prepared independently using distilled and degassed water ($\kappa < 1$ μS cm^{-1}), each in a 2 L volumetric flask. The bulk solution of concentration c is prepared by mixing 1 L of the top solution with 1 L of the bottom solution, accurately measured. LiCl (Riedel-de Haën, *pro analysis*) previously dried at 180 °C until constant weight was used.

Diffusion is followed by reading the electrical resistance ratio between the top and the bottom electrodes relative to the central electrode, every 5 minutes for about 7 hours, 1000 minutes after starting each run. The diffusion coefficient is evaluated using a computerized linear least-squares procedure fit equations to data.

Results and Discussion

Differential mutual diffusion coefficients of aqueous LiCl measured from 0.1 to 1 mol dm^{-3}, at 25 °C are shown in Table 1. The number of experimental readings, N, the standard deviation s and TR$_\infty$=10^5/(1 + w$_\infty$), where w$_\infty$ is the electrical resistance ratio w with the capillaries filled with bulk solution (conditions of infinite time), are also shown. The constancy of TR$_\infty$ from replicate experiments is a good indication of the high reproducibility in the experimental procedure. The fact that they are not far from 5 000 shows good symmetry in the capillary set up. The average diffusion coefficients, D_{exp}, are calculated from, at least, three independent experiments.

Table 1 - Mutual diffusion coefficients, D_{exp}, of LiCl solutions at 25 °C.

c / (mol dm^{-3})	N	TR$_\infty$	$D_{i,exp}$ / (10^{-9} m^2 s^{-1})	D_{exp} (s) / (10^{-9} m^2 s^{-1})
0.1014	55	5035.4	1.297	
	55	5034.0	1.296	1.294 (0.005)
	55	5034.0	1.288	
0.2000	57	5034.2	1.289	
	56	5033.9	1.276	1.288 (0.012)
	56	5033.0	1.300	
0.2976	56	5035.1	1.293	
	54	5035.2	1.294	1.285 (0.015)
	54	5036.1	1.268	
0.4963	55	5045.2	1.312	
	56	5042.5	1.313	1.310 (0.004)
	55	5045.5	1.305	
0.6971	54	5048.5	1.284	
	48	5047.5	1.350	
	52	5045.4	1.303	1.312 (0.027)
	56	5028.6	1.330	
	56	5039.0	1.292	
0.9961	54	5050.7	1.335	
	54	5052.7	1.312	1.322 (0.012)
	54	5052.7	1.319	

N is the number of experimental readings recorded in each experiment; TR$_\infty$ is defined as 10^4/(1+w), where w=R'/R'' is the resistance ratio of the diffusion capillaries at infinite time that is, in isoconcentrational conditions; D is the average of the measured differential diffusion coefficients D_i; s is the standard deviation.

The alterations carried out on the equipment, especially the considerable increase of capacitance in the electrical bridge [18], relative to the situation of concentrations up to 0.1 M, do not significantly change the precision of this measuring technique, as we may conclude from the low standard deviation shown in Table 1.

With the exception of one concentration, the standard deviations are ≤ 1 %, in a good agreement with the previous measurements in the concentration range 0.001 to 0.1 mol dm^{-3} (see for example [19]) before the above alterations. Even so, the electrical noise, as observed in the oscilloscope image, is greatly increased, probably as a consequence of the addition of new capacitance boxes. On the other hand, the TR values shown in Table 1 are very close to 5 000, which means that all experiments were carried out under very good experimental conditions. All these data indicate acceptable reliability of the measuring system.

There is a good agreement between our experimental diffusion coefficients and those published by other authors using different techniques [20,21], Fig. 1, with a maximum deviation of 3-2 %.
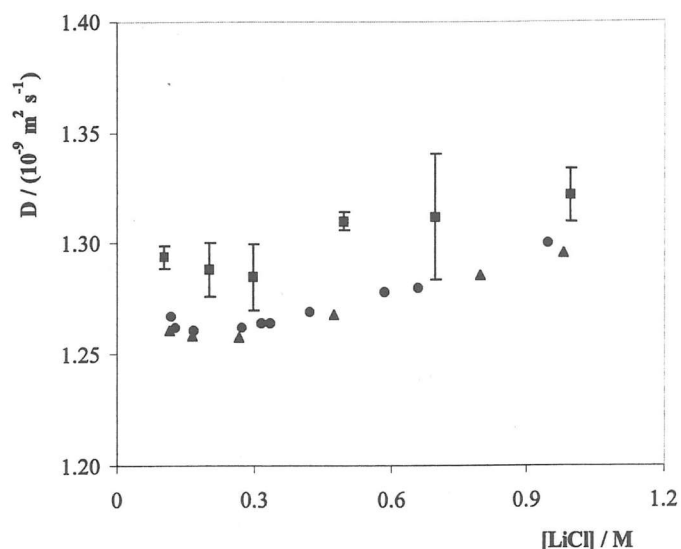
Figure 1 – Mutual diffusion coefficients of aqueous LiCl at 25 °C measured by: the capillary conductimetric method (■), Gouy interferometry (▲) (Vitagliano, 1960), and Rayleigh interferometry (●) (Rard & Miller, 1983).

In a recent paper [11], mutual diffusion coefficients of symmetric 1:1 non-associated salts were explained on basis of different contributions: resistance coefficient [22] and solution viscosity [23], but no direct correlation between these two factors was found. However, Agar [24,25] has developed the semi-empirical equation

$$D = (D^0 + \Delta_1 + \Delta_2) (1 + m \, d\ln \gamma_\pm / d \, m) (1 - 0.018 \, n \, m)$$
$$[1 + 0.018 \, m \, ((\nu \, D^*_w / D^0) - n)] \, \eta_0 / \eta \qquad (1)$$

to model diffusion in electrolyte solutions, taking into account thermodynamic and viscosity factors, $(1 + m \, d\ln \gamma_\pm / d \, m)$ and η / η_0, respectively, [as well as the electrophoretic terms Δ_1 and Δ_2]. Eq. (1) has been used to describe the variation of diffusion coefficients, D, with molality, m, of symmetrical non-associated electrolytes [10,14,18]. The application of Agar's equation to LiCl solutions, previously done by [24], is applied using more recent experimental values of some parameters, as for example the self-diffusion coefficient of water, and a comparison with mutual diffusion coefficient is carried out. The computation of diffusion coefficients using Eq. (1) was done using n = 2.8 for the hydration number [24], and D^*_w = 2.299 x 10^{-9} m^2 s^{-1} for the self-diffusion coefficient

of water [26]. Published densities [27] were used to convert molalities, m, to molarities, c. Relative viscosities, η / η_0, were taken from [27-29]. The Nernst limiting diffusion coefficient, D^0, was computed from $D^0(LiCl) = 2 \, D^0(Li^+) \, D^0(Cl^-) / [D^0(Li^+) + D^0(Cl^-)] = 1.367$ x 10^{-9} m^2 s^{-1}. The limiting ionic diffusion coefficients $D^0(Li^+) = 1.030$ x 10^{-9} m^2 s^{-1} and $D^0(Cl^-) = 2.033$ x 10^{-9} m^2 s^{-1} were calculated from limiting ionic conductivities [23]. The thermodynamic factor, TF = $(1 + m \, d\ln \gamma_\pm / d \, m)$, was directly computed using the experimental activity coefficients reported by [30], and the D_{OF} (Eq. 2) was calculated from Onsager-Fuoss' equation [31], according to a procedure described elsewhere [3], Table 2.

$$D_{OF} = (D^0 + \Delta_1 + \Delta_2) (1 + m \, d\ln \gamma_\pm / dm) \qquad (2)$$

Table 2 – Diffusion coefficients, D (eq. 1), thermodynamic factor, TF, and D_{OF}, eq. (2), at 25 °C for LiCl concentrations.

c / (mol dm^{-3})	TF	D_{OF} / (10^{-9} m^2 s^{-1})	D / (10^{-9} m^2 s^{-1})
0.0500	0.9376	1.2872	1.2744
0.0899	0.9373	1.2892	1.2659
0.1000	0.9382	1.2902	1.2648
0.1254	0.9414	1.2964	1.2648
0.1784	0.9509	1.3098	1.2657
0.2000	0.9555	1.3161	1.2661
0.2126	0.9583	1.3202	1.2670
0.2235	0.9607	1.3233	1.2679
0.3538	0.9929	1.3669	1.2777
0.4106	1.0079	1.3876	1.2838
0.4440	1.0169	1.4000	1.2894
0.5000	1.0321	1.4217	1.2991
0.7300	1.0959	1.5078	1.3204
0.9031	1.1446	1.5722	1.3353
1.0000	1.1720	1.6085	1.3404

Figure 2 compares diffusion coefficients computed from Agar's equation, with the present experimental data. The agreement seems to be good (> 98 %). Therefore Agar's equation may be used to simulate diffusion coefficients of non-associated electrolytes up to 1.0 mol dm^{-3}.
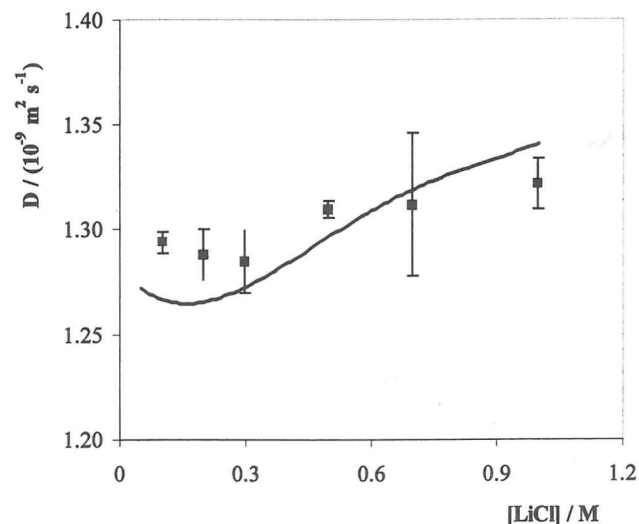
Figure 2 - Comparison of the measured diffusion coefficients (■) and those computed using Agar's equation (-) for aqueous LiCl at 25 °C.

Final Comments

Mutual diffusion coefficients of aqueous LiCl measured with an improved technique, from 0.1 mol dm^{-3} to 1.0 mol dm^{-3}, are in good agreement with the experimental data reported in the literature, using different reliable techniques, and the Agar's equation shows to be valid to simulate diffusion coefficients of LiCl solutions in the concentration range studied. We may point out that the diffusion coefficients of LiCl, in the concentration range 0.3 M to 1.0 M, computed from Agar's equation, show a better agreement with our experimental diffusion coefficients, than those obtained by other techniques.

Acknowledgements

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