

## Measurements of Tracer Diffusion Coefficients of Lithium Ions, Chloride Ions and Water in Aqueous Lithium Chloride Solutions

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Tracer diffusion coefficients of lithium ions, chloride ions and water in aqueous lithium chloride solutions over a wide range of concentrations at 298.2 K have been determined by means of the diaphragm-cell method using  $^6\text{Li}$ ,  $^{36}\text{Cl}$  and  $^2\text{H}$  as tracers. The experimental value of the tracer diffusion coefficient of lithium ion was equal to that of the chloride ion at  $18.6 \text{ mol kg}^{-1}$ , although at lower concentrations the values for the lithium ion were smaller than those of the chloride ion. This fact may indicate that the direct interaction between lithium and chloride ions is significant at  $18.6 \text{ mol kg}^{-1}$ .

It is of considerable interest to study the transport properties of highly concentrated aqueous electrolyte solutions where there are fewer water molecules than are needed to satisfy the hydration requirements of cations and anions. However, the experimental data for tracer diffusion coefficients of all constituent species in such solutions are rarely found in the literature.

The aim of this paper is to report tracer diffusion coefficients of two constituent ions and water in aqueous lithium chloride solutions over a wide range of concentrations up to near saturation. The data obtained are compared with published values<sup>1–3</sup> and discussed in relation to the structure of the solutions deduced from X-ray<sup>4</sup> and neutron diffraction studies.<sup>5–7</sup>

### Experimental

Measurements were made with a conventional diaphragm cell which incorporated a sintered glass disc. Details of the experimental procedure were as described in a previous paper.<sup>8</sup> The cell was calibrated by diffusion of  $0.5 \text{ mol dm}^{-3}$  potassium chloride solution into pure water at 298.2 K together with Stokes' data for the system.<sup>9</sup> The concentrations of potassium chloride were determined by weighing the residue obtained from evaporation of experimental solutions to dryness.

The enriched  $^6\text{LiCl}$  and  $^7\text{LiCl}$  were prepared from  $^6\text{LiCO}_3$  and  $^7\text{LiCO}_3$ , respectively (Tomiya Pure Chemical Institute Ltd, Japan) and aqueous hydrochloric acid.  $^{36}\text{Cl}$  was obtained from The Radiochemical Centre, Amersham. Deuterium oxide (99.75 atom % deuterium) was obtained from Junsei Pure Chemicals, Japan and diluted to 2 atom % with triply distilled normal water.

The isotope ratios of  $^6\text{Li}/^7\text{Li}$  were determined with the aid of a Varian MAT CH-5 mass spectrometer. The chloride ion in the sample was ion-exchanged for iodide before the measurements were taken. The radioactivity of  $^{36}\text{Cl}$  was counted by means of a standard liquid scintillation technique using ACSII (Amersham, U.S.A.) as a scintillant. The isotope ratios of  $^2\text{H}/^1\text{H}$  were determined densitometrically by means of a DMA60

**Table 1.** Tracer diffusion coefficients of lithium ion in aqueous 0.1 mol kg<sup>-1</sup> lithium chloride solutions at various initial concentrations of <sup>6</sup>Li in lower (l) and upper (u) compartments of the cell

[ <sup>6</sup> Li] <sub>l</sub> (atom %)	[ <sup>6</sup> Li] <sub>u</sub> (atom %)	$D_{Li}$ /10 <sup>-9</sup> m <sup>2</sup> s <sup>-1</sup>
95.44	7.57	1.022
81.80	7.57	1.016
24.00	7.57	1.014
1.81	66.81	1.025
1.81	95.42	1.020

Anton Paar density meter. The water in the sample was separated from LiCl by distilling the solution before the density measurements. To avoid isotope fractionation during the distillation, water in the solution was first separated from LiCl by distillation to dryness, then the water collected was distilled under nitrogen.

## Results and Discussion

The tracer diffusion coefficient of lithium ions in aqueous 0.1 mol kg<sup>-1</sup> lithium chloride at 298.2 K has been measured by varying the initial isotope ratios of <sup>6</sup>Li/<sup>7</sup>Li in the upper and lower compartments of the diaphragm cell and is given in table 1. Each value listed is the average of 2 to 4 measurements and the experimental error is estimated to be within 0.5%. The agreement of observed values within the limits of experimental error indicates that the isotope effect is not significant. This observation is supported by the result of Kunze and Fuoss,<sup>10</sup> who have found that at infinite dilution in water the ratio of self-diffusion coefficients of <sup>6</sup>Li<sup>+</sup> and <sup>7</sup>Li<sup>+</sup> is 1.0035, which is estimated from the limiting equivalent conductance of each isotope by means of the Nernst equation.<sup>11</sup>

Tracer diffusion coefficients for all constituent species in aqueous solutions of lithium chloride at 298.2 K over a wide range of concentrations are given in table 2. The initial isotope ratios of lower and upper compartments of the cell were 95.44 and 7.57 atom % of <sup>6</sup>Li, respectively, for the first five cases of the measurements of tracer diffusion coefficients of lithium ions. The values obtained at 13.8 and 18.6 mol kg<sup>-1</sup> are averages of the values obtained using the solutions containing several isotope ratios.

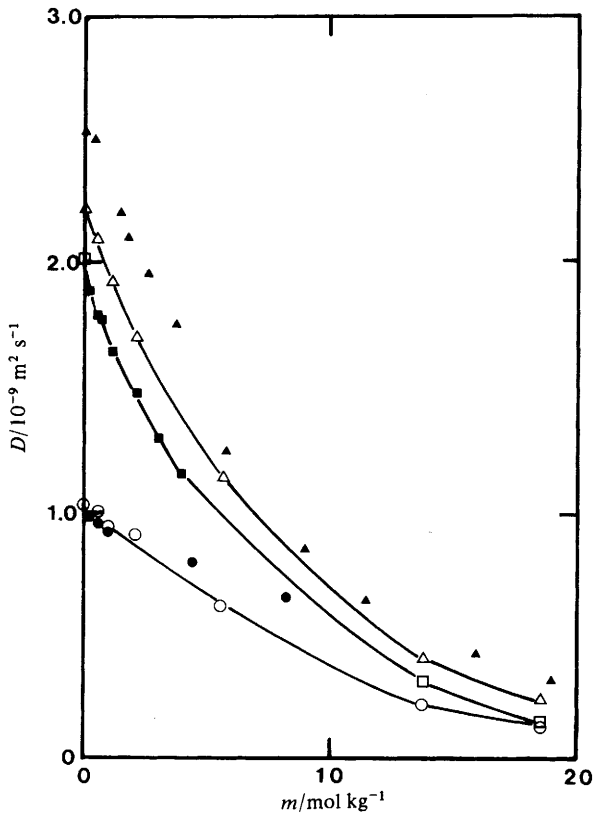
The measurements of tracer diffusion coefficients of chloride ion in aqueous solution of lithium chloride have been extended to include concentrations above 10 mol kg<sup>-1</sup> since the data obtained with medium concentrations are available in the literature and the values reported by Mills<sup>2</sup> and Turq *et al.*<sup>1</sup> are in good agreement.

Our data, together with the literature values, are plotted as a function of concentration in fig. 1. There is fairly good agreement between present data and Turq's data of tracer diffusion coefficients of the lithium ion at lower concentrations, although at higher concentrations the values reported by Turq *et al.*<sup>1</sup> are slightly larger than our values. The disagreement between the two sets of water diffusion data is mainly ascribed to the difference in the tracer diffusion coefficient of water in pure water that we used<sup>13</sup> and the value reported by Tamas *et al.*<sup>3</sup>

It is interesting to note that these tracer diffusion coefficients of component species in solution are related to the hydrated structure of lithium ion in the solution. It is generally accepted that although both lithium and chloride ions are hydrated, the lithium ion is more strongly hydrated than the chloride ion, and no significant change in the dynamical properties of water molecules around chloride ions was observed.<sup>14</sup> In this

**Table 2.** Tracer diffusion coefficients of lithium ion, chloride ion and water in aqueous lithium chloride solutions at 298.2 K

$m$ /mol kg <sup>-1</sup>	$D_{\text{Li}}$ /10 <sup>-9</sup> m <sup>2</sup> s <sup>-1</sup>	$D_{\text{Cl}}$ /10 <sup>-9</sup> m <sup>2</sup> s <sup>-1</sup>	$D_{\text{H}_2\text{O}}$ /10 <sup>-9</sup> m <sup>2</sup> s <sup>-1</sup>
0.10	1.022	—	2.183
0.50	1.005	—	2.114
1.03	0.931	—	1.934
2.10	0.914	—	1.701
5.60	0.615	—	1.144
13.8	0.232	0.321	0.400
18.6	0.141	0.143	0.241



**Fig. 1.** Concentration dependence of tracer diffusion coefficients of Li<sup>+</sup>, Cl<sup>-</sup> and water in aqueous LiCl solutions at 298.2 K; Li<sup>+</sup> (○), Cl<sup>-</sup> (□) and water (△), filled symbols designate respective literature values.

respect we assume that all the water molecules in highly concentrated lithium chloride solutions are hydrated to lithium ions. In concentrated solutions of lithium chloride the hydration number for the lithium ion is four, while in dilute solutions it is six.<sup>4, 7, 12</sup> Up to 13.8 mol kg<sup>-1</sup>, where the ratio of lithium ions to water molecules is one to four, the hydration requirement of lithium ions can be satisfied. Over this concentration range there are insufficient water molecules to complete the hydration shells of lithium ions and the direct interaction between lithium and chloride ions becomes significant.<sup>5, 6</sup>

This picture is reflected in the measured values of tracer diffusion coefficients of lithium and chloride ions as shown in table 2. At  $18.6 \text{ mol kg}^{-1}$  the value of tracer diffusion coefficient of chloride ions is equal to that of lithium ions. This may be an indication of direct interaction between lithium and chloride ions as a consequence of which they travel together in the solution. At concentrations lower than  $18.6 \text{ mol kg}^{-1}$  the values of tracer diffusion coefficients of lithium ions are much smaller than those of chloride ions, suggesting that the diffusional behaviour of lithium and chloride ions are for the most part independent. This is to be expected if the lithium ion is surrounded by four water molecules. At lower concentrations the complete hydration of lithium ions precludes any significant direct interaction between lithium and chloride ions.

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