A Physico-chemical Study of Concentrated Aqueous Solutions of Lithium Chloride

Kazuko Tanaka
The Institute of Physical and Chemical Research, 2-1 Hirosawa, Wako, Saitama, 351-01, Japan

Reita Tamamushi
Faculty of Education, Fukushima University, Asakawa, Matsukawa-machi,
Fukushima 960-12, Japan

Z. Naturforsch. **46a**, 141 – 147 (1991); received October 2, 1990

Dedicated to Dr. Karl Heinzinger on the occasion of his 60th birthday

The experimental values of density, viscosity, electric conductivity and diffusion coefficients of trace ions in aqueous solutions of lithium chloride in wide ranges of concentration and temperature are collected and discussed. The thermal expansivity and the activation energies of viscous flow, electric conductance and diffusion of trace ions show significant changes at a molality around 12 mol/kg, beyond which the hydration requirement is not satisfied.

Introduction

Lithium chloride, consisting of a small, univalent cation and a relatively large, univalent anion, and having a very large solubility in water, is one of the most suitable electrolytes for the physico-chemical study of concentrated aqueous solutions; the mole fraction of LiCl of a saturated aqueous solution is even greater than 0.25 at 25 °C.

We present the density, viscosity, and electrolytic conductivity data of aqueous LiCl solutions in the molality range 0.05 – 20 mol/kg and at different temperatures from 15 to 55 °C, and also the tracer diffusion coefficients of some metal ions in LiCl(aq) of different concentrations. The molar volume, thermal expansivity, and Arrhenius activation parameters for the viscous flow, conductivity and tracer diffusion will be discussed, including the osmotic and activity coefficients and the contact angle between glass and LiCl(aq).

Density, Viscosity, and Electrolytic Conductivity Data

The density and viscosity of LiCl(aq) were reported by Lengyel et al. [1] in the molality range 1.0090 – 19.584 mol/kg and at temperatures between 15 and 35 °C. Tables 1 – 3 summarize the density ϱ, viscosity η, and electrolytic conductivity $\varkappa$ of aqueous LiCl solutions, measured by Isono [2], at molalities 0.05 – 20 mol/kg and at temperatures 15 – 55 °C. The density data given in Table 1 are in very good agreement with [1]. However the viscosity data in Table 2 are generally larger than those given in [1]; at molalities below 10 mol/kg differences are less than 0.5%, but deviations up to about 10% are found at higher concentrations.

Volume of Solution

Consider an aqueous LiCl solution of molality m. The volume V of this solution containing 1 kg of water is calculated from the density ϱ by the equation

$$V/\mathrm{cm}^3 = \{1000 + (m/\mathrm{mol\ kg}^{-1})(M_2/\mathrm{g\ mol}^{-1})\}/(\varrho/(\mathrm{g\,cm}^{-3})), \tag{1}$$

where M_2 is the molar mass of the solute. The volume per kg of water of aqueous alkali chloride solutions of molalities from 0.5 mol/kg to saturation was found to obey with reasonable accuracy a second-order equation in the molality:

$$V = A + B\,(m/\mathrm{kg}^{-1}) + C\,(m/\mathrm{kg}^{-1})^2. \tag{2}$$

Table 4 gives the coefficients A, B, and C for LiCl and other alkali chlorides at 25 °C, together with the molar volumes of water, v_0^1, and those of crystals of the solutes, v_2^0.

Reprint requests to Dr. K. Tanaka, Institute of Physical and Chemical Research, 2-1 Hirosawa, Wako, Saitama, 351-01, Japan.

0932-0784 / 91 / 0100-0141 $ 01.30/0. – Please order a reprint rather than making your own copy.

Table 1. Density, $\varrho/(\mathrm{kg\ m^{-3}})$, of aqueous LiCl solutions [2].

$\frac{m}{\mathrm{mol\ kg^{-1}}}$	15.00 °C	20.00 °C	25.00 °C	30.00 °C	35.00 °C	40.00 °C	45.00 °C	50.00 °C	55.00 °C
0.050	1000.34	999.44	998.28	996.90	995.27	–	991.51	–	987.00
0.100	1001.54	1000.65	999.47	998.08	996.47	–	992.66	–	988.16
0.500	1011.21	1010.25	1009.02	1007.60	1005.96	–	1002.20	–	997.80
1.000	1022.47	1021.42	1020.08	1018.71	1017.09	–	1013.35	–	1009.01
2.000	1044.09	1043.07	1041.63	1040.14	1038.58	–	1034.93	–	1030.77
3.000	1064.10	1062.92	1061.53	1060.04	1058.48	–	1054.91	–	1050.90
4.000	1082.84	1081.57	1080.18	1078.69	1077.11	–	1073.62	–	1069.79
6.000	1117.96	1116.26	1114.82	1113.33	1111.75	–	1108.46	–	1104.82
8.000	1149.08	1147.71	1146.26	1144.71	1143.15	–	1139.81	–	1136.30
10.000	1178.88	1177.45	1175.89	1174.31	1172.68	–	1169.31	–	1165.74
12.00	1209.27	1207.68	1206.03	1204.38	1202.69	1200.92	1199.19	1197.40	1195.58
14.00	1234.79	1233.12	1231.39	1229.68	1227.92	1226.15	1224.33	1222.47	1220.63
16.00	1259.44	1257.64	1255.85	1254.04	1252.26	1250.41	1248.54	1246.64	1244.75
18.00	1282.37	1280.52	1278.67	1276.78	1274.92	1273.00	1271.07	1269.16	1267.18
20.00	–	–	1298.72	1296.77	1294.82	1292.84	1290.83	1288.85	1286.80

Table 2. Viscosity, $\eta/(\mathrm{mN\ s\ m^{-2}})$, of aqueous LiCl solutions [2].

$\frac{m}{\mathrm{mol\ kg^{-1}}}$	15.00 °C	20.00 °C	25.00 °C	30.00 °C	35.00 °C	40.00 °C	45.00 °C	50.00 °C	55.00 °C
0.050	1.1484	1.0105	0.8972	0.8036	0.7247	–	0.6005	–	0.5076
0.100	1.1562	1.0183	0.9048	0.8108	0.7310	–	0.6063	–	0.5128
0.500	1.2214	1.0765	0.9573	0.8583	0.7747	–	0.6415	–	0.5441
1.000	1.3028	1.1499	1.0232	0.9180	0.8291	–	0.6872	–	0.5832
2.000	1.4815	1.3103	1.1669	1.0484	0.9477	–	0.7888	–	0.6695
3.000	1.6810	1.4879	1.3270	1.1926	1.0788	–	0.8991	–	0.7643
4.000	1.905	1.678	1.505	1.354	1.225	–	1.021	–	0.8688
6.000	2.455	2.176	1.944	1.750	1.585	–	1.323	–	1.128
8.000	3.192	2.830	2.527	2.275	2.059	–	1.716	–	1.461
10.000	4.283	3.786	3.370	3.026	2.732	–	2.267	–	1.920
12.00	6.104	5.368	4.764	4.255	3.826	3.470	3.156	2.889	2.659
14.00	8.540	7.448	6.554	5.807	5.187	4.668	4.223	3.840	3.513
16.00	12.158	10.483	9.129	8.012	7.088	6.327	5.676	5.125	4.657
18.00	17.21	14.66	12.61	10.95	9.601	8.492	7.552	6.765	6.100
20.00	–	–	16.81	14.40	12.54	11.06	9.777	8.681	7.763

Table 3. Conductivity, $\varkappa/(\mathrm{S\ m^{-1}})$, of aqueous LiCl solutions [2].

$\frac{m}{\mathrm{mol\ kg^{-1}}}$	15.00 °C	20.00 °C	25.00 °C	30.00 °C	35.00 °C	40.00 °C	45.00 °C	50.00 °C	55.00 °C
0.050	0.3923	0.4409	0.4911	0.5418	0.5956	–	0.7049	–	0.8179
0.100	0.7647	0.8583	0.9544	1.053	1.155	–	1.364	–	1.581
0.500	3.260	3.654	4.054	4.467	4.888	–	5.761	–	6.655
1.000	5.800	6.484	7.188	7.911	8.654	–	10.16	–	11.72
2.000	9.666	10.80	11.94	13.14	14.37	–	16.86	–	19.42
3.000	12.31	13.74	15.18	16.70	18.20	–	21.35	–	24.63
4.000	14.00	15.63	17.27	18.96	20.69	–	24.28	–	27.93
6.000	15.34	17.09	18.92	20.76	22.68	–	26.66	–	30.64
8.000	14.76	16.47	18.25	20.09	21.97	–	25.88	–	29.93
10.00	13.10	14.67	16.32	18.03	19.81	–	23.50	–	27.37
12.00	10.86	12.25	13.73	15.26	16.86	18.54	20.27	22.03	23.89
14.00	8.99	10.24	11.55	12.94	14.41	15.93	17.53	19.21	20.88
16.00	7.41	8.52	9.70	10.96	12.30	13.71	15.18	16.72	18.33
18.00	6.21	7.19	8.27	9.42	10.65	11.96	13.35	14.80	16.30
20.00	–	–	7.23	8.31	9.46	10.68	11.99	13.38	14.84

Table 4. The coefficients in (2) for aqueous alkali chloride solutions, the molar volume of water v_1^0, and the molar volume of the solute v_2^0 at 25 °C.

Electrolyte	Coefficients in (2) *			Molar volume	
	A cm^3	B cm^3/mol	C cm^3 mol^2	v_1^0 cm^3/mol	v_2^0 cm^3/mol
LiCl	1001.65	20.46	0.0296	18.05	20.50
NaCl	1002.79	18.50	0.519	18.07	26.99
KCl	1002.80	28.65	0.597	18.07	37.68
RbCl	1002.68	34.34	0.433	18.06	43.18
CsCl	1002.31	42.16	0.317	18.06	42.21

* Coefficients A, B, and C for NaCl, KCl, RbCl, and CsCl were determined by using the density data given in [2].

Table 5. Temperature dependence of the density (cf. (6)) and the thermal expansion of LiCl(aq) at 25 °C (cf. (7)). The density data in [2] were used in the calculation.

$\frac{m}{\text{mol kg}^{-1}}$	ϱ (25 °C) g cm^{-3}	$-10^3 a$ g cm^{-3}	$-10^6 b$ g cm^{-3}	10^3 (s.d.) * g cm^{-3}	$10^4 \alpha$ (25 °C) K^{-1}
0	0.997047	0.2539	4.318	0.073	2.55
0.05	0.99828	0.2529	4.242	0.073	2.53
0.1	0.99947	0.2547	4.211	0.070	2.55
0.5	1.00902	0.2630	3.838	0.074	2.61
1.0	1.02008	0.2715	3.133	0.076	2.66
2.0	1.04163	0.2842	2.574	0.080	2.73
3.0	1.06153	0.2845	2.325	0.029	2.68
4.0	1.08017	0.2873	1.970	0.010	2.66
6.0	1.11488	0.3065	0.904	0.075	2.75
8.0	1.14624	0.2975	1.133	0.016	2.60
10.0	1.17589	0.3118	0.890	0.024	2.65
12.0	1.20603	0.3301	0.619	0.012	2.74
14.0	1.23139	0.3434	0.532	0.011	2.79
16.0	1.25585	0.3591	0.373	0.016	2.86
18.0	1.27867	0.3730	0.321	0.010	2.92
20.0	1.29872	0.3867	0.303	0.016	2.98

* Standard deviation.

The values of v_1^0 given in Table 4 were obtained from the coefficients A by assuming the relation

$$A = 1000\, v_1^0 / M_1 \tag{3}$$

with M_1 the number mass of water. They are found to be very close to the molar volume of pure water, 18.07 cm^3/mol at 25 °C, as determined from the density data of pure water.

The molar volumes of solute, v_2^0, in Table 4 were calculated from the crystal density ϱ_2 and the molar mass of the solute:

$$v_2^0 = M_2 / \varrho_2 . \tag{4}$$

It is interesting to note that, in case of LiCl and CsCl, the molar volume v_2^0 is practically identical with coefficient B, whereas in solutions of NaCl, KCl and RbCl the coefficient B is significantly smaller than v_2^0.

The apparent molar volume of solute, ϕ_2^v, is given by the relation (cf. (2))

$$\phi_2^v = \mathrm{d}V / \mathrm{d}(m/\mathrm{kg}^{-1}) = B + 2C\,(m/\mathrm{kg}^{-1}) . \tag{5}$$

Due to the very small C value for LiCl, the apparent molar volume of LiCl is practically constant in the range 0.05 mol/kg $\leqq m \leqq$ 20 mol/kg. This behaviour shows that the volume of the LiCl(aq) solution is additive with v_2^0 as given by (4) being the intrinsic volume of LiCl in the solution.

Thermal Expansivity

Temperature dependence of the density can be represented by the equation,

$$\varrho = \varrho(25\ ^\circ\mathrm{C}) + a(t/^\circ\mathrm{C} - 25) + b(t/^\circ\mathrm{C} - 25)^2 \tag{6}$$

and the thermal expansivity is given by

$$\alpha = -(1/\varrho)(\mathrm{d}\varrho/\mathrm{d}t) . \tag{7}$$

The coefficients a and b in (6) and the thermal expansivity of LiCl(aq) at 25 °C are given in Table 5. The thermal expansivity of LiCl(aq) remains nearly unchanged in the molality range 0–10 mol/kg but shows a gradual increase with molality from about 12 mol/kg.

Figure 1 shows the thermal expansivity of LiCl(aq) at 25 °C as a function of molality of the solute; the data for aqueous solutions of other alkali chlorides are included for comparison. The very small thermal expansivity of LiCl(aq) suggests that the volume fraction of free space in the structure of liquid water does not change appreciably with increasing concentration of LiCl.

Activation Parameters for the Viscous Flow and Electrolytic Conductivity

The molar conductivity of LiCl and the conductivity-fluidity correlation were discussed in [3]. In this study attention will be focused to the temperature dependence of the viscosity and electrolytic conductivity. Arrhenius plots for the viscosity and electrolytic conductivity of aqueous electrolyte solutions are not strictly linear [4]. In the following, however, the average activation parameters in the temperature range 15–55 °C will be discussed.

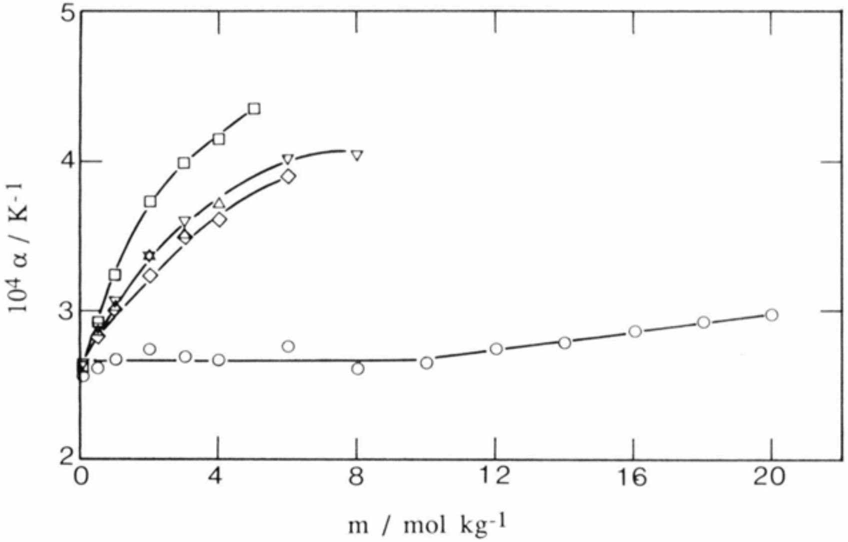

Fig. 1. Thermal expansivities of aqueous solutions of alkali chlorides at 25.0 °C as functions of the molality of the solute: ○, LiCl; □, NaCl; △, KCl; ◇, RbCl; ▽, CsCl. The density data in [2] were used in the caclulation.

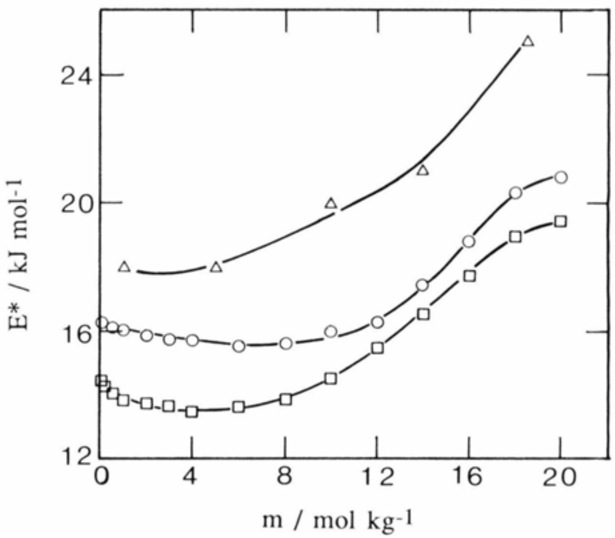

Fig. 2. Activation energies of the viscosity (○), conductivity (□) and tracer diffusion coefficients of metal ions (△) as functions of the molality of LiCl(aq).

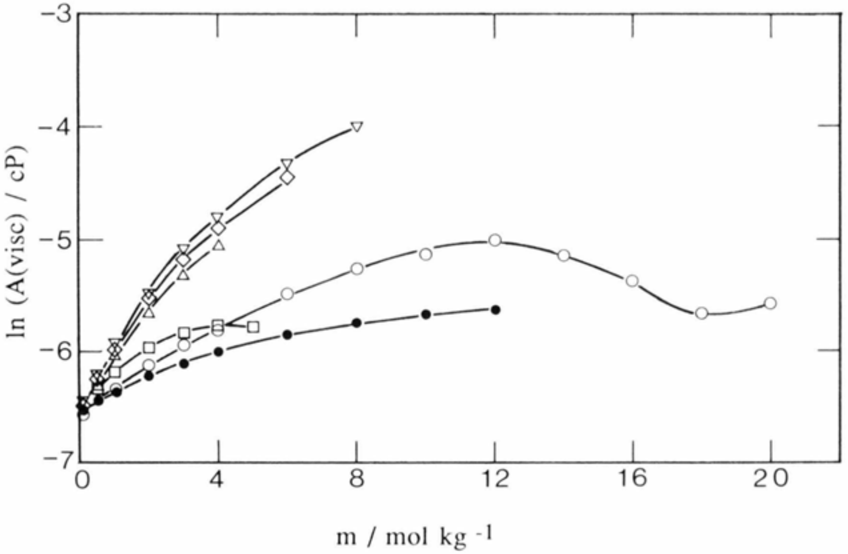

Fig. 3. Pre-exponential factors of the viscosity of aqueous solutions as functions of the molality of the solute: ○, LiCl; □, NaCl; △, KCl; ◇, RbCl; ▽, CsCl; ●, urea. Data from [2]

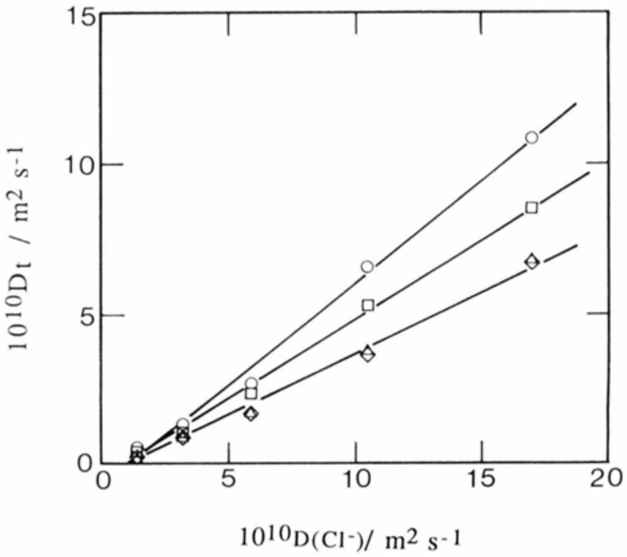

Fig. 4. Correlation between the tracer diffusion coefficients of metal ions, D_t, and chloride ions, $D(Cl^-)$, in LiCl(aq) of different concentrations at 25 °C: ○, Tl(I); □, Cd(II); △,

Table 6. Tracer diffusion coefficients of some ions and water molecule in LiCl(aq) at 25 °C.

m (LiCl) mol/kg	10^{10} *D*/m^2 s^{-1}							*E** kJ/mol
	Tl(I) [6]	Cd(II) [6]	Zn(II) [6]	Co(II) [6]	Li^+ [5]	Cl^- [5]	H_2O [5]	
1	10.8	8.50	6.76	6.75	9.31	17.0	19.3	18
5	6.60	5.28	3.72	3.70	6.70	10.5	12.8	18
10	2.65	2.36	1.74	1.70	3.7	5.9	6.8	20
13.9	1.28	1.12	0.98	0.99	2.3	3.2	4.0	21
18.5	0.54	0.45	0.42	0.42	1.4	1.4	2.4	25

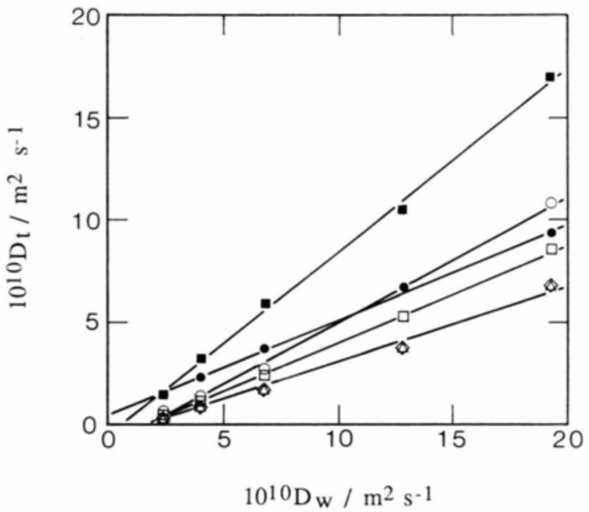

Fig. 5. Correlation between the tracer diffusion coefficients of some ions, D_t, and that of water molecule, D_w, in LiCl(aq) of different concentrations at 25 °C: ○, Tl(I); □, Cd(II); △, Zn(II); ◇, Co(II); ●, Li^+; ■, Cl^-. Data from [5].

The activation energies for the viscous flow and electrolytic conductivity of LiCl(aq) change with concentration in a similar manner, as shown in Fig. 2, although the values for the viscous flow are always larger than those for the conductivity. With increasing concentration, the energies first show a slight decrease but then begin to increase from about 6 mol/kg, which is followed by a larger increase starting from about 10–12 mol/kg. A more significant change at 12 mol/kg occurs with the pre-exponential factor for the viscous flow, *A*(visc), as seen in Fig. 3, which includes *A*(visc) of aqueous solutions of other alkali chlorides and urea for comparison.

Diffusion of Tracer Ions in Concentrated LiCl(aq)

Tracer diffusion coefficients of lithium ions, chloride ions and water in LiCl(aq) of 0.1–18.6 mol/kg at 25 °C were reported in [5]. The tracer diffusion coefficients of Tl(I), Cd(II), Co(II), and Zn(II), their concentrations being less than 1 mmol/dm^3, in LiCl(aq) of 1–18.5 mol/kg at different temperatures from 15 to 55 °C were obtained from the analysis of pulse-polarographic diffusion-controlled limiting currents with the Ikeuchi-Galvez equation [6]. The results at 25 °C are summarized in Table 6, in which the tracer diffusion coefficients of Li^+, Cl^- and H_2O in LiCl(aq) are taken from [5].

The tracer diffusion coefficients of the metal ions decrease with increasing concentration of LiCl, and they become significantly smaller than those of Li^+ and Cl^- at higher concentrations of LiCl, which suggests the formation of metal-chloro complexes and also the association of the chloro complex ions with lithium ions. This argument may be supported by the linear correlation observed between the tracer diffusion coefficients of the metal ions and that of the chloride ion, as can be seen in Figure 4. Another interesting finding is that, in LiCl(aq), the tracer diffusion coefficient of each ion depends linearly on that of water, as shown in Figure 5.

The Arrhenius activation energy for diffusion of tracer ions was found to be almost independent of the type of metal ion, but to vary with the LiCl concentration in a similar way as does the activation energy of viscous flow and electrolytic conductivity of LiCl(aq), cf. Figure 2. This is in contrast with fused sodium chloride media, where different metal ions give different activation energies [7].

Discussion

Lithium ions are strongly hydrated in aqueous solutions. In concentrated solutions of LiCl the hydration number for the lithium ion is reported to be four, while in dilute solutions it is six [8–10]. The hydration requirement of lithium ions can be satisfied up to 13.8 mol/kg where the ratio of lithium ions to water molecules is one to four. Beyond this concentration, however, there are insufficient water molecules to complete the hydration shells of lithium ions and direct interaction between lithium and chloride ions becomes significant [11–14].

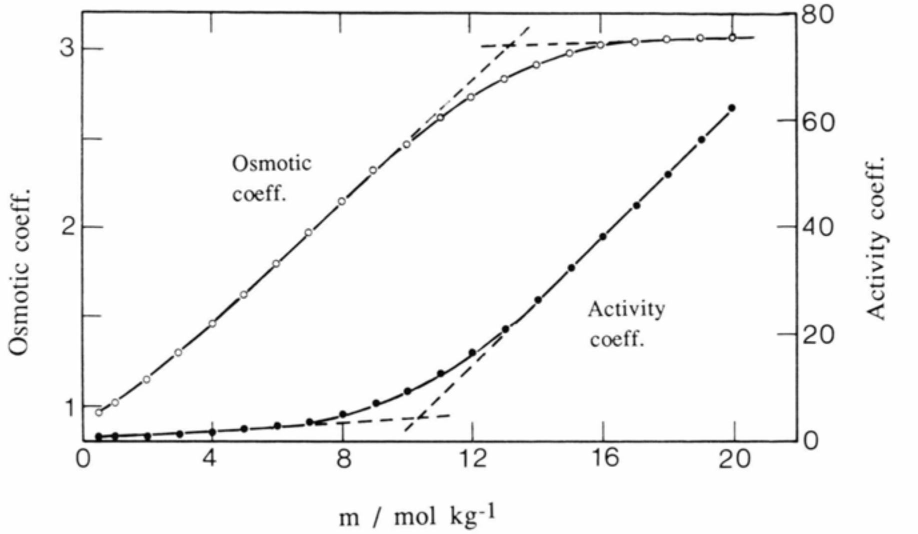

Fig. 6. Osmotic coefficients, ϕ, and activity coefficients, γ, of LiCl at 25 °C as functions of the molality of LiCl. Data from [15].

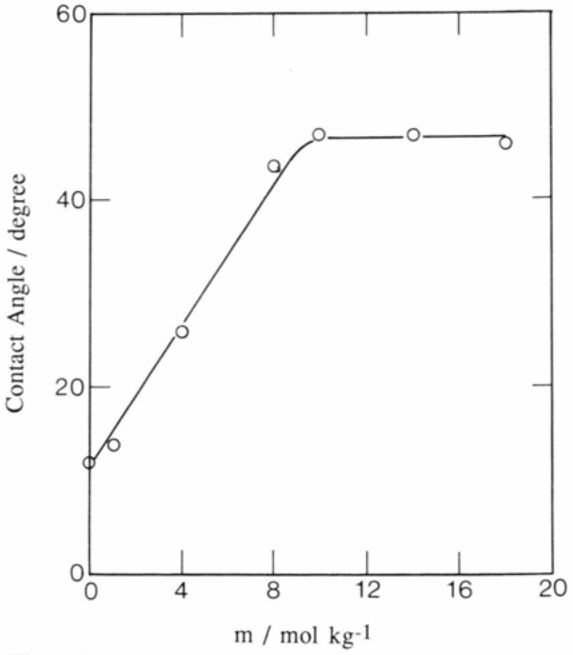

Fig. 7. Contact angle between a glass plate and LiCl(aq) as a function of te molality of LiCl at room temperature. Data from [16].

This structural picture is in accordance with the following thermodynamic and transport evidences, which suggest that the water molecules in LiCl(aq) in the higher concentration range behave quite differently from those in the bulk water.

(a) The thermal expansivity of LiCl(aq) begins to increase linearly with concentration from about 12 mol/kg, while it remains almost constant at lower concentrations (Figure 1).

(b) The Arrhenius activation parameters, i.e., the activation energy and pre-exponential factor, for the viscous flow of LiCl(aq) show significant changes at concentrations around 12 mol/kg as can be seen in Figs. 2 and 3.

(c) The concentration dependence of some thermodynamic quantities in the concentration range 13–20 mol/kg is different from that at lower concentrations. Figure 6 illustrates the osmotic coefficient ϕ and activity coefficient γ of LiCl in aqueous solutions as a function of the molality of LiCl [15]. The osmotic coefficient increases linearly with concentration in the range 2–10 mol/kg but it tends to become nearly constant at concentrations higher than about 14 mol/kg. In the case of the activity coefficient of LiCl, its concentration dependence in the range 12–20 mol/kg is clearly different from that in the lower concentration range as shown in Figure 6.

(d) The contact angle between glass and LiCl(aq) at room temperature also exhibits a significant change at a concentration about 10 mol/kg: the contact angle increases linearly in the range 0–10 mol/kg but remains almost constant at higher concentrations, as illustrated in Fig. 7 [16]. The contact angle is a measure of the relative strengths of the interaction of the water molecules with the constituents of glass and with the ions and molecules in the solution. Pure liquid water forms small contact angles with clean glass, indicating a strong adhesion of the water to the glass. The relatively large and constant contact angles observed with LiCl(aq) of $m > 10$ kg/mol suggest that most of the water molecules in the solutions are coordinated to the lithium ions.

A recent MD study [14] of 18.5 mol/kg LiCl(aq) shows that the Born-Mayer-Huggins potentials with parameters proposed by Tosi and Fumi, which proved to be successful to describe the structural and dynamical properties of various molten salts, give tracer diffusion coefficients for water and the solved ions which are in reasonably good agreement with experimental values. The tracer diffusion of Tl(I), Cd(II), Zn(II) and Co(II) in concentrated LiCl(aq) gave a common activation energy which is dependent only on the LiCl concentration, while the activation energy differs from ion to ion in fused NaCl media. There exists a relatively good correlation between the tracer diffusion coefficients of ions and that of the water molecule as shown in Fig. 5, which suggests that the water molecules play an important role even in such concentrated solutions where the hydration requirement of lithium ions is not satisfied.

[1] S. Lengyel, J. Tamas, J. Giber, and J. Holderith, Acta Chim. Hung. **40,** 125 (1964).
[2] K. Takahashi and T. Isono, Rikagaku Kenkyusho Hokoku **61,** 47 (1985). – T. Isono, ibid. **61,** 53 (1985). Unpublished data at molalities $m > 10$ mol/kg are included in Tables 1–3.
[3] R. Tamamushi and K. Tanaka, Electrochim. Acta **33,** 1445 (1988).
[4] For example, E. C. Bingham, Fluidity and Plasticity, McGraw-Hill, New York 1922, Chapt. III. – E. A. Moelwyn-Hughes, Physical Chemistry, Pergamon, Oxford 1964, pp. 715–717. – R. Tamamushi, Denki Kagaku **54,** 344 (1986).
[5] K. Tanaka and M. Nomura, J. Chem. Soc., Faraday Trans. 1 **83,** 1779 (1987).
[6] H. Ikeuchi, H. Uchida, and G. P. Sato, Anal. Sci. J. **6,** 239 (1990).
[7] J. O'M. Bockris, S. Yoshikawa, and S. R. Richards, J. Phys. Chem. **68,** 1838 (1964).
[8] I. Okada, Y. Kitsuno, H.-Y. Lee, and H. Ohtaki, Ions and Molecules in Solution (N. Tanaka, H. Ohtaki, and R. Tamamushi, eds.), Elsevier, Amsterdam 1983, p. 81.
[9] J. R. Newsome, G. W. Neilson, and J. E. Enderby, J. Phys. C: Solid State Phys. **13,** L923 (1980).
[10] J. E. Enderby and G. W. Neilson, Rep. Progr. Phys. **44,** 38 (1981).
[11] K. Ichikawa, Y. Kameda, T. Matsumoto, and M. Misawa, J. Phys. C: Solid State Phys. **17,** L725 (1984).
[12] A. P. Copestake, G. W. Neilson, and J. E. Enderby, J. Phys. C: Solid State Phys. **18,** 4211 (1985).
[13] K. Tanaka, N. Ogita, Y. Tamura, I. Okada, H. Ohtaki, G. Palinska, E. Spohr, and K. Heinzinger, Z. Naturforsch. **42a,** 29 (1987).
[14] Y. Tamura, K. Tanaka, E. Spohr, and K. Heinzinger, Z. Naturforsch. **43a,** 1103 (1988).
[15] R. A. Robinson and R. H. Stokes, Electrolyte Solutions, Rev. Ed., Butterworths, London 1965, Appendix 8.10.
[16] K. Tanaka and R. Tamamushi, unpublished data.