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Lawrence Livermore Laboratory

AQUEOUS LiOH: PHYSICAL, THERMODYNAMIC, AND TRANSPORT PROPERTIES

Robert V. Homsy

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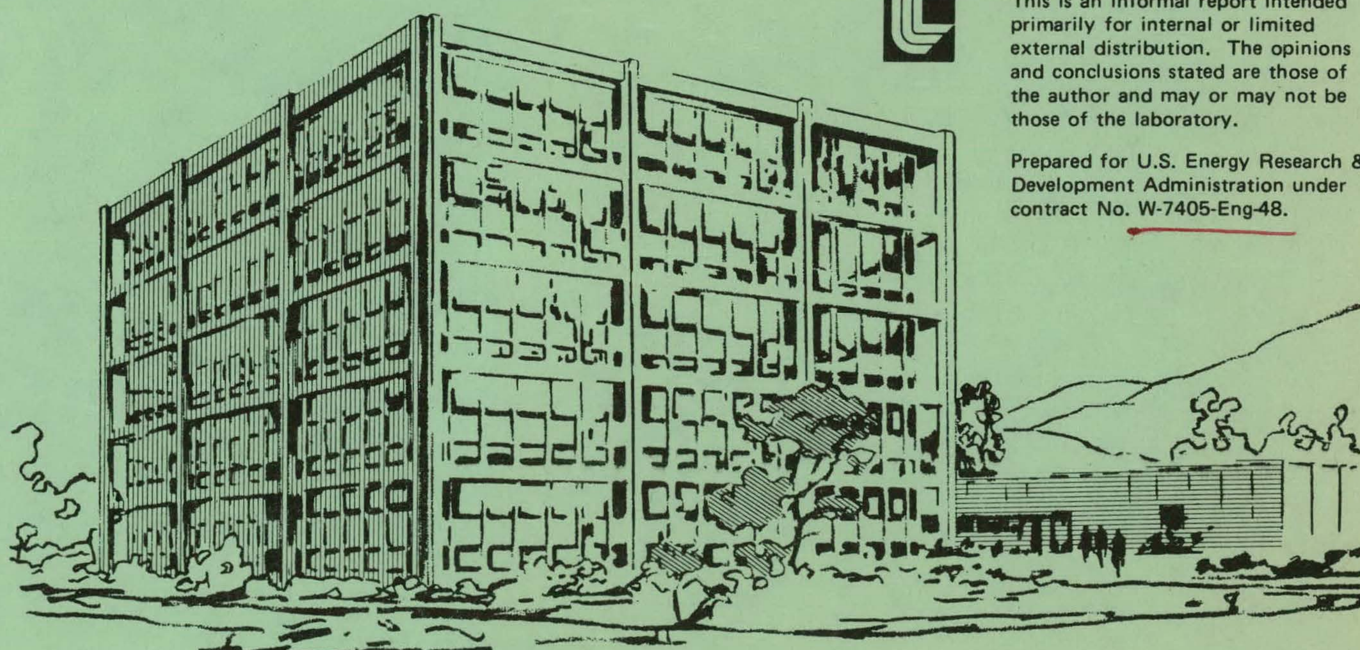

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CONTENTS

SYMBOLS

a	ion size parameter
B_2	constant in Eq. (2), equals 60.65
c	molar concentration of LiOH, mole/liter
C_p	heat capacity at constant pressure, J/g-°C
D	diffusion coefficient of LiOH in water, cm^2/sec
$\mathcal{D}_{oi}$	diffusion coefficient of species i in water, cm^2/sec
m	molal concentration of LiOH, mole/kg
M	molecular weight of LiOH, equals 23.95 g/mole
Sc	Schmidt number, ν/D
t_+	transference number of Li^+ in aqueous LiOH
T	temperature, K
$\overline{V}_o$	partial molal volume of water, liter/mole
w	weight fraction of LiOH
$\gamma_\pm$	mean molal activity coefficient of aqueous LiOH
κ	parameter in Eq. (2)
λ_i	equivalent conductance of species i, cm^2/ohm-equivalent
Λ	equivalent conductance of aqueous LiOH, cm^2/ohm-equivalent
μ	dynamic viscosity, Pa-sec
ν	kinematic viscosity, cm^2/sec
ρ	density, g/cm^3
σ	surface tension, dyn/m
ϕ	osmotic coefficient

Subscripts

calc	calculated value
exp	experimental value
i	species i
0	solvent, water
s	saturation condition
T	temperature, K
+	cation, Li^+
-	anion, OH^-

Superscripts

0	at infinite dilution

AQUEOUS LiOH:
PHYSICAL, THERMODYNAMIC, AND TRANSPORT PROPERTIES

ABSTRACT

Experimental data in the literature on the physical, thermodynamic, and transport properties of aqueous LiOH are summarized. The behavior of some properties is predicted beyond the range of the data.

INTRODUCTION

Aqueous solutions of LiOH are being studied at Lawrence Livermore Laboratory in connection with the lithium-water-air battery electric vehicle project.[1] The purpose of this effort is to summarize literature data on aqueous LiOH properties. This is intended to provide a ready reference for laboratory and design calculations. When the last digit in experimental data is reported in parentheses, it may or may not be significant and should not be considered necessarily accurate.

PHYSICAL PROPERTIES

Density

Table 1 summarizes data on density[2] at various concentrations and temperatures. Concentration appears in the literature as weight fraction, denoted by w; molality (mole/kg water), denoted by m; or molarity (mole/liter of solution), denoted by c. I express the concentration as molarity, unless inappropriate to do so. The relationship among the three concentration bases is given by the expression

$$c = \frac{10^2 \rho w}{M} = \frac{\rho m}{1 + 10^{-3} mM} , \qquad (1)$$

where M = 23.95 g/mole is the molecular weight of LiOH. Figure 1 shows the relationship between molality and molarity at various temperatures. As concentration and temperature decrease, molality becomes equal to molarity (indicated by dashed line in the figure). Table 2 summarizes the density at 25°C; Figure 2 shows the same data.

Solubility

Table 3 gives data on the solubility[3] of LiOH in water; Figure 3 illustrates this data.

Viscosity

Figure 4 and Table 4 show the ratio of the viscosity of aqueous LiOH to that of water at the same temperature.[4] Viscosity increases rapidly with increasing concentration and decreasing temperature.

Table 5 summarizes kinematic viscosity, defined as μ/ρ; Figure 5 shows this for various concentrations at 25°C.

Heat Capacity

Table 6 and Fig. 6 list and depict heat capacity at constant pressure[5] at 20°C.

Surface Tension

Table 7 and Fig. 7 list and picture the variation of surface tension[6] with concentration at 18°C.

THERMODYNAMIC PROPERTIES

This section reports concentration in terms of molality, since this is the base for which the properties are defined.

Osmotic Coefficient

Table 8 summarizes experimental data on the osmotic coefficient[7] for aqueous LiOH at 25°C.

Activity Coefficient

Table 8 also shows data on the mean molal activity coefficient[8] at 25°C. Figure 8 shows a log-log data plot, which is nearly linear over the concentration range reported.

TRANSPORT PROPERTIES

Electrical Conductivity

Table 9 summarizes data on the specific conductance[9] of aqueous LiOH at various concentrations and temperatures.

Ionic Equivalent Conductance

Table 10 reports the equivalent conductance at infinite dilution for Li^+ and OH^- at 25°C[10] and various other temperatures.[11]

Transference Number

Only scanty experimental data are available on the transference number[12] of Li^+ in aqueous LiOH. I estimated values of the transference number from existing data using a method given by Robinson and Stokes.[13] (See Appendix A for details.) The results for 18°C appear in Table 11 and Fig. 9.

Diffusion Coefficient

The value of the diffusion coefficient of LiOH in water at infinite dilution may be calculated from the equivalent conductance and diffusion coefficient of the ions in water. (See Appendix B for details.)

The only reported experimental measurements at higher concentrations were performed in a solution containing 2% agar in a 0.3-mole/liter, aqueous LiOH solution,[14] and are thus of questionable accuracy. I estimated the diffusion coefficient by a method that uses data on thermodynamic and physical properties. (Details may be found in Appendix B.) See Table 12 and Fig. 10 for all the results.

Schmidt Number

Although strictly not a transport property, the Schmidt number has been included. This dimensionless group is given by $Sc = \nu/D$. Table 13 and Fig. 11 list and show the predicted values for the Schmidt number at 25°C.

APPENDIX A

PREDICTION OF TRANSFERENCE NUMBER OF Li^+ IN AQUEOUS LiOH

Robinson and Stokes[13] report that for a 1:1 electrolyte the transference number is related to the concentration by the expression

$$t_+ = \frac{\lambda_+^0 - \dfrac{B_2\sqrt{c}}{2\ (1 + \kappa a)}}{\Lambda^0 - \dfrac{B_2\sqrt{c}}{(1 + \kappa a)}} \quad , \tag{2}$$

where $\Lambda^0 = \lambda_+^0 + \lambda_-^0$ is the equivalent conductance of the electrolyte at infinite dilution. For an aqueous solution at 25°C, $B_2 = 60.65$ and $\kappa = 0.3291\ \sqrt{c}$, while a is the ion size parameter, which is determined from an experimental measurement of t_+ at some concentration. I used the experimental value of $t_+ = 0.11$ at c = 1.5 mole/liter (from Table 11) to determine a = 3.18. Substitution of the ionic equivalent conductances from Table 10 and the other parameters into Eq. (1) yields, after some simplification

$$t_+ = \frac{3.81 + \sqrt{c}}{23.3 + 18.4\ \sqrt{c}} \quad . \tag{3}$$

This equation was used to determine the values of $t_{+_{calc}}$ in Table 11.

APPENDIX B

DIFFUSION COEFFICIENT OF LiOH IN WATER

Diffusion Coefficient at Infinite Dilution

The diffusion coefficient at infinite dilution may be calculated from the equivalent conductance and diffusion coefficient of the respective ions in water. Table 14 lists the ionic diffusion coefficients[10] at 25°C. At infinite dilution

$$D^0 = 2t_+^0 \mathcal{D}_{0-}^0 = 2(1 - t_+^0) \mathcal{D}_{0+}^0 \quad . \qquad (4)$$

I used this equation to calculate the value of the diffusion coefficient at infinite dilution (Table 12) with the appropriate ionic transport properties.

Estimation of Diffusion Coefficient

Reid and Sherwood[15] report that the diffusion coefficient for electrolytic systems may be estimated by the expression

$$D = D^0 \left(\frac{1}{c_0\overline{V}_0}\right)\left(\frac{\mu_0}{\mu}\right)\left(1 + \frac{d \ln \gamma_\pm}{d \ln m}\right) \quad , \qquad (5)$$

where c_0 and $\overline{V}_0$ are the molar concentration and partial molal volume of the solvent. From the data in Fig. 2, we see that density increases almost linearly with concentration. This means that the concentration of the solvent (water) is essentially constant and equal to $1/\overline{V}_0$,[16] so that $c_0 \overline{V}_0 \cong 1$. I differentiated the data in Table 8 and Fig. 8 to obtain values for $d \ln \gamma_\pm / d \ln m$. Figure 12 shows the results. I used these results and the viscosity data shown in Table 4 to predict by Eq. (5) the diffusion coefficients listed in Table 12.

Correction of Diffusion Coefficient for Temperature

Reid and Sherwood[15] suggest the following expression for estimating the diffusion coefficient at temperature, T:

$$D_T = D_{25} \frac{T}{298} \frac{\mu_{25}}{\mu_T} \quad . \qquad (6)$$

I used this equation to estimate the values in Table 12 at 18°C.

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Table 1. Density in g/cm^3 at various concentrations and temperatures.

w	T (°C) 0	10	20	25	30	40	50	60	80
0[a]	0.9999	0.9997	0.9982	0.9971	0.9957	0.9922	0.9881	0.9832	0.9718
0.01	1.0122	1.0115	1.0102	1.0090	1.0075	1.0041	1.0000	0.9958	0.9860
0.02	1.0240	1.0230	1.0217	1.0203	1.0188	1.0155	1.0114	1.0072	0.9973
0.04	1.0468	1.0456	1.0437	1.0422	1.0407	1.0371	1.0331	1.0286	1.0189
0.06	1.0690	1.0674	1.0650	1.0636	1.0621	1.0582	1.0541	1.0496	1.0397
0.08	1.0908	1.0888	1.0862	1.0847	1.0830	1.0790	1.0747	1.0701	1.0600
0.10	1.1125	1.1102	1.1074	1.1057	1.1038	1.0996	1.0952	1.0906	1.0803

[a]Data for pure water.[17]

Table 2. Density of aqueous LiOH at 25°C.

w	c (mole/liter)	ρ (g/cm^3)
0	0	0.9971[a]
0.01	0.4213	1.0090
0.02	0.8520	1.0203
0.04	1.741	1.0422
0.06	2.665	1.0636
0.08	3.623	1.0847
0.10	4.617	1.1057

[a]Data for pure water.[17]

Table 5. Kinematic viscosity of aqueous LiOH at 25°C.

c (mole/liter)	$\nu \times 10^2$ (cm^2/sec)
0	0.897(5)[a]
0.500	0.991
1.00	1.08
2.00	1.3(7)
3.99	2.3(6)

[a]Calculated from the data for pure water,[18] $\mu_0 = 8.94(9) \times 10^{-4}$ Pa-sec.

Table 6. Heat capacity at constant pressure at 20°C.

w	c (mole/liter)	C_p (J/g-°C)
0	0	4.1819[a]
0.005	0.2097	4.17
0.010	0.4218	4.12
0.025	1.072	4.06
0.050	2.201	3.99

[a]Data for pure water.[19]

Table 7. Surface tension at 18°C.

c (mole/liter)	σ (dyn/m)
0	0.7305[a]
0.7	1.19
1.5	2.46

[a]Data for pure water.[20]

Table 3. Solubility of LiOH in water at various temperatures.

T (C°)	c_s (mole/liter)
10	5.29
20	5.29
30	5.31
40	5.35
50	5.44
60	5.59
80	5.81

Table 4. Ratio of viscosity of aqueous LiOH to that of water at the same temperature, μ/μ_0.

m	T (°C)			
(mole/kg)	0	25	50	75
0.5	1.13	1.12	1.11	1.10
1	1.24	1.23	1.22	1.21
2	1.6(7)	1.6(1)	1.5(6)	1.5(1)
4	3.4(0)	2.8(8)	2.5(8)	2.3(0)

Table 8. Osmotic coefficient and mean molal activity coefficient at 25°C.

m (mole/kg)	ϕ	$\gamma_{\pm}$
0	1.000	1.000
0.1	0.894	0.718
0.2	0.889	0.663
0.3	0.881	0.628
0.4	0.874	0.603
0.5	0.870	0.583
0.6	0.865	0.566
0.7	0.862	0.553
0.8	0.860	0.541
0.9	0.858	0.532
1.0	0.857	0.523
1.2	0.861	0.512
1.4	0.864	0.503
1.6	0.868	0.496
1.8	0.871	0.489
2.0	0.874	0.485
2.5	0.881	0.475
3.0	0.885	0.467
3.5	0.888	0.460
4.0	0.891	0.454

Table 9. Specific conductance in mho/cm.

m (mole/kg)	T (°C) 18	30	50	60
0.100	180.5	---	---	---
0.200	172.2	---	---	---
0.500	156.9	---	---	---
0.700	149.1	---	---	---
1.000	139.0	---	---	---
1.925	---	---	---	206.(6)
1.933	---	---	184.(7)	---
1.955	---	112.(3)	---	---
2.000	113.3	---	---	---
3.000	94.4	---	---	---
4.000	78.7	---	---	---
4.465	---	---	---	145.(6)
4.483	---	---	127.(6)	---
4.535	---	71.2	---	---
5.000	65.3	---	---	---

Table 10. Ionic equivalent conductance in cm^2/ohm-equiv. at infinite dilution and 25°C.

	T (°C)									
i	0	5	15	18	25[a]		35	45	55	100
Li^+	19.4	22.7(6)	30.2(0)	32.8	38.6(8)	38.69	48.0(0)	58.0(4)	68.7(4)	115
OH^-	105	---	---	171	198.3	197.6	---	---	---	450

[a]Data from Ref. 10; all other data from Ref. 11.

Table 11. Transference number at 18°C.

c (mole/liter)	t_{+calc}	t_{+exp}
0	0.161	0.161
0.1	0.142	0.150
0.2	0.135	0.150
0.5	0.125	0.140
1.0	0.116	0.13
1.5	0.110	0.11
2.0	0.106	---
2.5	0.103	---
3.0	0.101	---
3.5	0.0986	---
4.0	0.0968	---
4.5	0.0953	---
5.0	0.0939	---
5.29	0.0932	---

Table 12. Experimental and predicted values of the diffusion coefficient of LiOH in water in cm^2/sec.

c	T (°C)				
(mole/liter)	0	18	20	25	40
0	---	1.419	---	1.722	---
0.(3)[a]	0.(8)	---	1.(4)	---	2.(3)
0.500	---	1.07	---	1.30	---
1.00	---	0.981	---	1.20	---
2.00	---	0.766	---	0.970	---
3.99	---	0.356	---	0.539	---

[a]Data from Ref. 14.

Table 13. Schmidt number at 25°C.

c (mole/liter)	$Sc \times 10^{-3}$
0	0.521
0.500	0.763
1.00	0.896
2.00	1.4(2)
3.99	4.3(8)

Table 14. Ionic diffusion coefficient at infinite dilution and 25°C.

i	$\mathcal{D}_{oi} \times 10^5$ (cm^2/sec)
Li^+	1.030
OH^-	5.260

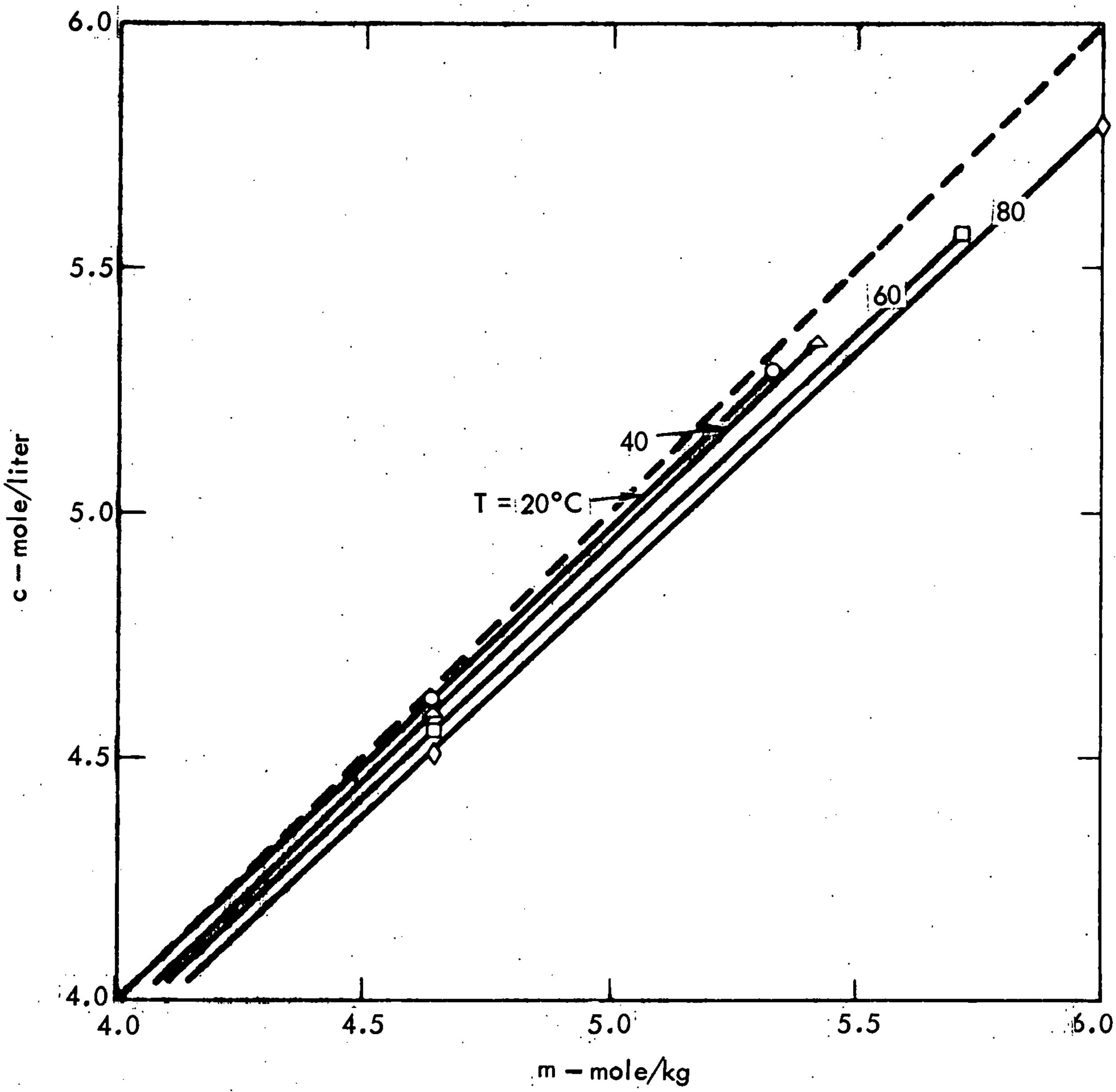

Fig. 1. Relationship between molality and molarity at various temperatures.

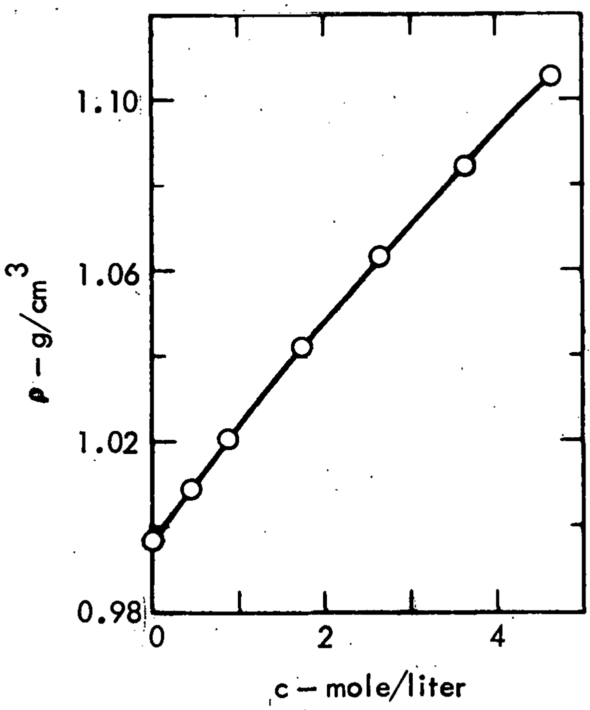

Fig. 2. Density of aqueous LiOH at 25°C.

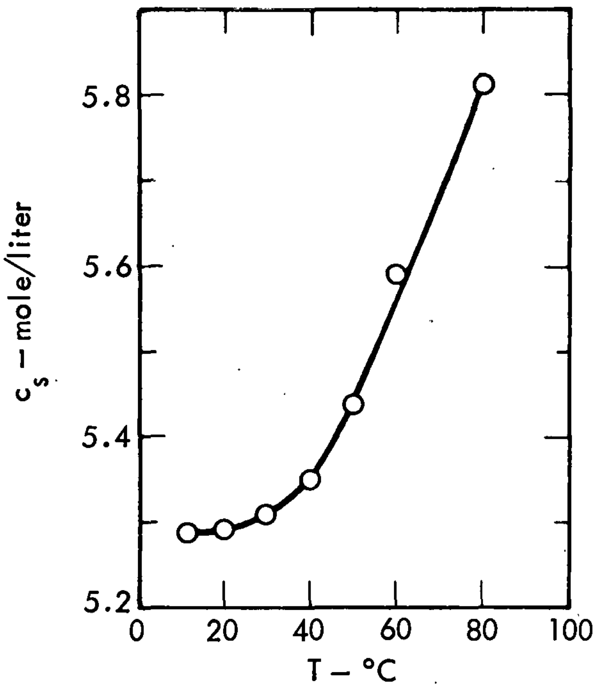

Fig. 3. Solubility of LiOH in water.

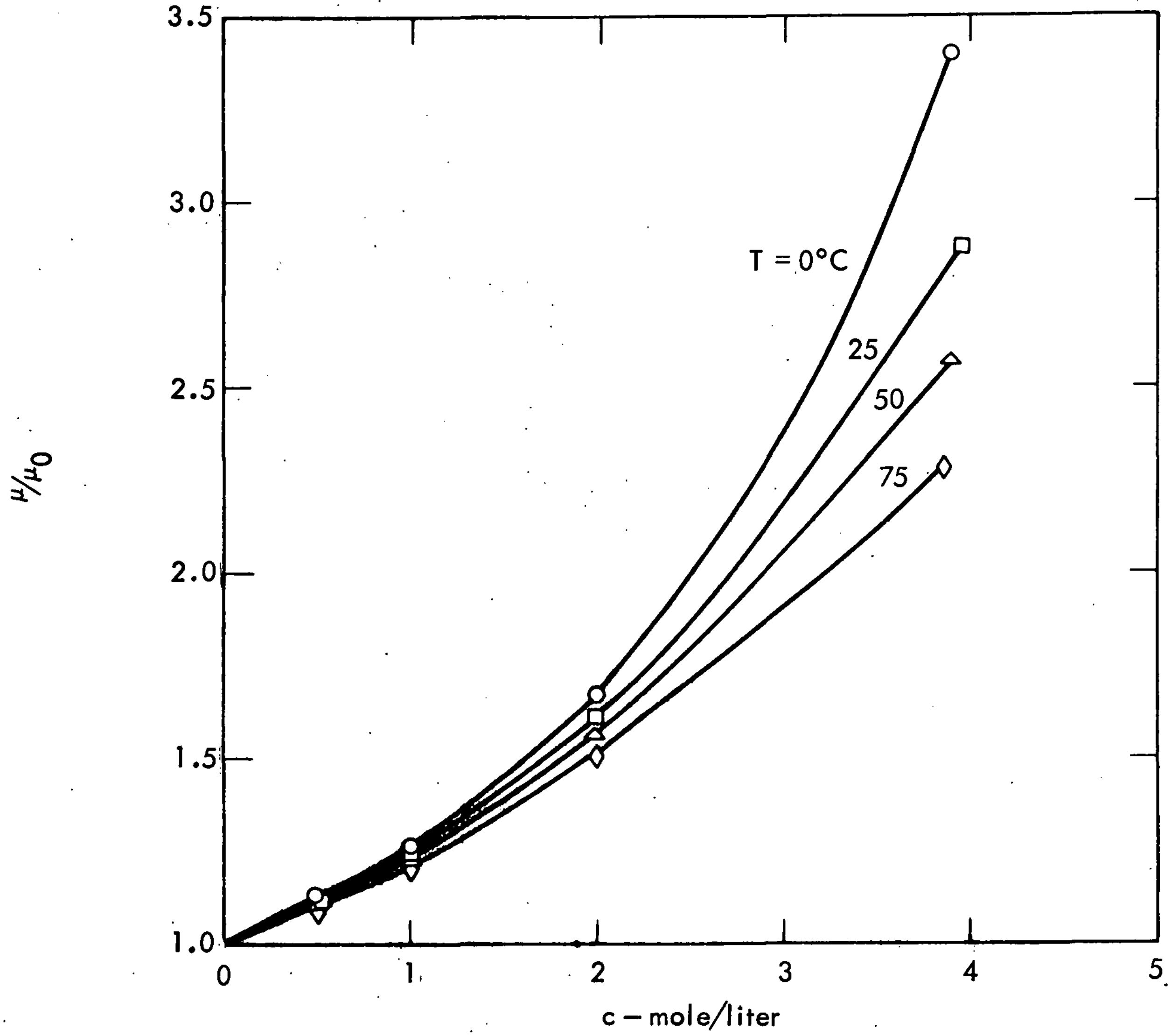

Fig. 4. Dependence of viscosity on concentration at various temperatures.

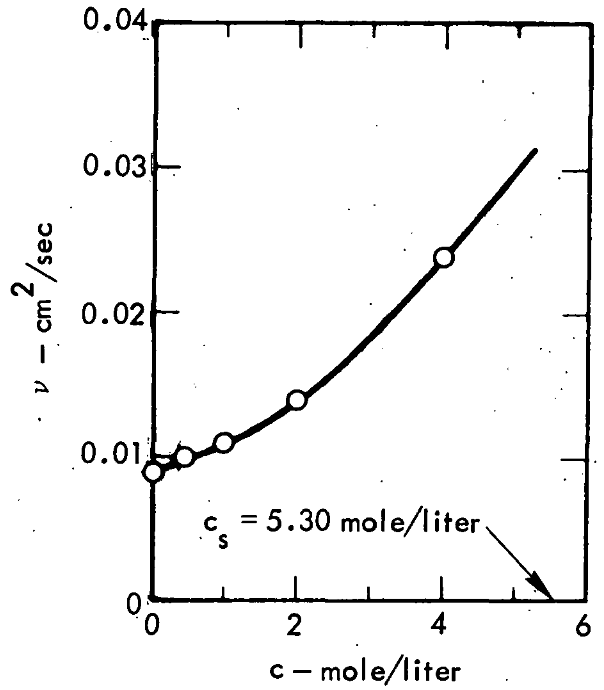

Fig. 5. Kinematic viscosity of aqueous LiOH at 25°C.

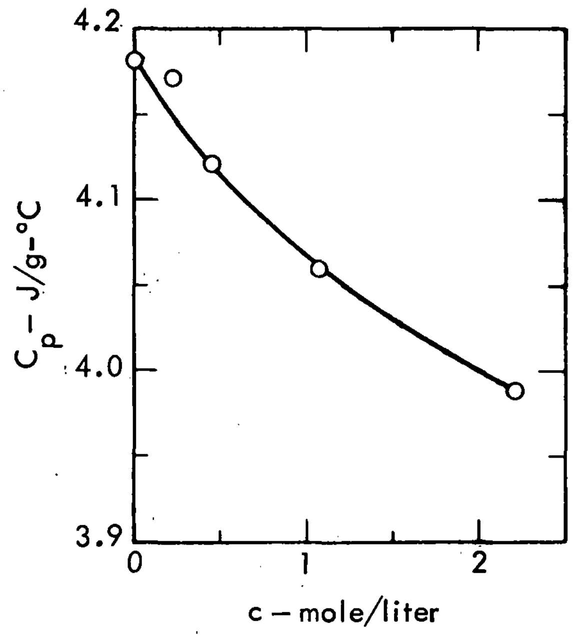

Fig. 6. Heat capacity at constant pressure at 20°C.

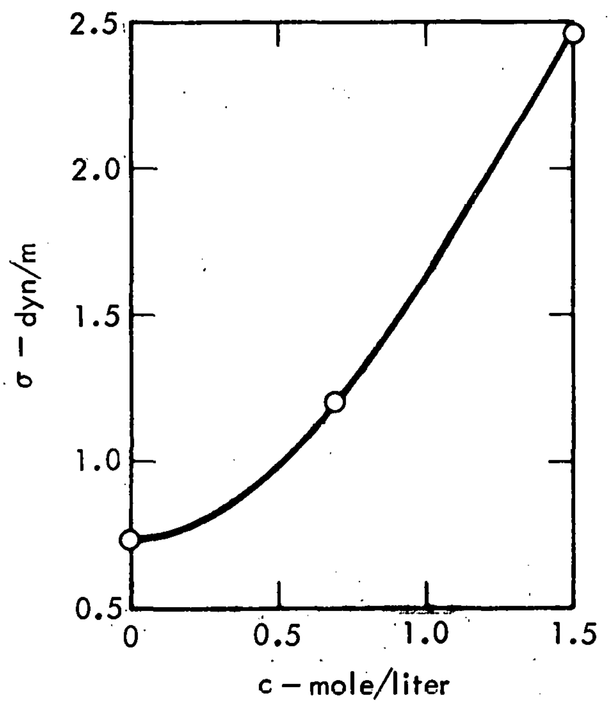

Fig. 7. Surface tension at 18°C.

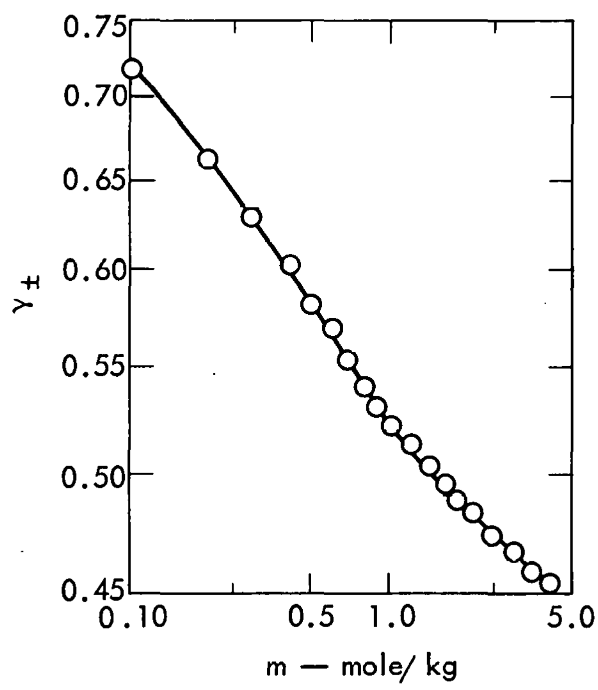

Fig. 8. Mean molal activity coefficient at 25°C.

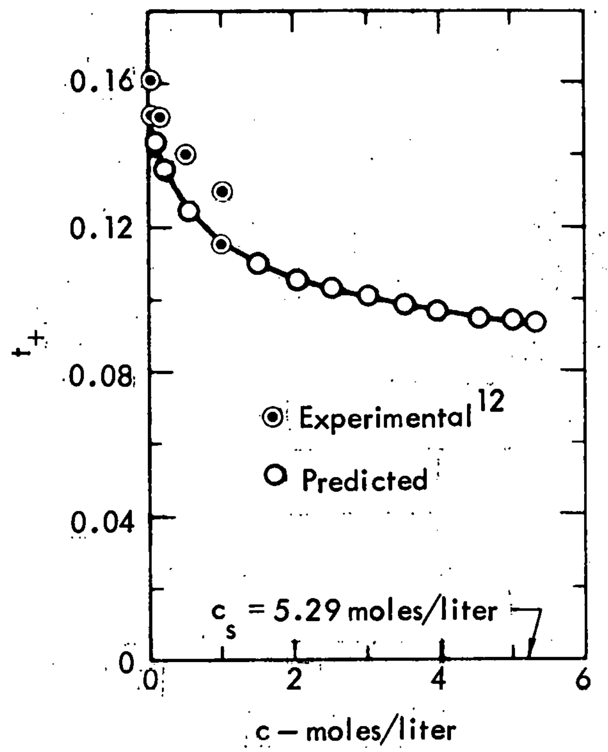

Fig. 9. Transference number at 18°C.

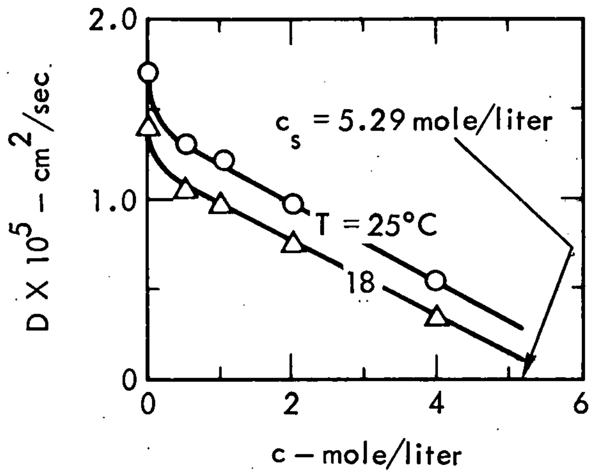

Fig. 10. Diffusion coefficient of LiOH in water.

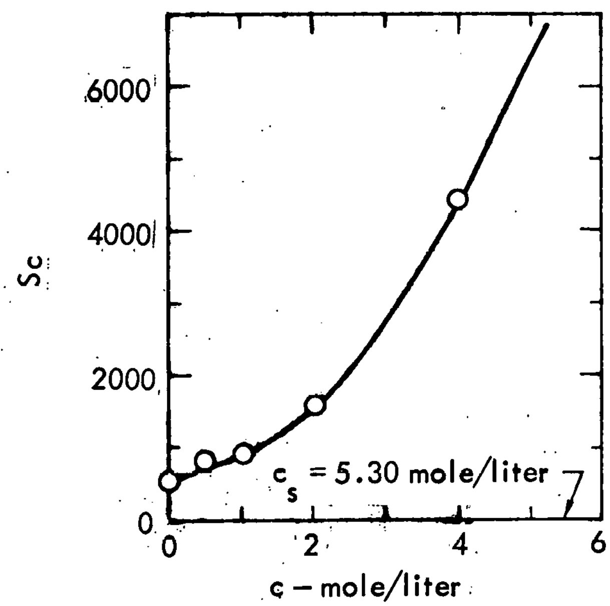

Fig. 11. Schmidt number at 25°C.

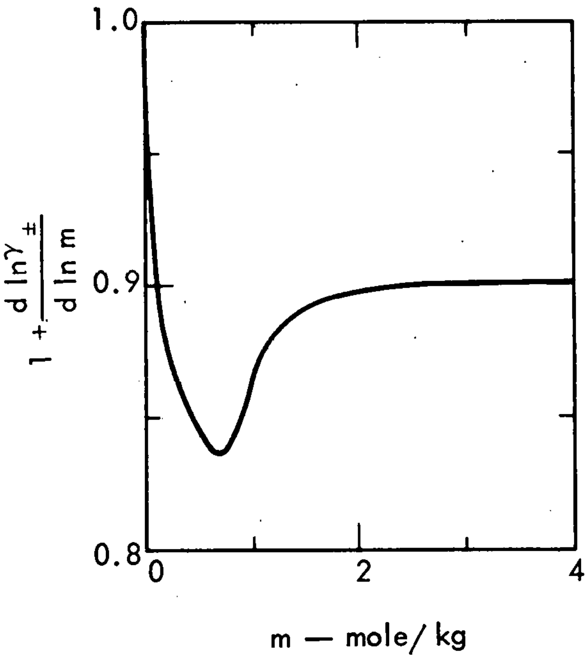

Fig. 12. Variation of mean molal activity coefficient with concentration.

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