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Research Article

Conductivity and Molar Conductivity of LiOD Heavy Water Solution

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Abstract

In cold fusion research, the LiOD heavy water solution has been used as electrolyte in Pd-D_2O electrolytic systems for over 30 years. The conductivity of LiOD not only affects the electrical and thermal properties but also can be used to determine the LiOD concentration. In this paper, conductivities of LiOD heavy water solution (0.01409 $\sim$ 0.09721 mol·L^{-1}) at 10 $\sim$ 70°C were measured. Changes of conductivity κ in mS·cm^{-1} with concentration c in mol·L^{-1} and temperature T in °C can be expressed by the quadratic form: $\kappa = 60.56c - 14.25c^2 + 2.514cT - 0.5459c^2T$. This relationship can be simplified to $\kappa = 123.41c - 27.90c^2$ or $c = 8.1031 \times 10^{-3}\ \kappa + 1.484 \times 10^{-5}\ \kappa^2$ at 25°C.
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Keywords: LiOD heavy water solution, Conductivity, Molar conductivity, Lithium, Cold fusion

1. Introduction

In 1989, Fleischmann and Pons reported anomalous excess heat in the electrolytic system of LiOD heavy water solution with a Pd cathode [1]. Since then, for more than 30 years, many researchers around the world have focused on this system [2]−[5]. Recently, our lab explored excess heat in a Pd-LiOD+D_2O open system, similar to that used by Fleischmann-Pons [1] and Miles [2], with Seebeck envelope calorimetry. During open electrolysis, it was found that the LiOD concentration decreased, while the cell voltage increased with time in the constant current mode. To quickly determine the LiOD concentration, and to understand the electric and thermal behaviors of electrochemical

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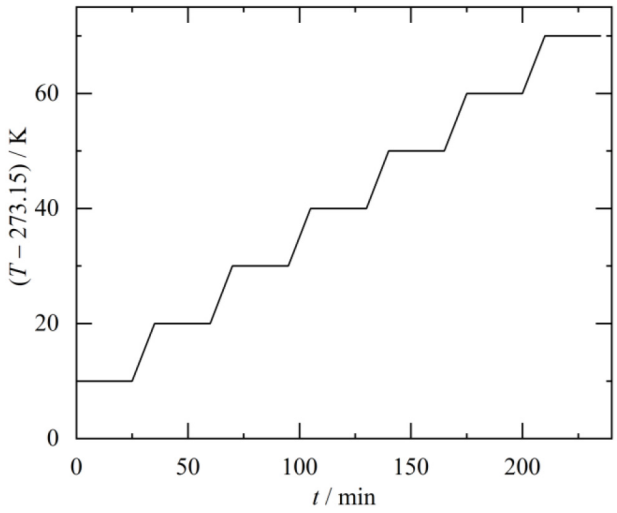

Figure 1. Heating curve of LiOD+D_2O solution.

cells, the electrolyte conductivities of LiOD heavy water solutions under different concentrations and temperatures must be obtained first. However, there was only data of 0.1 mol·L^1 LiOD solution, from 1990 [7]. In this paper, the conductivities of LiOD heavy water solution at various concentrations and temperature are measured. At the same time, the molar conductivities are also given. We hope these data can support future works on the Pd-LiOD+D_2O electrolytic system.

2. Experimental

The LiOD heavy water solution is made before conductivity measurements. The method is as follows. First, weigh 0.14524 g Li_2O powder (Alfa, 99.5%, Order #41832; Lot #S23G011) with balance (Mettler Toledo XPR205R. max. 220 g, d = 0.01 mg) and put it into a 5 mL beaker, then add heavy water (J&K, 99.8 at.%D, Order #261750; Lot #L240U16) and ultrasonically mix for 10 minutes to ensure that Li_2O is completely dissolved. Finally, transfer the solution from the beaker to a volumetric flask with capacity of 10 ± 0.02 mL at 20°C and add heavy water to the graduation line. After these procedures, we get 0.9721 mol·L^{-1} LiOD heavy water solution. Solutions of 0.07279, 0.1126, 0.1215, 0.2411 and 0.4867 mol·L^{-1} are obtained by diluting the 0.9721 mol·L^{-1} LiOD solution. The solution of 0.1126 mol·L^{-1} is further diluted to that of 0.01409, 0.02816 and 0.05630 mol·L^{-1}, respectively. In the end, nine different concentrations of LiOD heavy water solutions are obtained.

Each solution is placed in a centrifuge tube, which is immersed in a water bath (PolyScience AP15R-30-A12E) with temperature stability of ± 0.005°C. The conductivity of the solution is directly measured by Mettler Toledo S230 conductivity meter equipped with InLab®731-ISM using a 4-ring graphite electrode. Its measurement range is 0.01 to 1,000 mS·cm^{-1} at temperature of 0 ∼ 100°C (The unit of conductance is S (Siemens), which is the inverse of Ω (Ohm), i.e., 1 S = 1 Ω^{-1}).

The measurement is started at 10°C and heated at a rate of 1°C per minute, then the temperature is kept at a constant value for 25 minutes at 10, 20, 30, 40, 50, 60 and 70°C, respectively, as shown in Fig. 1. The conductivity meter is set to measure every 5 minutes and it automatically saves the data.

Before the formal measurement, the conductivity meter was calibrated with a conductivity standard solution of 111.3 mS·cm^{-1} at 25°C (Shanghai Inesa Scientific Instrument Co., Ltd, Order #624101; Lot #9028N002102F00023).

Table 1. Conductivities (κ/mS·cm^{-1}) of LiOH aqueous solution at 25°C.

c/mol·L^{-1} / **References**	0.1	0.5
Ritley *et al*. [7]	13.5	82.6
Darken *et al*. [8]	20.51	89.72
This work	19.17 ± 0.07	86.27 ± 0.01

Table 2. Conductivities (κ/mS·cm^{-1}) and activation energies (E_a) of LiOD heavy water solution at different temperatures and concentrations.

T/°C / **c**/mol·L^{-1}	10	20	30	40	50	60	70	E_a/ J·mol^{-1}
0.01409	1.364	1.714	2.103	2.506	2.920	3.343	3.758	13,647
0.02816	2.673	3.357	4.122	4.908	5.736	6.591	7.520	13,863
0.05630	5.273	6.594	8.080	9.615	11.213	12.80	14.460	13,574
0.07279	6.567	8.232	10.074	11.954	13.954	16.034	18.195	13,672
0.1126	9.938	12.437	15.195	18.034	20.954	23.851	26.885	13,369
0.1215	10.692	13.379	16.356	19.425	22.529	25.851	29.230	13,496
0.2411	20.218	25.276	30.839	36.483	42.264	48.149	54.391	13,262
0.4867	38.218	47.690	58.161	68.736	79.253	89.816	101.115	13,040
0.9721	67.6667	84.287	102.977	122.069	141.379	160.345	181.954	13,255

Then we measured another standard solution with conductivity of 12.88 mS·cm^{-1} ± 1.5% at 25°C (Mettler Toledo InLab® Solutions, Order #51350094; Lot #1F325A). The result was 13.28 ± 0.01 mS·cm^{-1} at 25°C and it is consistent with the standard value within 3.1%.

At the same time, we made a LiOH aqueous solution by mixing Li_2O and H_2O and measured conductivities at two different LiOH concentrations at 25°C as shown in Table 1. We found that our results are consistent with the interpolated values based on data in [8] within 6.5%. This means our measurement method is reliable and the sample preparation of LiOD heavy water solution using Li_2O instead of lithium metal as in [2]−[7] is not a problem. However, conductivities of 0.1 and 0.5 mol·L^{-1} LiOH aqueous solution measured by Ritley *et al*. [7] are 34% and 8%, respectively, less than the accepted values in [8]. Therefore, their results of the LiOD heavy water solution are only for reference here.

3. Results

3.1. Conductivity

The conductivities κ of LiOD heavy water solution at different temperatures T and concentrations c are listed in Table 2 and shown in Fig. 2.

Although the linearity is not obvious on the logarithmic scale, it can be observed from Fig. 2(a) that the electrical conductivity increases linearly with increasing temperature at a constant concentration as described by:

$$\kappa = a_0 + a_1 T \tag{1}$$

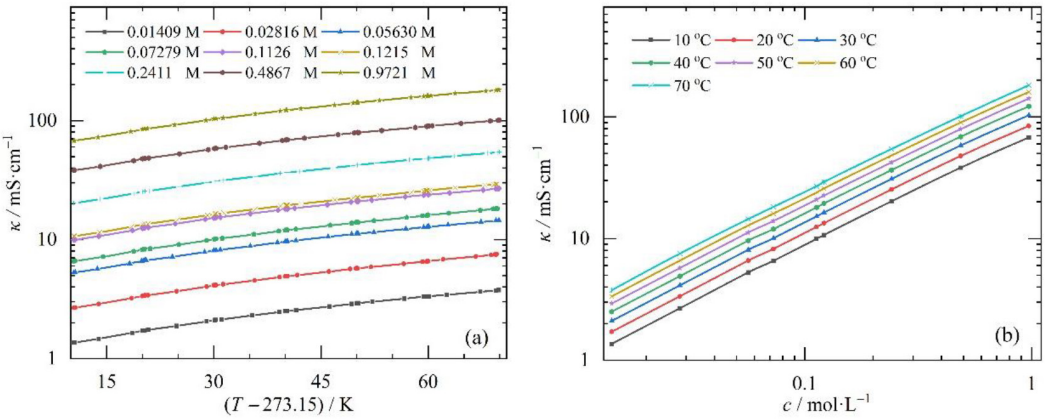

Figure 2. Conductivities of LiOD heavy water solution at different temperatures (a) and concentrations (b).

In addition, we find that a quadratic function can be used to express the relationship between conductivity and LiOD concentration at a constant temperature as shown in Fig. 2(b) and described by:

$$\kappa = b_1 c + b_2 c^2 \tag{2}$$

Considering the simultaneous influences of temperature and concentration, the relationship between these three parameters can be expressed as:

$$\kappa = d_1 c + d_2 c^2 + d_3 cT + d_4 c^2 T \tag{3}$$

where d_1, d_2, d_3 and d_4 are constants. A program is used for fitting the data listed in Table 2 and we obtain the expression:

$$\kappa = 60.56c - 14.25c^2 + 2.514cT - 0.5459c^2 T \tag{4}$$

with T in °C, $R^2 = 0.9997$ and RMSE $= 0.7193$. The fitting results are shown in Fig. 3, where X, Y and Z axes refer to the LiOD concentration (mol·L^{-1}), temperature (°C) and conductivity (mS·cm^{-1}), respectively.

At 25°C, Eq. (4) can be simplified to:

$$\kappa = 123.41c - 27.90c^2 \tag{5}$$

The conductivity of 0.1 mol·L^{-1} LiOD heavy water solution at 25°C is 12.08 mS·cm^{-1}. It is $\sim 40\%$ lower than the conductivity of LiOH aqueous solution at the same alkali concentration as listed in Table 1. On the other hand, this value is 37% higher than 8.8 mS·cm^{-1} in [7]. Because their conductivity at 0.1 mol·L^{-1} LiOH aqueous solution is 34% less than the accepted value in [8], this means their results have prominent negative shifts both for LiOH+H_2O and LiOD+D_2O solutions.

The LiOD concentration can be determined from conductivity based on Eq. (5) at 25°C:

$$c = 8.1031\times10^{-3}\kappa + 1.484\times10^{-5}\kappa^2 \tag{6}$$

This equation can be used to calculate the LiOD concentration from conductivity data in experiments. In crude estimation, the first term is sufficient for dilute solutions.

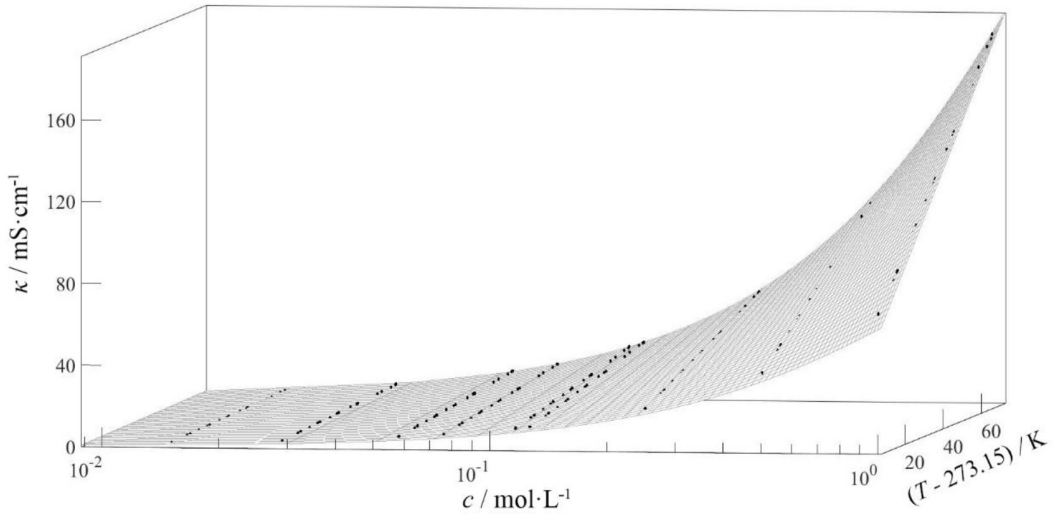

Figure 3. The fitting surface among conductivity, temperature and LiOD concentration.

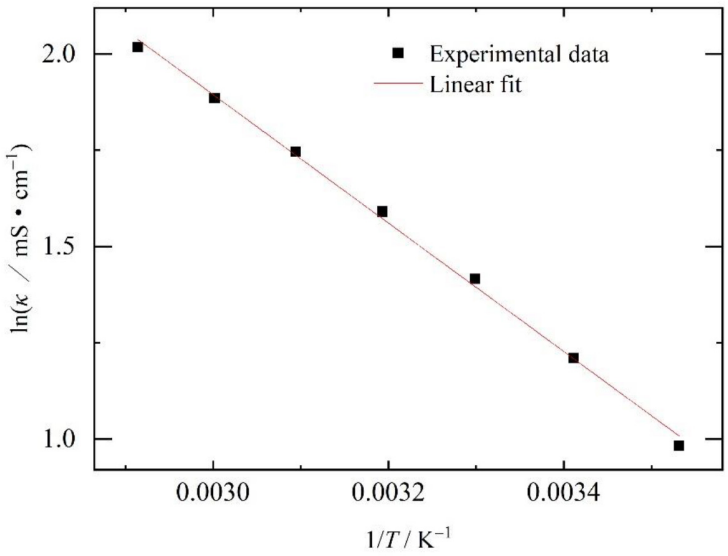

Figure 4. Arrhenius plot of conductivities of LiOD heavy water solution at $10 \sim 70°C$ ($c = 0.02816$ mol·L^{-1}).

On the other hand, the increase of electric conductivity of LiOD+D_2O solution with temperature can be described by the Arrhenius law [9], whose logarithmic form is:

$$\ln\kappa = \ln\kappa_0 - \frac{E_a}{RT} \tag{7}$$

Table 3. Molar conductivity (Λ/S·cm^2·mol^{-1}) of LiOD+D_2O solution at different temperatures and concentrations.

T/°C / *c*/mol·L^{-1}	10	20	30	40	50	60	70
0.01409	96.80625	121.64656	149.25479	177.85664	207.23918	237.26047	266.71398
0.02816	94.92188	119.21165	146.37784	174.28977	203.69318	234.0554	267.04545
0.05630	93.65897	117.12256	143.51687	170.78153	199.16519	227.35346	256.83837
0.07279	90.21844	113.09246	138.39813	164.22586	191.70216	220.27751	249.96565
0.1126	88.25933	110.45293	134.94671	160.15986	186.09236	211.8206	238.76554
0.1215	88	110.11523	134.61728	159.87654	185.42387	212.76543	240.57613
0.2411	83.85732	104.83617	127.90958	151.31895	175.29656	199.70552	225.59519
0.4867	78.52476	97.98644	119.50072	141.22868	162.83748	184.54078	207.75632
0.9721	69.60879	86.7061	105.93252	125.57247	145.43668	164.94702	187.17622

Table 4. The limiting molar conductivities (Λ_0) and slopes of fitting (β) at different temperatures.

T / °C	Λ_0 / S·cm^2·mol^{-1}	β / S·cm^2·L$^{1/2}$·mol$^{-3/2}$
10	99.62	30.87
20	125.07	39.56
30	153.35	49.20
40	182.54	59.56
50	213.06	71.38
60	244.56	84.41
70	276.59	95.52

where κ_0 is the pre-exponential factor, E_a, the activation energy, R, the universal gas constant and T, the absolute temperature in K. Fig. 4. shows the experimental data and the fit of Eq. (7) at 0.02816 mol·L^{-1}. The slope of line enables the determination of activation energy, 13.863 kJ·mol^{-1}. As listed in the last column of Table 2, $E_a = 13.2 \sim 13.6$ kJ·mol^{-1} while $c = 0.01409 \sim 0.9721$ mol·L^{-1}, which are greater than the estimated value of 12.6 kJ·mol^{-1} for LiOH aqueous solution in [9].

3.2. Molar Conductivity

Molar conductivity Λ refers to the electrical conductivity of a solution of different concentrations converted to unit molar concentration:

$$\Lambda = \kappa / c \tag{8}$$

Table 3 lists the calculated molar conductivity at different temperatures and concentrations based on data in Table 2.

The limiting molar conductivity (Λ_0) is defined as the molar conductivity of a solution at infinite dilution. The molar conductivity of a strong electrolyte solution has a linear relationship with the square root of the concentration [10] is:

$$\Lambda = \Lambda_0 - \beta\sqrt{c} \tag{9}$$

where β is constant in S·cm^2·L$^{1/2}$·mol$^{-3/2}$. Λ_0 can be obtained by extrapolation to infinite dilution as shown in Fig. 5. The limiting molar conductivities Λ_0 and slopes *k* obtained from these curves are listed in Table 4.

It can be seen from Fig. 5 and Table 4 that with the increase of temperature, the limiting molar conductivity and the slope of the fitting increase at the same time.

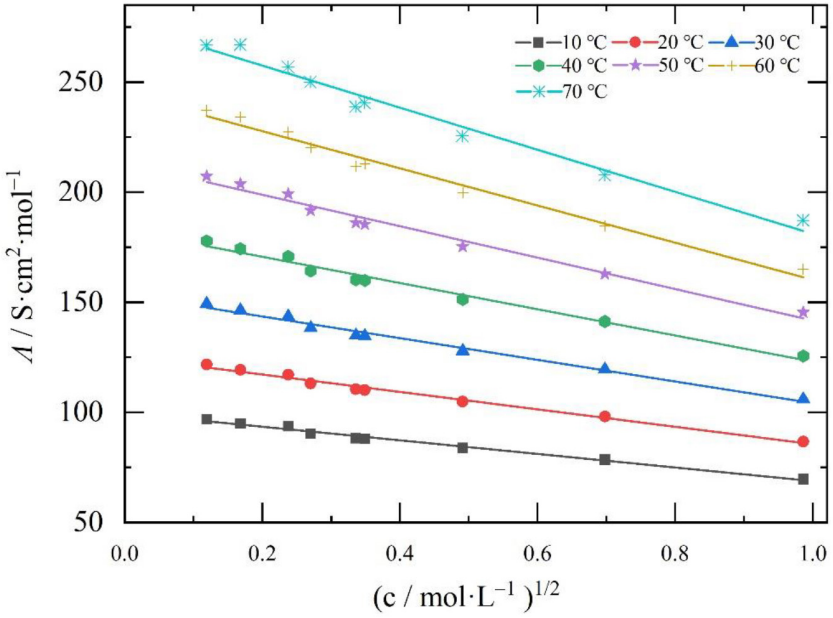

Figure 5. The fitted lines of molar conductivity against the square root of LiOD concentration at different temperatures.

4. Summary

We measured the conductivity of LiOD heavy water solution at temperatures of 10 $\sim$ 70°C and concentrations of 0.01409 $\sim$ 0.9721 mol·L^{-1}, and obtained a quadratic relationship among the conductivity, the temperature, and the concentration. The LiOD concentration can be calculated by equations we obtained using temperature and conductivity. This provides a method for understanding the properties of the Pd-LiOD+D_2O solution in electrolysis experiments.

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