BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 43 1377—1379 (1970)

Measurement of the Lyonium Ion Concentration in a H_2O-D_2O Mixed Solvent by Means of a Glass Electrode[*1, *2]

Hidetake KAKIHANA, Masunobu MAEDA and Toshihiko AMAYA

Research Laboratory of Nuclear Reactor, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo

(Received August 20, 1969)

In the present work, experiments were carried out for the systems of 20, 80 and 99.8% heavy water. It has turned out that the relationship between the emf and the lyonium ion concentration in a H_2O–D_2O mixed solvent can be expressed at 25°C by the so-called Nernst equation within the limits of experimental accuracy of ± 0.1 mV. This means that the lyonium ion concentration in a H_2O–D_2O mixed solvent can be measured with the same experimental accuracy (uncertainty of ± 0.1 mV) as that in light water by the use of a glass electrode.

The measurement of the lyonium ion concentration is of great importance to the studies of solution chemistry in a H_2O–D_2O mixed solvent. Thus far, the concentration of the lyonium ions has been measured with a H_2O–D_2O mixed gas electrode, a quinhydrone electrode, a glass electrode, and several other techniques.

It would, though, be very convenient for the studies of solution chemistry if the lyonium ion concentration in a H_2O–D_2O mixed solvent could be determined accurately with a glass electrode, which is rather cheap and easy to handle. The acidity in a H_2O–D_2O mixed solvent has been measured by several investigators.[1,2] They have standardized the pH meters with light water buffers and determined the values for pL by the addition of some experimental values to the readings of the pH meter. On the other hand, few determinations have been made by the direct measurement of emf with a glass electrode.[3] The determination of the lyonium ion concentration by the direct measurement of emf is of considerable importance to the investigation of complex ionic equilibria in a H_2O–D_2O mixed solvent containing background salt of a high concentration.[4-7]

This work has been undertaken to determine whether the electromotive-force-lyonium-ion dependence is the same as for the hydrogen ion and whether the lyonium-ion concentration can be determined with the same accuracy as the hydrogen-ion concentration by electromotive-force measurements employing a glass electrode.

Symbols

$[L_3O^+]$	concentration of free lyonium ions M (mol/*l*)
E, E_0, E_0', E_{0g}	emf's (mV)
E_j	liquid junction potential
n	deuterium atom fraction
m	equilibrium constant of the following reaction: $1/3H_3O^+ + 1/2D_2O = 1/3D_3O^+ + 1/2H_2O$
$f_{L_3O^+}$	activity coefficient of the lyonium ion in a test solution
$f^g_{L_3O^+}$	activity coefficient of the lyonium ion in a gel layer of a glass electrode
C^g_0	total ion-exchange capacity of a gel layer of a glass electrode
$K_{L_3O^+}$	equilibrium constant of the following reaction: $H_2O(\text{glass}) + L_3O^+(\text{soln.}) = H_3O^+(\text{soln.}) + L_3O^+(\text{glass})$
V	volume of a test solution added (m*l*)
V_0	initial volume of a test solution (m*l*)
v	number of μF passed through a test solution
ω, C	constants

L will be used to mean H and D.

Experimental

Reagents and Apparatus. *All the reagents used* were prepared and analyzed by procedures similar to those described in Refs. 4 and 5.

A Wilhelm-type half cell[8] was used for the emf measurement, and a modified one for constant-current coulometry.

Glass electrodes of the Beckman type No. 40498 were employed.

[*1] Ionic Equilibria in Heavy Water, Part IV.

[*2] Part III: H. Kakihana and M. Maeda, This Bulletin, **43**, 1097 (1970).

1) P. K. Glasoe and F. A. Long, *J. Phys. Chem.*, **64**, 188 (1960).

2) P. Salomaa, L. L. Schaleger and F. A. Long, *J. Amer. Chem. Soc.*, **86**, 1 (1964).

3) R. S. Tobias and M. Yasuda, *J. Phys. Chem.*, **68**, 1820 (1964).

4) H. Kakihana and M. Maeda, This Bulletin, **42**, 1458 (1969).

5) H. Kakihana and M. Maeda, *ibid.*, **43**, 109 (1970).

6) M. Maeda and H. Kakihana, *ibid.*, **43**, 1097 (1970).

7) H. Kakihana, M. Maeda and T. Amaya, to be published.

8) W. Forsling, S. Hietanen and L. G. Sillén, *Acta Chem. Scand.*, **6**, 901 (1952).

Emf was measured with *a Radiometer PHM-4C(Copenhagen)*. The reading accuracy of this instrument is ±0.1 mV.

Silver-silver chloride electrodes were used as references.

A coulometric analyzer(Leeds & Northrup Co., Philadelphia) was employed as a constant-current power source. In the present work, 6.43 mA was used as a constant current.

Procedures. All the measurements were carried out in a paraffin-oil thermostat kept at 25.00±0.01°C and placed in a room thermostated at 25±1°C. All the test solutions were made so as to contain 3M ClO_4^- as an ionic medium by the addition of $NaClO_4$.

The lyonium-ion concentration in a H_2O–D_2O mixed solvent was measured by means of the cell:

$$\mathrm{Ref}|L\,\mathrm{M}\ \mathrm{L}^+,\ (3-L)\,\mathrm{M}\ \mathrm{Na}^+,\ 3\,\mathrm{M}\ \mathrm{ClO_4}^-|\mathrm{GE} \qquad \text{(A)}$$

where GE denotes a glass electrode, and Ref, the reference half cell:

|3M $NaClO_4$ in a H_2O–D_2O mixed solvent|2.99M $NaClO_4$ and 0.01M $AgClO_4$ in light water|AgCl-Ag

The lyonium-ion concentration in the cell (A) was varied by two procedures; one was the technique of constant-current coulometry, whose experimental details are similar to those presented in Ref. 9, and the other was the technique of titration by the use of a buret.

A steady emf was usually attained within ten minutes. This means that the time required to reach equilibrium is the same as that for the system of light water. During the measurements, a test solution was stirred by a vigorous stream of nitrogen gas which had been purified by leading through a H_2O–D_2O mixed solvent and 3M $NaClO_4$ in a H_2O–D_2O mixed solvent.

Results

1) Relationship between the emf and the Lyonium-ion Concentration. The emf-lyonium-ion dependence was derived on the basis of the assumptions that a gel layer of a glass surface acts as a cation exchanger,[10,11] which adsorbs exclusively the ions of hydrogen isotopes when a glass electrode is brought into equilibrium with a H_2O–D_2O mixed solvent, that H^+ and D^+ ions are present in the forms of H_3O^+, H_2DO^+, HD_2O^+, and D_3O^+ in a H_2O–D_2O mixed solvent,[12,13] and that the rule of the geometric mean[14] is applicable as a first approximation to acid-base equilibria in a H_2O–D_2O mixed solvent. On the basis of the above assumptions, it was found that the emf of a glass electrode could be represented approximately by Eq. (1a):

$$E = E_0' - \boldsymbol{R}T/F(\ln C_0^{\mathrm{g}}) + \boldsymbol{R}T/F\Bigg(\ln\Bigg(\frac{f_{\mathrm{H_2O^+}}(1-n)^3}{f^{\mathrm{g}}_{\mathrm{H_2O^+}}(1-n+nm)^3} + \frac{f_{\mathrm{D_3O^+}}K_{\mathrm{D_3O^+}}n^3m^3}{f^{\mathrm{g}}_{\mathrm{D_3O^+}}(1-n+nm)^3} + \frac{3f_{\mathrm{HD_2O^+}}K_{\mathrm{HD_2O^+}}(1-n)n^2m^2}{f^{\mathrm{g}}_{\mathrm{HD_2O^+}}(1-n+nm)^3} + \frac{3f_{\mathrm{H_2DO^+}}K_{\mathrm{H_2DO^+}}(1-n)^2nm}{f^{\mathrm{g}}_{\mathrm{H_2DO^+}}(1-n+nm)^3}\Bigg)\Bigg) + \boldsymbol{R}T/F(\ln[\mathrm{L_3O^+}]) \qquad (1a)$$

Since the first, second, and third terms on the right-hand side are constant provided that the temperature of the cell, the activity coefficients of the lyonium ions, and the deuterium atom fraction in a H_2O–D_2O mixed solvent are held constant, Eq. (1a) can be restated in this form:

$$E = E_0 + \boldsymbol{R}T/F(\ln[\mathrm{L_3O^+}]) \qquad (1b)$$

On the other hand, the emf of a cell with a liquid-junction that corresponds to cell(A) is given by:

$$E = E_0 + \boldsymbol{R}T/F(\ln[\mathrm{L_3O^+}]) + E_{\mathrm{J}} \qquad (2a)$$

On the basis of the assumption that Henderson's equation for a continuous-mixture boundary and the rule of the geometric mean[14] are applicable as a first approximation to equilibria in which the ions of hydrogen isotopes take part, it was proved that the liquid-junction potential for the system of a 3M $NaClO_4$ solution of a H_2O–D_2O mixed solvent was approximated by a linear function of the lyonium-ion concentration. Therefore, the emf of a cell with a liquid-junction is given by:

$$F = E_0 + \boldsymbol{R}T/F(\ln[\mathrm{L_3O^+}]) + \omega[\mathrm{L_3O^+}] \qquad (2b)$$

Eq. (2b) is expressed at 25°C as follows:

$$E = E_0 + 59.15 \log[\mathrm{L_3O^+}] + \omega[\mathrm{L_3O^+}] \qquad (3)$$

2) Experimental Proof of the Reliability of Eq. (3). In this section, we will examine experimentally whether Eq.(3), which holds as a first approximation, is true within the limits of experimental error. 20, 80, and 99.8% heavy-water systems were used as the solvents. Since the liquid-junction potential for the system of light water containing 3M $NaClO_4$ has been found to be negligible in the acid region less than 0.01M[15] it was examined experimentally whether the $E=E_0+59.15\log[\mathrm{L_3O^+}]$ term in Eq.(3) held within the limits of experimental accuracy. It was then examined, at an acidity of more than 0.01M, whether the liquid-junction potential in the cell (A) had a linear dependence on the lyonium-ion concentration.

When the liquid-junction potential is negligible, Eq.(3) is transformed as follows:[16]

$$(V_0+V)\times 10^{E/59.15} = C(V_0(\mathrm{L})_0 - V(\mathrm{OL})) \qquad (4)$$

when an alkaline solution is added from a buret to a test solution, and

$$V_0 \times 10^{E/59.15} = C(V_0(\mathrm{L})_0 - v\times 10^{-3}) \qquad (5)$$

---

[9] L. Ciavatta, *Ark. Kemi*, **20**, 417 (1962).

[10] T. Okada, T. Nishi and H. Takahashi, *Kogyo Kagaku Zasshi*, **61**, 931 (1958).

[11] N. Kishimoto, H. Matsushita, H. Hironaka and H. Maruyama, *Denki Kagaku*, **30**, 355 (1962).

[12] V. Gold, *Proc. Chem. Soc.*, **1963**, 141.

[13] K. Heinzinger and R. E. Weston, *J. Phys. Chem.*, **68**, 744 (1964).

[14] J. Bigeleisen, *J. Chem. Phys.*, **23**, 2264 (1955).

[15] G. Biedermann and L. G. Sillén, *Ark. Kemi*, **5**, 425 (1952).

[16] G. Gran, *Analyst*, **77**, 661 (1952).

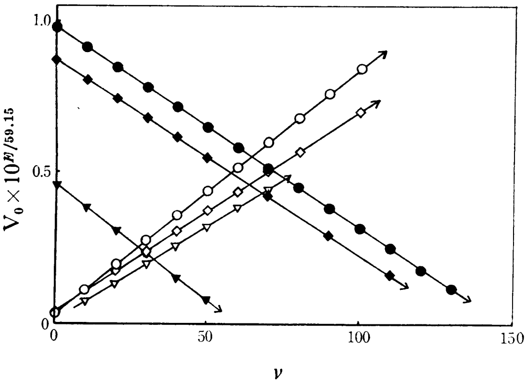

Fig. 1. $V_0\times10^{E/59.15}$ as a function of microfaraday.
▼, ●, ◆ generation of OL^- ion for the system of 99.8% heavy water, 80% heavy water and 20% heavy water, respectively.
▽, ○, ◇ generation of L_3O^+ ion for the system of 99.8% heavy water, 80% heavy water and 20% heavy water, respectively.

when an alkali is generated by constant-current coulometry.

A glass-electrode function in the higher acid region was investigated by the titration method, and one in the lower acid region was investigated by constant-current coulometry capable of generating a very small amount of acid or alkali.

If Eq. (3) is valid, plots of $(V_0+V)\times10^{E/59.15}$ as a function of V, or of $V_0\times10^{E/59.15}$ as a function of γ, should show straight lines.

The results obtained by means of constant-current coulometry for the systems of 20, 80 and 99.8% heavy water are visualized in Fig. 1.

From this figure, it is obvious that the experimental plots show straight lines. In addition, the values for E_0 calculated at each point were kept constant within the exprimental error of ±0.1 mV, and there was no systematic error in the value of E_0. These things were also true for the results obtained by the titration method.

Next, it was examined experimentally, by plotting$(E-59.15\times\log[L_3O^+])$ as a function of $[L_3O^+]$, whether the liquid-junction potential could be approximated as a linear function of the lyonium-ion concentration. The experiments were carried out by the titration method. The results obtained thereby are pictured in Fig. 2. This figure shows that the liquid-junction potential for the system of a H_2O-D_2O mixed solvent is expressed approximately as a linear function of the lyonium-ion concentration.

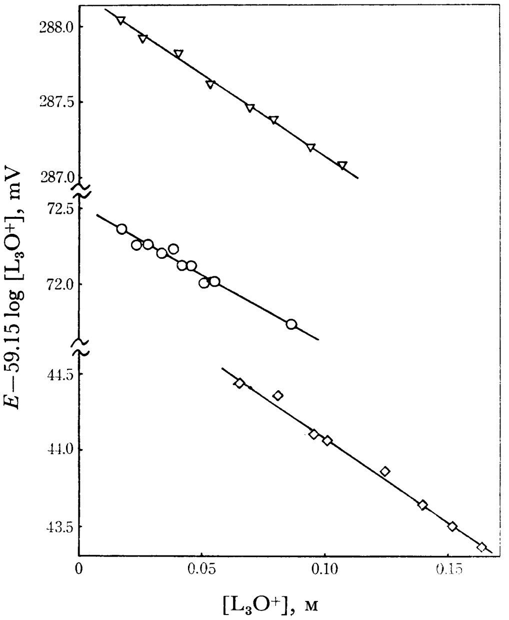

Fig. 2. $(E-59.15\log[L_3O^+])$ as a function of $[L_3O^+]$;
▽, for the system of 99.8% heavy water;
○, 80% heavy water; ◇, 20% heavy water

From the slopes of the straight lines, the liquid-junction potentials for the systems of 20, 80 and 99.8% heavy water were found to be approximated by $-13._2\times[L_3O^+]$, $-8._4\times[L_3O^+]$, and $-10._9\times[L_3O^+]$mV respectively.

From the results described above, it has been found that Eq.(3) is valid within the experimental error of ±0.1 mV.

Conclusion

In this work, it has been verified that the relationship between the emf of a glass electrode and the lyonium-ion concentration in a H_2O-D_2O mixed solvent is given at 25°C by the so-called Nernst equation with an experimental accuracy of ±0.1 mV. This means that the lyonium-ion concentration in a H_2O-D_2O mixed solvent can be measured with the same experimental accuracy (an uncertainty of ±0.1 mV) as that in light water by the use of a glass electrode.