

## On the Liquid Junction Potential

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The tip potential of microelectrode widely used in an electrophysiological experiment is a sort of liquid junction potential or diffusion potential. An applicability of Henderson's equation for the interpretation of the tip potential was recently discussed by Kawabata and Nakamura (1). It must, however, be noted that the "continuous mixing boundary" between the two electrolyte solutions is assumed in deriving the equation. Although we have no method directly to assure this boundary, it is usual to relate the practice and theory by comparing the experimental points with a theoretical curve. In the present paper, the liquid junction potential between a hydrochloric acid in a beaker and potassium chloride solution in a glass capillary was measured. It was compared with the curve drawn by the Henderson's equation, as Cumming already reported in 1912 (2), in order to criticize the previous reports from this laboratory (1, 3, 4, 5,).

### METHODS

An arrangement to obtain the electro-motive force is shown in the Fig. 1. The agar-bridge was not used for the electrical connection to avoid an unexpected result caused by the negative charge of the agar. The glass capillary made by a conventional puller and filled with the potassium chloride (KCl) solution was connected to the end of three-way glass tube, which was also filled with the same solution. The concentration of KCl was ranged between 3 and 0.015 molar. (See the Table 1 below). If the diameter of the capillary-tip were less than  $1 \mu$ , the potential difference would frequently be resulted between the two KCl solution, the one is in the capillary and the other is at the outside, having the same concentration (3). The tip was, therefore, artificially broken and the used capillary had the tip-diameter of 3~5 micra.

A balancing circuit of the tube-potentiometer was the Du Bridge and Braum's one using the special tube for the measurement of the weak current (Toshiba UX-54A), and its detail had previously reported (2). The relationship between the applied voltage and the deflection of galvanometer was strictly linear, with the input series-resistance of 10 megohms. When the input was 1 mV., the maximum deflection on the scale was 26 mm. The measurements were made at the room temperature between 20° and 23°C.

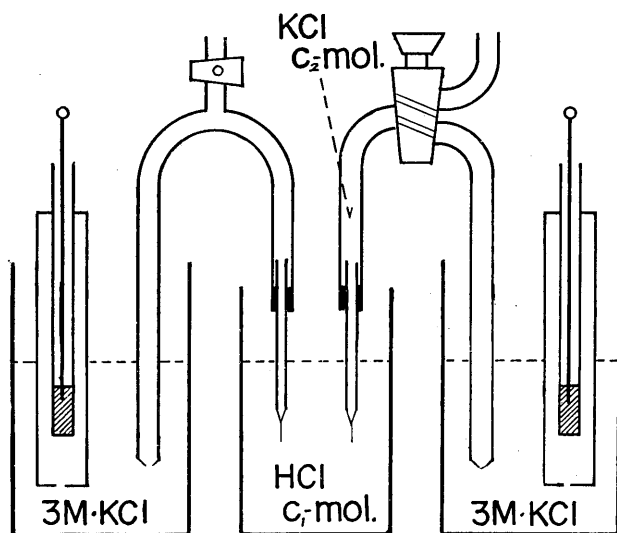


Fig. 1 Simplified Diagram of Recording Arrangement for the Liquid Junction Potential between HCl and KCl Solution. Agar is not used in the Bridge, because of its negative Charge.

## RESULTS

The experimental results are summarized in the following table.

In the Table 1, the first and the second columns ( $C_1$  and  $C_2$ ) are the concentrations of HCl and KCl solution, in millimolar. As is well known, one of the factors determining the liquid junction potential between the two electrolyte solutions is an ionic activity of respective solution and not a concentration. Those activities in the used

Table 1 The electro-motive force measured with the arrangement shown in the Fig. 1.

$C_1$ (mM)	$C_2$ (mM)	$\frac{a_1}{a_2}$	measured potential (mV)		
3	15	0.22	11.8	13.0	—
15	//	1.0	20.7	22.0	19.3
150	//	8.8	48.0	52.0	48.0
5	50	0.12	6.7	8.0	8.7
50	//	1.1	20.0	25.6	23.3
500	//	9.3	50.0	47.3	44.7
3	150	0.025	3.6	—	2.8
15	//	0.13	9.3	6.0	6.7
150	//	1.0	22.0	20.0	20.7
5	500	0.015	1.3	1.3	—
50	//	0.014	5.3	4.7	8.7
500	//	1.17	16.7	17.3	22.0

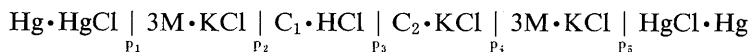
solutions are quoted from a monograph of physical chemistry (6), and the ratio is shown in the third column.

Each figure of the electro-motive forces was obtained with one pair of the glass capillaries, the one was filled with 3M·KCl solution and the other, with its

solution having the concentration shown in the second column. When both the concentration of HCl in the beaker and that of KCl in the capillaries were unchanged, the resulted figures well agreed in each measurement, and there was no need of repeating the experiment under the same condition.

### DISCUSSION

The following is the scheme of the electro-motive force of the cell as shown in the Fig. 1.



In this scheme, the vertical line denotes the boundary where the electro-motive force would be generated and is represented by these symbols as  $p_1$  or  $p_2$  etc. If the two calomel-electrodes at the end had the same physico-chemical character,  $p_1$  and  $p_5$  would be cancelled out mutually and they would not be included in the measurement. That we cannot practically get such electrodes does not matter, because those are eliminated by the following procedure. When the KCl ( $\text{C}_2$ -molar) is used instead of the HCl ( $\text{C}_1$ -mol.) solution,  $p_3$  is zero,  $p_2$  and  $p_4$  are cancelled out together and the resulted potential is the algebraic sum of  $p_1$  and  $p_5$ . This potential is a standard one (O-potential) in the present experiment. The potential values in the above table, therefore, shows the algebraic sum of  $p_2$ ,  $p_3$  and  $p_4$ .

The liquid junction potential between the two electrolyte solutions is determined by the mobilities and the activities of ions. In the present case, as the mobility of K-ion is approximately the same with that of Cl-ion, the potential between the two KCl-solutions ( $p_4$  in the above scheme) can be neglected. Those between the 3M·KCl solution and the used HCl solutions ( $p_2$ ) are calculated from Henderson's equation and shown in the Table 2. It must be noticed that the potential cannot be neglected when the concentration of HCl solution is more than 50 mM.

Table 2 The calculated liquid junction potential between 3M·KCl and HCl solution. The ionic activity coefficient of the former is estimated to be 0.57 (KCl-side is positive).

Concentration of HCl (mM.)	3	5	15	50	150	500
Activity Coefficient	1.0	1.0	1.0	0.9	0.79	0.76
L. J. Potential (mV.)	<1	<1	1.6	3.5	6.7	13.2

The theoretical curve drawn by the equation concerning the arbitral KCl and HCl solution is shown in the Fig. 2; where, and in the above Table 2 also, the potential at the KCl-side is higher than that at the HCl. The potential, however, listed in the Table 1 is not the liquid junction potential between the respective

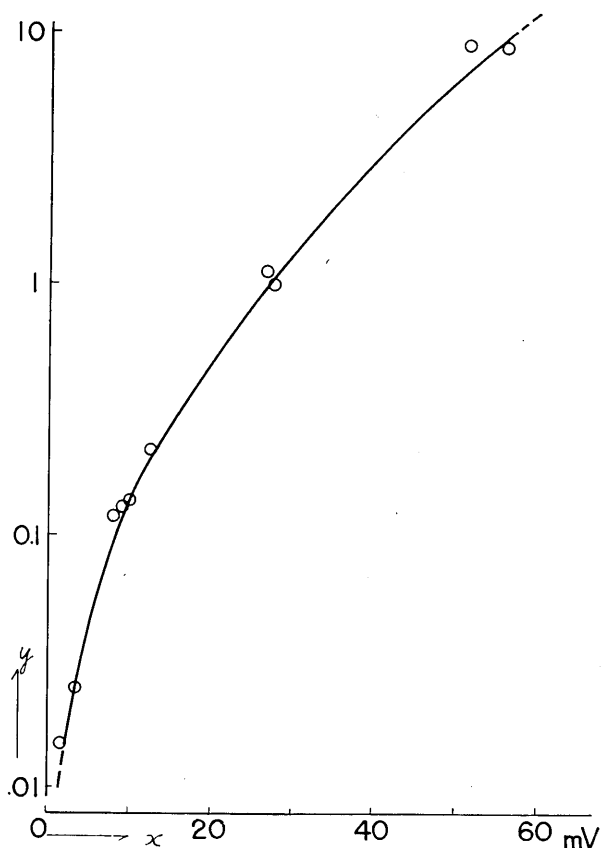


Fig. 2 Relationship between the Liquid Junction Potential

(Abscissa) and Activity Ratio (Ordinate).  $y = \frac{a_1}{a_2}$ ,  $a_1$  and  $a_2$  are the Activities of HCl and KCl Solution, respectively.  $k = \frac{u_1}{u_2} + 1$ ,  $k' = \frac{u_1}{u_2} - 1$ ;  $u_1$  and  $u_2$  are the Mobilities of H and K-ion, resp. Those of Cl and K-ion are assumed to be the same.

The curve is the theoretical one drawn by the Henderson's equation. The circles represent the experimental points. These are the average of 2 or 3 measurements.

HCl and KCl solution, but the potential difference of the two, the one is the potential just mentioned and the other is the liquid junction potential between that HCl and the 3M·KCl solution. As the direction is opposite and the KCl-side is positive in both, the addition of the latter listed in the Table 2 to the respective figure in the Table 1 gives the former experimentally obtained. The open circles in the Fig. 2 represent these results and the coincidence with the theoretical curve is good.

#### ADDENDUM (CALCULATION)

The Henderson's equation of the liquid junction potential between the electrolyte solution I and II is:

$$E = \frac{RT}{F} \cdot \frac{\sum u_i(a_2 - a_1)}{\sum u_i z_i(a_2 - a_1)} \ln \frac{\sum u_i z_i a_1}{\sum u_i z_i a_2} \dots \dots \dots (1)$$

when the solution I is HCl and II, KCl:

$$E = \frac{RT}{F} \cdot \frac{(u_1 a_1 - v a_1) - (u_2 a_2 - v a_2)}{(u_1 a_1 + v a_1) - (u_2 a_2 + v a_2)} \ln \frac{u_1 a_1 + v a_1}{u_2 a_2 + v a_2} \dots \dots \dots (2)$$

where, not including the dimension;

- $R$ : gas constant ( $3.8144 \times 10^7$ )                       $u_1$ : the mobility of H-ion (315)
- $T$ : the absolute temperature                               $u_2$ : the mobility of K-ion (64.6)
- $F$ : Faraday constant (96488)                               $v$ : the mobility of Cl-ion (65.15)

Substituting these figures, and assuming  $u_2 = v$ ;

$$E(mV) = 57.7 \frac{k' y}{k y - 2} \log \frac{k y}{2} \dots\dots\dots (3)$$

(where:

$$y = \frac{a_1}{a_2} \quad k = \frac{u_1}{u_2} + 1 \quad k' = \frac{u_1}{u_2} - 1 \quad t = 18^\circ\text{C})$$

In the above equation 3,  $a_1$  and  $a_2$  are the ionic activities of HCl and KCl solution, respectively. Each is equal to the concentration times activity coefficient. The curve in the Fig. 2 is drawn from this equation.

Another calculation to investigate the applicability of the Henderson's equation to the present experiment is as follows, i.e. in equation 3, changing the variable as;

$$Y \equiv \frac{k}{2} y \quad \text{and rearranging,}$$

$$E \cdot \frac{k}{k'} \left(1 - \frac{1}{Y}\right) = 57.7 \log Y \dots\dots\dots (4)$$

Introducing another variable and a constant as,

$$X \equiv E \left(1 - \frac{1}{Y}\right) \quad k'' \equiv 57.7 \frac{k'}{k} \doteq 38.0$$

$$X = k'' \log Y \dots\dots\dots (5)$$

From the equation 5, it is clear that the relationship between  $X$  and  $\log Y$  is linear. The straight line in the Fig. 3 shows this relationship and the circles, experimental points obtained from the results in the Tables 1 and 2 by the above calculation. In the low range of activity ratio, small variation of the measured potential affects the calculated  $X$ -value greatly. As an accuracy of the present potential measurement was estimated to be 1 millivolt, the disagreement of the lowest point in the figure could not be ruled out.

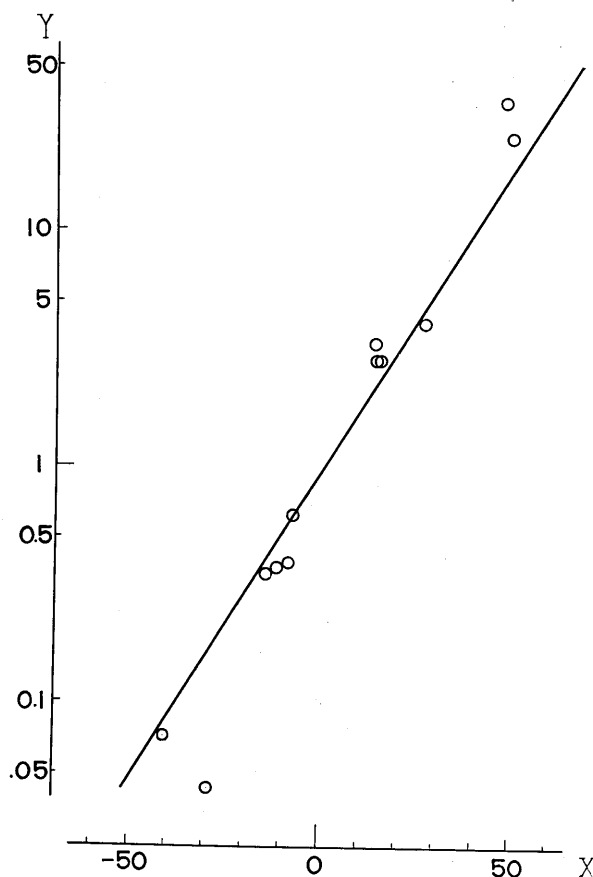


Fig. 3 Using the appropriate variables, the equation 3 in the text can be modified as straight line in this figure. Y (Oridinate) =  $\frac{u_1+u_2}{2u_2} y$  X (Abscissa) =  $E\left(1 - \frac{1}{Y}\right)$ ,  $k'' = 57.7 \frac{u_1-u_2}{u_1+u_2}$ . The symbols  $y$ ,  $u_1$  and  $u_2$  are the same with Fig. 2. The circles represent the experimental points.

### SUMMARY

A liquid junction potential between the HCl solution in a beaker and KCl in glass capillary was measured with a tube-potentiometer. When the concentration of HCl was more than 0.05 molar, the potential generated by 3 mol. KCl solution could not be neglected (Table 2). The experimental results well agreed with a theoretical curve drawn by Henderson's equation.

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## REFERENCES

1. KAWABATA, G. and Y. NAKAMURA: On the Henderson's Equation concerning the Tip-Potential of Microelectrode. *Bull. Yamaguchi Med. School*, **12**; 1-4, 1965.
2. CUMMING: *Trans. Faraday Soc.*, **8**; 1912. (cited from 7)
3. KAWASAKI, M. and M. OKI: Tip-Potential of the Microelectrode and the Intracellular Potential of *Nitella Flexilis*. *Bull. Yamaguchi Med. School*, **8**; 329-333, 1951.
4. TANIKUNI, K., K. FUJIMOTO and G. KAWABATA: On the Measurement of Intracellular Potential. Part 1. The Potential Changes at the Ag-AgCl Electrode. Part 2. The Liquid Junction Potential of Microelectrode. *J. Physiol. Soc. Jap.*, **27**; 446-453, 1965. (in Japanese)
5. Dittos: Part 3. The Liquid junction Potential of the Protein Solution. *ibid*, 454-462.
6. ROBINSON, R. A. and R. H. STOKES: *Electrolyte Solution*. Butterworth Sci. Pub., London, 1955.
7. YOSHIMURA, H.: On the Diffusion Potential. In the "*Theory and the Measurement of pH.*", Maruzen Co., Tokyo, 1942 (in Japanese).