Communication to the Editor

Comparison of Polarographic Diffusion Current with that calculated using Tracer-Diffusion Coefficient

by

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It has been frequently pointed out that the tracer-diffusion coefficient of an ion present in vanishingly small amounts in a solution of another electrolyte can be identified with the polarographic diffusion coefficient¹⁻⁴⁾ and is applicable to the Ilkovic equation for the polarographic diffusion current, as the diffusion conditions in both cases are similar. On this stand-point Wang and Polestra⁵⁻⁶⁾ measured the tracer-diffusion coefficients of Zn(II), Pb(II) and Tl(I) ions in various supporting electrolytes and examined the validity of the modified Ilkovic equation. But their examination was made only in one concentration of the supporting electrolyte with varying the capillary characteristics. In the present work the diffusion currents of Tl(I), Pb(II) and Zn(II) ions were measured with the varying concentrations of the supporting electrolytes under the same experimental conditions as those of their works and the results were compared with the calculated values by the modified Ilkovic equation using the tracer-diffusion coefficient measured by them.

In the case of a single salt present at a concentration of c moles per liter, the tracer-diffusion coefficient of an tracer ion is given by the following formula according to Onsager equation⁷⁾

$$D_j = D_j^\circ - Bc^{1/2} \quad (1)$$

where D is the diffusion coefficient at any concentration and D° that at infinite dilution, and j represents the diffusing ion and B a constant containing the term of the relaxation effect due to the ion-ion interaction. The relationship between the polarographic diffusion current and the concentration of supporting electrolyte can be therefore derived in the following manner. When D_j° is larger than B and the concentration of supporting electrolyte is smaller than about 1 mole per liter, the equation (1) takes approximately the following form.

$$D_j^{1/2} = D_j^{\circ 1/2} - \frac{1}{2} D_j^{\circ -1/2} Bc^{1/2} \quad (2)$$

When this equation is substituted into the following modified Ilkovic equation

$$i_d = 607nD_j^{1/2} c_j m^{2/3} t^{1/6} \frac{(1 + AD_j^{1/2} t^{1/6})}{m^{1/3}} \quad (3)$$

the diffusion current is given by the simplified form

$$i_d = i_d^\circ - \alpha c^{1/2} \quad (4)$$

where

$$i_d^\circ = 607nD_j^{-1/2}c_jm^{2/3}t^{1/6} + 607nAD_j^{-1/2}c_jm^{1/3}t^{1/3} \quad (5)$$

$$\alpha = \frac{1}{2}607nD_j^{-1/2}Bc_jm^{2/3}t^{1/6} + 607nABc_jm^{1/3}t^{1/3} \quad (6)$$

In the above equations the numerical value of the constant A differs by the authors, as well known, and is assigned to be 17 or 39 $\text{mg}^{1/3}\text{cm}^{-1}$.

Unless the ionic species change their forms with variation of the concentration of supporting electrolyte, it is expected that the diffusion current decreases proportionally with the square root of the concentration of supporting electrolyte.

The measurements of average diffusion current were made by using blunt and vertical capillaries in 0.002 mole/liter TlCl and PbCl_2 and 0.005 mole/liter ZnCl_2 aqueous solutions containing potassium chloride of various concentrations as supporting electrolyte and 0.01% gelatine as maximum suppressor. The capillary characteristics of the dropping mercury electrode were $m=1.612 \text{ mg/sec}$, $t=5.14 \text{ sec}$ in the case of Tl(I) ion, $m=1.618 \text{ mg/sec}$, $t=5.00 \text{ sec}$ in the case of Pb(II) ion and $m=1.612 \text{ mg/sec}$, $t=5.14 \text{ sec}$ in the case of Zn(II) ion. By plotting i_d against the square root of the concentration of supporting electrolyte, Fig. 1, 2, and 3 were obtained. In the figures the experimentally observed diffusion currents are represented by solid circles, and the diffusion currents calculated from the data of tracer-diffusion by equation (3) using 0, 17 and 39 $\text{mg}^{1/3}\text{cm}^{-1}$ as constant A are represented by open circles. The solid lines represent the theoretical values of equation (4).

In the case of Tl(I) ion, the observed values agreed fairly with the calculated and

Fig. 1. Diffusion currents of Tl(I) ion in KCl solution at 25° . The solid circles represent the observed values, the open circles the calculated values and the solid lines the theoretical values of the diffusion current when the values of 0, 17 and 39 were used as constant A, respectively. The lines are $i_d = 9.69 - 1.13c^{1/2}$ for $A=0$, $i_d = 10.50 - 1.32c^{1/2}$ for $A=17$ and $i_d = 11.55 - 1.56c^{1/2}$ for 39.

Fig. 2. Diffusion currents of Pb(II) ion in KCl solution at 25° . The solid circles represent the observed values, the open circles the calculated values and the solid lines the theoretical values of the diffusion current when the values of 0, 17 and 39 were used as constant A, respectively. The lines are $i_d = 13.35 - 3.66c^{1/2}$ for $A=0$, $i_d = 14.12 - 4.08c^{1/2}$ for $A=17$ and $i_d = 15.12 - 4.63c^{1/2}$ for 39.

Fig. 3. Diffusion currents of Zn (II) ion in KCl solution at 25°. The solid circles represent the observed values, the open circles the calculated values and solid lines the theoretical values of the diffusion currents when the values of 0, 17 and 39 were used as constant A, respectively. The lines are $i_d = 30.99 - 6.88 c^{1/2}$ for A=0, $i_d = 32.56 - 7.58 c^{1/2}$ for A=17 and $i_d = 34.60 - 8.48 c^{1/2}$ for A=39

theoretical values at $17 \text{ mg}^{1/2} \text{ cm}^{-1}$ for A. On the other hand, in the case of Pb(II) and Zn(II) ions, the observed values agreed fairly with the calculated values at 17 for A, but not with the theoretical values. This may mean that the ionic species changed their forms with variation of the concentration of supporting electrolyte for Pb(II) and Zn(II) ions. The abnormally high value at $\sqrt{c} = 0.1 \text{ mol}^{1/2} \text{ l}^{-1/2}$ may be due to migration current, since the concentrations of metal ions are relatively as high as 0.002 to 0.005 mole/liter.

In conclusion, the polarographic diffusion currents of the metal ions investigated in the present study are sufficiently close to that calculated from tracer-diffusion coefficients by using only the value of $17 \text{ mg}^{1/2} \text{ cm}^{-1}$ for A just as Wang's reports, and these diffusion currents fall on the line of the theoretical values calculated from Onsager equation for the case of Tl(I) ion, while not for the case of Pb(II) and Zn(II) ions, being probably due to change in form of the ionic species. However, it is concluded that the condition of the average diffusion current in polarography is the same as that of the tracer diffusion.

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