

# The Liquid Junction Potential in Potentiometric Titrations. 3. Determination of Ionic Molar Conductivities in Mixtures of $\text{Cd}(\text{ClO}_4)_2 + \text{HClO}_4 + \text{NaClO}_4$ Under the Experimental Condition that $[\text{ClO}_4^-] = 3 \text{ M}$ is Kept Constant

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Ionic molar conductivities were determined in the test solutions of some emf cells containing the mixtures of  $\text{Cd}(\text{ClO}_4)_2 + \text{HClO}_4 + \text{NaClO}_4$  under the experimental condition that  $[\text{ClO}_4^-] = 3 \text{ M}$  is kept constant.

It was found that the ionic molar conductivities are either constant or a linear function of  $[\text{H}^+]$  or  $[\text{Cd}^{2+}]$ , respectively. The trace ionic molar conductivities of the  $\text{Cd}^{2+}$  ions ( $\lambda_{\text{Cd}^{2+}}^{\text{tr}}$ ) and the  $\text{H}^+$  ions ( $\lambda_{\text{H}^+}^{\text{tr}}$ ) are different in the different mixtures studied and they cannot be interchanged.

Once the ionic molar conductivities had been obtained, the systematic errors present in the determined  $E_{0\text{J}}$  values of the Nernst equations could be calculated. These errors are:  $-0.63 \text{ mV}$  in Mixture 1, where  $[\text{H}^+] = 0.025 \text{ mol dm}^{-3}$  was also kept constant, and  $0.56 \text{ mV}$  in Mixture 2, where  $[\text{Cd}^{2+}] = 0.050 \text{ mol dm}^{-3}$  was also kept constant. The systematic errors in the equilibrium constants ( $\log \beta_{p,q,r}$ ) have been estimated caused by the systematic errors in  $E_{0\text{J}}$ .

This work is Part 3 of the series. The earlier parts are presented in Refs. 1 and 2.

In Ref. 1, potential functions were derived for the calculation of potentials across liquid junctions of constant ionic medium types, for emf cells<sup>1</sup> containing mixtures of strong electrolytes with the junction types  $\text{AY} | \text{AY} + \text{BY}_{z(\text{B})} + \text{HY}$  under the experimental conditions  $[\text{A}^+] = C \text{ mol dm}^{-3}$  constant,  $[\text{Y}^-] = C \text{ mol dm}^{-3}$  constant and  $I = C \text{ mol dm}^{-3}$  is kept constant, respectively. For the calculation of the total potential anomalies in these cells, the ionic molar conductivities are needed for every electrolyte mixture studied. Definitions and symbols used throughout this series are also presented in Ref. 1.

In Ref. 2, ionic molar conductivities were determined in the mixtures of  $\text{Cd}(\text{ClO}_4)_2 + \text{HClO}_4 + \text{NaClO}_4$  under the experimental condition  $[\text{Na}^+] = 3 \text{ mol dm}^{-3}$  is kept constant. The influence of the neglect of the liquid junction potential terms on the equilibrium constants studied ( $\log \beta_{p,q,r}$ )<sup>2</sup> was discussed too.

In the present part, the ionic molar conductivities will be estimated from the measurements of the conductivity

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( $10^3 \kappa$ ) of the electrolyte mixtures defined above, under the experimental condition  $[\text{Y}^-] = C \text{ mol dm}^{-3}$ , is kept constant. These mixtures are used for the determination of the constants of the Nernst equation,  $E_{0\text{B}}$  and  $E_{0\text{H}}$ . The total emf cell for these cells studied can be given as

$$E_{\text{J}} = E_{0\text{J}} + (g/z_{\text{J}}) \log c_{\text{J}} f_{\text{JTS2}} + E_{\text{D}} + E_{\text{Df}} \quad (1a)$$

The total potential anomalies in the cells are

$$\Delta E_{\text{J}} = (g/z_{\text{J}}) \log f_{\text{JTS2}} + E_{\text{D}} + E_{\text{Df}} \quad (1b)$$

In the present practice, conditional constants are determined in the emf cells

$$E_{0\text{B}\alpha} = E_{0\text{B}} + g c_{\text{H}} d_2 \quad (1c)$$

in Mixture 1, and

$$E_{0\text{H}\alpha} = E_{0\text{H}} + g c_{\text{B}} d_3 \quad (1d)$$

in Mixture 2, with the compositions of the test solutions given below. Here, the terms  $d_2$  and  $d_3$  are functions<sup>1</sup> with constant values, in terms of some ionic molar conductivities and interaction coefficients.

In studies of complex formation reactions through emf cells, the constants  $E_{0\text{B}}$  and  $E_{0\text{H}}$  are needed. Therefore,

the systematic errors  $gc_H d_2$  and  $gc_B d_3$  must be determined.

The composition of the mixtures studied are given here.

Mixture 1:  $c_H = 0.025 \text{ mol dm}^{-3}$ , is kept constant,  $c_B$  is varied within the range  $0-0.1 \text{ mol dm}^{-3}$ ,  $X \text{ mol dm}^{-3}$  AY as ionic medium at the experimental condition  $[Y^-] = 3 \text{ mol dm}^{-3}$ , is kept constant.

Mixture 2:  $c_B = 0.050 \text{ mol dm}^{-3}$ , is kept constant,  $c_H$  is varied within the range  $0.003-0.1 \text{ mol dm}^{-3}$ ,  $X' \text{ mol dm}^{-3}$  AY at the experimental condition  $[Y^-] = 3 \text{ mol dm}^{-3}$ , is kept constant. Here,  $B = \text{Cd}^{2+}$ ,  $Y^- = \text{ClO}_4^-$ ,  $A^+ = \text{Na}^+$  and  $c_H \equiv [\text{H}^+] = [\text{HClO}_4] \text{ mol dm}^{-3}$ ,  $c_B \equiv [\text{Cd}^{2+}] = [\text{Cd}(\text{ClO}_4)_2] \text{ mol dm}^{-3}$ .

The ionic strength in these mixtures can be given, with the concentration condition  $[Y^-] = z_B c_B + c_H + c_A$ , as

$$I = c_H + c_A + [(z_B^2 + z_B)/2]c_B \quad (1e)$$

### Estimation of the ionic molar conductivities

In order to calculate the different potential functions which describe the total potential anomalies, derived in Ref. 1, in the mixtures noted, we have to know the ionic molar conductivity values  $\lambda_H^{\text{tr}}$ ,  $\lambda_{\text{Cd}}^{\text{tr}}$ ,  $\lambda_{\text{Na}}^{\text{tr}}$  and  $\lambda_Y$ . Here, tr denotes trace. These values have been estimated by the author through the measurements of the conductivity in Mixtures 1 and 2 at  $25.000 \pm 0.005^\circ\text{C}$ . The uncertainty of the resistance measurements, in general, is ca. 0.02%. The measurements have been carried out as forward and back titrations.

All molar conductivities ( $\lambda$  and  $\Lambda$ ), in this section, are expressed in  $\text{S cm}^2 (\text{g-mol})^{-1}$  and the conductivity ( $\kappa$ ) in  $\text{S cm}^{-1}$  units, and are generally omitted in the text for simplicity.

1. Conductivity measurements in mixtures where  $c_H$  is varied while  $c_B$  is kept constant. The conductivity was measured in Mixture 2. This data have been interpreted in terms of the ionic conductivities with the help of several plots, as presented below. A similar treatment has already been used in Ref. 2.

1.1. The percentage deviations of the conductivity from additivity. The mentioned deviations for the system studied can be investigated through the plot  $10^2 (10^3 \kappa - 10^3 \kappa_{\text{add}})/10^3 \kappa$  vs.  $c_H$ . Here,  $10^3 \kappa$  stands for the measured conductivity of the solution studied and  $10^3 \kappa_{\text{add}}$  is calculated according to the additivity, in the same way as shown in Ref. 2 [cf. eqns. (17)–(19)]. This plot is given in Fig. 1. As seen from this figure, the deviation function is linear, positive and almost constant. The deviations are small,  $< 2.5\%$ . As the deviations here are practically of the same magnitude in the whole range of  $c_H$  studied, it means that they appear due to the presence of either the  $\text{Cd}^{2+}$  or the  $\text{ClO}_4^-$  ions, as the concentration of these ions is constant. Owing to the experiences gained in this laboratory during the study<sup>3</sup> of the conductivity of the systems  $\text{HClO}_4\text{-NaClO}_4$  or  $\text{LiClO}_4$  and  $\text{HCl-NaCl}$ , moreover, the authors investi-

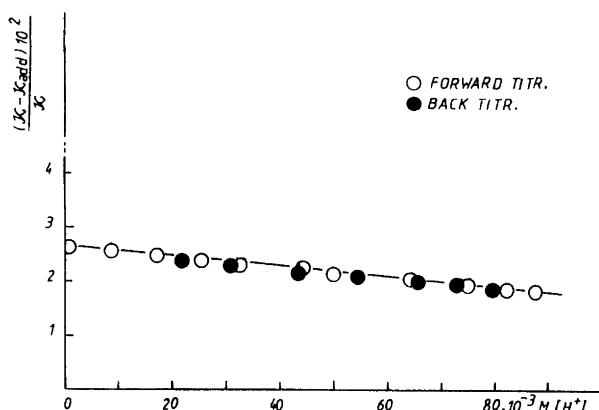


Fig. 1. The percentage deviation of the measured conductivity ( $10^3 \kappa$ ) from additivity ( $10^3 \kappa_{\text{add}}$ ) as a function of  $[\text{H}^+]$ , in the system  $0.050 \text{ M Cd}(\text{ClO}_4)_2$ ,  $2 \times 10^{-3} \leq [\text{HClO}_4] \leq 0.1 \text{ M}$ ,  $X \text{ M NaClO}_4$ , using  $[\text{ClO}_4^-] = 3 \text{ M}$  constant, at  $25.000 \pm 0.005^\circ\text{C}$ .

gations made on the  $\text{Cd}(\text{ClO}_4)_2\text{-HClO}_4\text{-NaClO}_4$  system,<sup>2</sup> we can assume, first, that the ionic molar conductivity of the common anion follows the additivity. This can mean that the  $\text{Cd}^{2+}$  ions seem to be responsible for the noticed deviations and  $\lambda_{\text{Cd}}^{\text{tr}}$  is significantly larger, here, than in  $1.5 \text{ M Cd}(\text{ClO}_4)_2$ . The linearity of the deviation function means that the ionic molar conductivities are either constant or a linear function of the composition, in this system.

1.2. The plot  $10^3 \kappa$  versus  $c_H$  at  $c_B = 0.050 \text{ mol dm}^{-3}$ , constant. This plot is presented in Fig. 2. The basic equation, which is valid here, in the three-component system, is

$$10^3 \kappa = z_B [\text{B}^{z(\text{B})+}] \lambda_B^{\text{tr}} + [\text{H}^+] \lambda_H^{\text{tr}} + [\text{Y}^-] \lambda_{Y(3)} + [\text{A}^+] \lambda_A \quad (2)$$

At the use of this equation, we must know how  $\lambda_{Y(3)}$  varies with the composition. We obtain, according to the

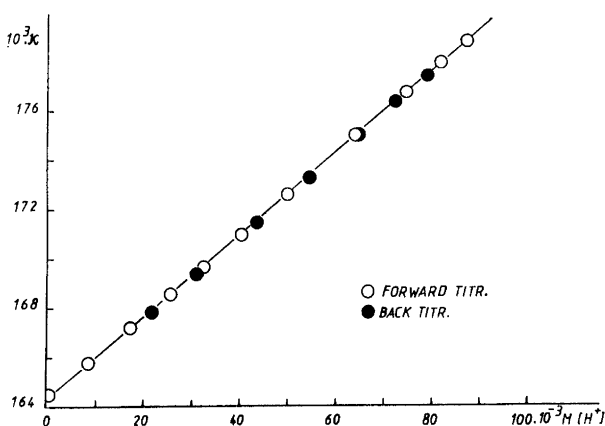


Fig. 2.  $10^3 \kappa$  vs.  $[\text{H}^+]$ , for the determination of the ionic molar conductivities in the system  $0.050 \text{ M Cd}(\text{ClO}_4)_2$ ,  $2 \times 10^{-3} \leq [\text{HClO}_4] \leq 0.1 \text{ M}$ ,  $X \text{ M NaClO}_4$ , using  $[\text{ClO}_4^-] = 3 \text{ M}$  constant, at  $25.000 \pm 0.005^\circ\text{C}$ .

additivity, for the present three-component mixture

$$\lambda_{Y(3)} = 30.38 + 2.76[H^+] \simeq 30.38 = \lambda_{Y(2)} \quad (3a)$$

Here, the constant value 30.38 represent  $\lambda_{Y(2)}$ , the ionic molar conductivity of the perchlorate ions in the two-component system 0.050 mol dm<sup>-3</sup> Cd(ClO<sub>4</sub>)<sub>2</sub>, constant, and 2.900 M NaClO<sub>4</sub> (= [Na<sup>+</sup>]<sub>2</sub>) at [H<sup>+</sup>]=0. This value can be estimated as given below.

As the concentration of the ClO<sub>4</sub><sup>-</sup> ions is constant and that of the H<sup>+</sup> ions is very low ([H<sup>+</sup>] ≤ 0.1 M), it can be assumed that  $\lambda_Y$  is constant in this mixture and is equal to  $\lambda_{Y(2)}$ . On the basis of this assumption, we can redefine eqn. (2). Inserting the concentration condition

$$[Y^-] = z_B[B^{z(B)^+}] + [H^+] + [A^+] \quad (3b)$$

into eqn. (2), we obtain

$$10^3 \kappa = z_B[B^{z(B)^+}](\lambda_B^{tr} + \lambda_{Y(2)}) + [H^+](\lambda_H^{tr} + \lambda_{Y(2)}) + [A^+](\lambda_A + \lambda_{Y(2)}) \quad (4)$$

Hence the intercept of the plot 10<sup>3</sup> κ versus [H<sup>+</sup>], at constant c<sub>B</sub>, is

$$z_B[B^{z(B)^+}](\lambda_B^{tr} + \lambda_{Y(2)}) + [A^+]_2(\lambda_A + \lambda_{Y(2)}) = 164.30 \quad (5)$$

The intercept represents the conductivity of the two-component system 0.050 mol dm<sup>-3</sup> Cd(ClO<sub>4</sub>)<sub>2</sub> constant, [Na<sup>+</sup>]<sub>2</sub> = 2.900 mol dm<sup>-3</sup> NaClO<sub>4</sub>. First, the ionic molar conductivities in this system should be estimated.

Here  $\lambda_{Na}$  can be considered as constant, being equal to the value valid in 3 mol dm<sup>-3</sup> NaClO<sub>4</sub>. We assume that  $\lambda_{Y(2)}$  can be calculated due to the additivity, in terms of the ionic strength fractions [cf. eqn. (19) in Ref. 2]. Hence, we obtain

$$\lambda_{Na} = t_{Na}(3 \text{ M NaClO}_4) \wedge (3 \text{ M NaClO}_4) \\ = 0.43 \times 54.60 = 23.48 \quad (6a)$$

$$\lambda_{Y(2)} = [Na^+]_2 \lambda_Y(3 \text{ M NaClO}_4) / I \\ + 3[Cd^{2+}] \lambda_Y[1.5 \text{ M Cd(ClO}_4)_2] / I = 30.38 \quad (6b)$$

$$\lambda_Y(3 \text{ M NaClO}_4) = 0.57 \times 54.60 = 31.12 \quad (6c)$$

$$\lambda_Y[1.5 \text{ M Cd(ClO}_4)_2] = 0.681 \times 23.6 = 16.1 \quad (6d)$$

Hence, the first estimated value for  $\lambda_{Cd}^{tr}$  can be obtained from the intercept

$$\lambda_{Cd(1)}^{tr} = 50.7$$

This value is much higher than  $\lambda_{Cd}$  in 1.5 M Cd(ClO<sub>4</sub>)<sub>2</sub>: 0.319 × 23.6 = 7.5. Here, the transport numbers and the molar conductivity of 3 M NaClO<sub>4</sub> were taken from Ref. 1. The molar conductivity of 1.5 M Cd(ClO<sub>4</sub>)<sub>2</sub> was measured by the author.<sup>2</sup> Moreover, the approximation  $t_{Cd}[1.5 \text{ M Cd(ClO}_4)_2] \simeq t_{Zn}[1.5 \text{ M Zn(ClO}_4)_2] = 0.319$  (Ref. 4) was introduced.

The value of  $\lambda_{Cd}^{tr}$  cannot be obtained with a high accuracy through the suggested procedure. The reason is that a small uncertainty in the position of the intercept influences the value of  $\lambda_{Cd}^{tr}$  very strongly. This uncertainty can be noticed if we compare the 10<sup>3</sup> κ values belonging to the special common measuring point: [Cd(ClO<sub>4</sub>)<sub>2</sub>] =

0.050 mol dm<sup>-3</sup> and [HClO<sub>4</sub>] = 0.025 mol dm<sup>-3</sup> in Mixtures 1 and 2.

For these points we have

$$10^3 \kappa = 167.97 \text{ in Mixture 1}$$

and

$$10^3 \kappa = 168.51 \text{ in Mixture 2.}$$

These numbers show that there is a 0.54 unit uncertainty in the position of the intercept which denotes 0.3% deviation in the conductivity. This means that the measured intercept in the plot of 10<sup>3</sup> κ vs. c<sub>H</sub> could also have the following value: 164.30 - 0.54 = 163.76. From this intercept, an alternative value can be calculated for  $\lambda_{Cd(2)}^{tr}$ :

$$\lambda_{Cd(2)}^{tr} = 45.28$$

Taking the average value as the result (denoted R) we have

$$\lambda_{Cd(R)}^{tr} = 48.0 \pm 2.7$$

As seen, this result includes ± 5.6% uncertainty.

For the estimation of  $\lambda_H^{tr}$  we can use the value of the slope of the plot in question. In order to give the correct mathematical equation of the slope valid here, eqn. (2) must be redefined by inserting into it the special concentration condition valid in this cell (a three-component system):

$$[A^+]_3 = \{[Y^-] \equiv C\} - z_B[B^{z(B)^+}] - [H^+] \quad (7)$$

Therefore, we have

$$10^3 \kappa = z_B[B^{z(B)^+}](\lambda_B^{tr} - \lambda_A) + [H^+](\lambda_H^{tr} - \lambda_A) \\ + C\lambda_A + C\lambda_{Y(3)} \quad (8)$$

Assuming that the constant value of  $\lambda_{Y(2)}$  is valid in this system, the slope of the plot 10<sup>3</sup> κ vs. c<sub>H</sub>, at constant c<sub>B</sub>, is according to this equation

$$\lambda_H^{tr} - \lambda_A = 166.25 \quad (9)$$

This difference of the two ionic molar conductivities in question is very accurate. Hence,  $\lambda_H^{tr}$  can be calculated from eqn. (9):

$$\lambda_H^{tr} = 166.25 + 23.48 = 189.73$$

Equations (8) and (9) are not valid if  $\lambda_Y$  is not constant. In this case,  $\lambda_{Y(2)}$  is valid in the intercept and  $\lambda_{Y(3)}$  in the three-component system, which means that eqn. (2) must be used for the interpretation of the conductivity data, using  $\lambda_{Y(3)}$ . The same value can also be obtained for  $\lambda_H^{tr}$  through the interpretation of the plot  $\Delta(\lambda_H^{tr})$  vs. c<sub>H</sub>, introduced by eqn. (25) in Ref. 2, if the constant value of  $\lambda_{Y(2)}$  is used in the calculation for the ionic molar conductivity of the perchlorate ions. The assumption  $\lambda_Y \sim \text{constant}$ , in this mixture, can be verified by the shape of the deviation function, shown in Fig. 1. Here the function has essentially the same values through the entire [H<sup>+</sup>] range studied. Hence we can assume that  $\lambda_{Na}$ ,  $\lambda_Y$  and  $\lambda_{Cd}^{tr}$  have essentially the same values as at

$[H^+] = 0$ . The negative sign of the almost flat slope we have shows that  $\lambda_H^{tr}$  is slightly lower than in 3 M  $HClO_4$  (cf. Ref. 1):  $\lambda_H(3 \text{ M } HClO_4) = 233.1 \times 0.83 = 193.5$ .

2. Conductivity measurements in mixtures where  $c_{Cd}$  is varied and  $c_H$  is kept constant. The conductivity was measured in Mixture 1. These data have been interpreted in terms of the ionic molar conductivities  $\lambda_{Cd}^{tr}$ ,  $\lambda_H^{tr}$ ,  $\lambda_{Na}$  and  $\lambda_Y$ . The treatment of the data is partly similar to that used in Section 1.

2.1. The percentage deviations of the conductivity from additivity. The deviation function, defined in Section 1 and Ref. 2 [cf. eqns. (17)–(19)] has been plotted as a function of  $[Cd^{2+}]$ . This plot is shown in Fig. 3. As seen, the deviations are positive, a linear function of the concentration of the  $Cd^{2+}$  ions and are  $< 4\%$  in the concentration range studied.

In principle, both the  $Cd^{2+}$  and the perchlorate ions can be responsible for the noticed deviations in the range of  $[Cd^{2+}]$  studied, as both  $\lambda_{Cd}^{tr}$  and  $\lambda_Y$  (calculated according to the additivity) are dependent on  $[Cd^{2+}]$ . However, on considering the data, given as a plot of  $10^3 \kappa$  vs.  $[Cd^{2+}]$  in Fig. 4, it is seen that the measured conductivity does not increase with the concentration of the  $Cd^{2+}$  ions. On the contrary, it decreases. This is an unexpected result, and it allows us to assume that the positive deviations of Fig. 3 are most probably due to the increase of  $\lambda_Y$ . Such deviations have not been observed in the other systems studied (cf. Refs. 2 and 5). The linearity of the deviation function shows that the ionic molar conductivities are either constant or a linear function of  $c_B$  in this system.

2.2. The plot of  $10^3 \kappa$  vs.  $c_{Cd}$  at  $c_H = 0.025 \text{ mol dm}^{-3}$ , constant. This plot is presented in Fig. 4, which is a complete straight line. According to eqn. (4), the intercept of this plot is

$$[H^+](\lambda_H^{tr} + \lambda'_{Y(2)}) + [A^+](\lambda_A + \lambda'_{Y(2)}) = 168.55 \quad (10)$$

The intercept represents the conductivity of the two-

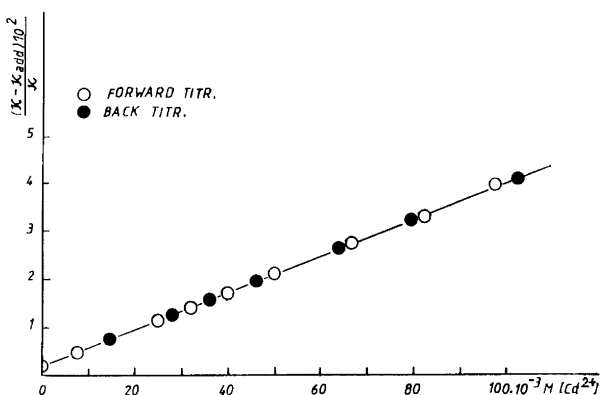


Fig. 3. The deviation of the measured conductivity ( $10^3 \kappa$ ) from additivity ( $10^3 \kappa_{add}$ ) (in %) as a function of  $[Cd^{2+}]$ , in the system  $0.025 \text{ M } HClO_4$ ,  $0 \leq [Cd(ClO_4)_2] \leq 0.1 \text{ M}$ ,  $X \text{ M } NaClO_4$ , using  $[ClO_4^-] = 3 \text{ M}$  constant, at  $25.000 \pm 0.005^\circ C$ .

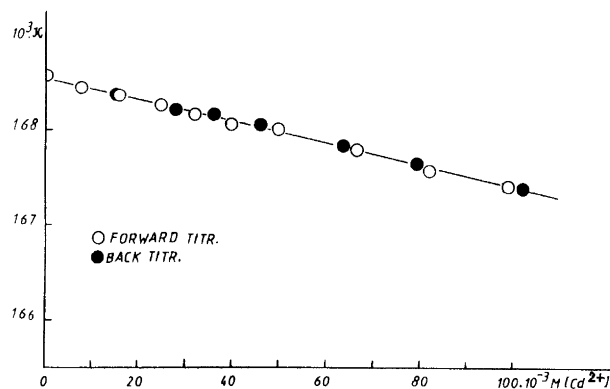


Fig. 4.  $10^3 \kappa$  vs.  $[Cd^{2+}]$ , for the determination of the ionic molar conductivities in the system  $0.025 \text{ M } HClO_4$ ,  $0 \leq [Cd(ClO_4)_2] \leq 0.1 \text{ M}$ ,  $X \text{ M } NaClO_4$ , using  $[ClO_4^-] = 3 \text{ M}$  constant, at  $25.000 \pm 0.005^\circ C$ .

component system:  $0.025 \text{ mol dm}^{-3} HClO_4$ , constant, and  $2.975 \text{ mol dm}^{-3} NaClO_4$ . This value can be used for the estimation of  $\lambda_H^{tr}$ ,  $\lambda'_{Y(2)}$  and  $\lambda_{Na}$ . We can assume, again, that  $\lambda_{Na}$  has the same value as in  $3 \text{ mol dm}^{-3} NaClO_4$ . Moreover,  $\lambda'_{Y(2)}$  will be calculated due to the additivity, as before. Therefore, we have for this system

$$\lambda_{Na} = 23.48$$

$$\lambda'_{Y(2)} = 31.19$$

Hence the first value for  $\lambda_H^{tr}$  can be obtained from the intercept in question:

$$\lambda_{H(1)}^{tr} = 205.1$$

Taking into account the 0.54 unit uncertainty in the position of the intercept, with  $168.55 + 0.54 = 169.09$  an alternative value can be calculated for  $\lambda_H^{tr}$ :

$$\lambda_{H(2)}^{tr} = 226.80$$

Taking the average value as the result,

$$\lambda_{H(R)}^{tr} = 215.9 \pm 10.9$$

This result includes  $\pm 5.0\%$  uncertainty.

For the estimation of  $\lambda_{Cd}^{tr}$  the slope of the plot in question can be used. Therefore, an accurate mathematical equation of the slope must be known. On the basis of the deviation function presented in Section 2.1, we shall assume that  $\lambda_{Y(3)}$  is the linear function of the concentration of the  $Cd^{2+}$  ions and can be described as

$$\lambda_{Y(3)} = 31.19 \pm f_1 z_B [B^{z(B)+}] \quad (11)$$

Inserting this expression into eqn. (8) we obtain

$$10^3 \kappa = z_B [B^{z(B)+}] (\lambda_B^{tr} - \lambda_A \pm Cf_1) + C\lambda_A + [H^+](\lambda_H^{tr} - \lambda_A) + C31.19 \quad (12)$$

Hence, the slope of a plot of  $10^3 \kappa$  vs.  $[Cd^{2+}]$ , at  $[H^+] = 0.025 \text{ mol dm}^{-3}$  constant, is in the present system

$$z_B (\lambda_B^{tr} - \lambda_A \pm Cf_1) = -11.60 \quad (13)$$

As seen, now we have two unknown quantities,  $\lambda_H^{tr}$  and

$f_1$ , and only one equation. For the determination of these quantities we can use eqn. (13), and the experimental slope function  $SL(H, c_B)$  is defined by eqns. (77) and (75) in Ref. 1, which was also determined in this mixture by emf measurements.

The slope of the plot of  $E_H - g \log[H^+]$  vs.  $[Cd^{2+}]$ , at  $[H^+] = 0.025 \text{ mol dm}^{-3}$  constant, was found to be in a forward and back titration

$$SL(H, c_B)_{\text{exp}} = 18.4 \text{ mV (M Cd}^{2+})^{-1}$$

as shown in Fig. 4 of Ref. 1. Here, exp denotes experimental. The estimation of  $\lambda_{Cd}^{\text{tr}}$  and  $f_1$  was done as follows.

As a first step, we assume that  $\lambda_{Y(3)}$  decreases with an increase in  $c_{Cd}$ . On the basis of  $\lambda_{Y_{\text{add}}}$  [cf. eqn. (19) in Ref. 2] we can write

$$\lambda_{Y(3)} = 31.19 - f_1 z_B [B^{z(B)+}] \quad (14a)$$

$$= 31.19 - [(z_B + 1)/2] z_B \lambda_Y (z_B/2 \text{ M BY}_{z(B)}) [B^{z(B)+}] / I \quad (14b)$$

$$= 31.19 - 7.25 \times 2 [Cd^{2+}] \quad (14c)$$

at  $c_{Cd} = 0.1 \text{ M}$ . The value  $f_1 = 7.25$  results in

$$\lambda_{Y(3)} = 29.74$$

$$\lambda_{Cd}^{\text{tr}} = 39.43$$

using eqn. (13) for the calculation. With these ionic molar conductivities, the slope function

$$SL(H, c_B) = 11.8 \text{ mV/M Cd}^{2+}$$

can be calculated from eqns. (77) and (75) in Ref. 1 at  $c_{Cd} = 0.1 \text{ M}$ . As seen, this slope value differs very much from the experimental one. It seems that the conclusion of the deviation function is valid, namely that the deviations are positive in this system.

As a second step, it was assumed that the equation

$$\lambda_{Y(3)} = 31.19 + f_1 z_B [B^{z(B)+}] \quad (15)$$

describes correctly the ionic molar conductivity of the ClO<sub>4</sub><sup>-</sup> ions. This means that the positive sign is valid in eqns. (11) and (13). Then several values were assumed for  $\lambda_{Cd}^{\text{tr}}$ , and the corresponding  $f_1$  values were calculated from eqn. (13). With these values of  $\lambda_{Cd}^{\text{tr}}$  and  $\lambda_{Y(3)}$ , the corresponding slope values,  $SL(H, c_B)$ , were calculated at  $[Cd^{2+}] = 0.1 \text{ mol dm}^{-3}$ , using eqns. (77) and (75) of Ref. 1, and were compared with the experimental one, as shown in Table 1. As seen, assumption (c) gives the correct value. It means that at  $[Cd^{2+}] = 0.1 \text{ M}$

$$\lambda_{Cd}^{\text{tr}} = 0, \quad f_1 = 5.89$$

$$\lambda_{Y(3)} = 32.37, \quad t_Y = 0.58$$

Table 1. Estimation of the value of  $\lambda_{Cd}^{\text{tr}}$  in Mixture 1.<sup>a</sup>

Assumption	$\lambda_{Cd}^{\text{tr}}$	$f_1$	$SL(H, c_B)_{\text{calc.}}/\text{mV (M Cd}^{2+})^{-1}$
a	5.0	4.22	17.41
b	1.00	5.56	18.03
c	0	5.89	18.18

<sup>a</sup>Here, calc. denotes calculated.

in this mixture. This is a very unusual result. The concentration condition  $[ClO_4^-] = 3 \text{ M}$  constant, results in such a strong retardation of the Cd<sup>2+</sup> ions in this mixture that they do not move at all to any of the electrodes. This result is consistent with the plot of  $10^3 \kappa$  vs.  $[Cd^{2+}]$  at  $[H^+] = 0.025 \text{ M}$  constant (cf. Fig. 4). In this figure the conductivity is almost constant (in fact it is decreasing), while the concentration of the Cd<sup>2+</sup> ions is changing in the range  $0 \leq [Cd^{2+}] \leq 0.1 \text{ M}$ . This can happen only if the Cd<sup>2+</sup> ions do not contribute at all to the value of  $10^3 \kappa$ .

In order to see the effect of the slight change of  $\lambda_{Y(3)}$  with  $[Cd^{2+}]$  on the value of the slope function,  $SL(H, c_B)$  was calculated at  $[Cd^{2+}] = 0.050 \text{ M}$  also. The result is

$$\lambda_{Cd}^{\text{tr}} = 0, \quad \lambda_{Y(3)} = 31.78, \quad t_Y = 0.57$$

$$SL(H, c_B) = 18.17 \text{ mV (M Cd}^{2+})^{-1}$$

As seen, we obtain the same result as at  $[Cd^{2+}] = 0.1 \text{ M}$ , because the ratios of the ionic molar conductivities in eqns. (77) and (75) of Ref. 1 are constant, as was also noticed earlier (cf. Ref. 2).

3. *Conductivity measurements in mixtures where both  $c_B$  and  $c_H$  are varied.* If both  $E_{OB}$  and  $E_{OH}$  are to be determined within one titration, in this case both  $c_B$  and  $c_H$  should be varied. The  $\lambda_j$  values, which can be obtained from these data, should be used at the estimation of the total potential anomalies in emf cells. The measured conductivity data,  $10^3 \kappa$ , can be interpreted in terms of the ionic molar conductivities only with the help of a curve-fitting computer program, e.g. MLAB.<sup>6</sup> In order to establish a suitable theoretical function which can be fitted to the data, we can assume, again, that  $\lambda_{Na}$  is constant and equal to its value in  $C \text{ M NaClO}_4$ . Moreover,  $\lambda_{Cd}^{\text{tr}}$  and  $\lambda_Y$  can be defined in general, as follows:

$$\lambda_B^{\text{tr}} = f_2 - f_3 [B^{z(B)+}] \quad (16)$$

$$\lambda_Y = \lambda_Y^\circ - f_4 [B^{z(B)+}] \quad (17)$$

where

$$\lambda_Y^\circ = t_Y (C \text{ M AY}) \Lambda (C \text{ M AY}). \quad (18)$$

Hence, we can transform the data, on the basis of eqn. (2), to the form  $10^3 \kappa - [A^+] \lambda_A$ , according to

$$\begin{aligned} F_0 &\equiv 10^3 \kappa - [A^+] \lambda_A \\ &= z_B [B^{z(B)+}] \{ f_2 - f_3 [B^{z(B)+}] \} \\ &\quad + [H^+] \lambda_H^{\text{tr}} + [Y^-] \{ \lambda_Y^\circ - f_4 [B^{z(B)+}] \} \end{aligned} \quad (19)$$

We assume that  $\lambda_H^{\text{tr}}$  does not change with  $[B^{z(B)+}]$ .

The function  $F_0$  should be fitted to the transformed experimental data  $\{F_{0\text{exp}}, [B^{z(B)+}], [H^+], [Y^-]\}$  with the help of a computer program, e.g. MLAB,<sup>6</sup> by adjusting the four unknown parameters:  $f_2, f_3, f_4$  and  $\lambda_H^{\text{tr}}$ . As a starting value for  $f_2$ , we can take the value  $\lambda_B^\circ$ , valid in  $C/z(B) \text{ M BY}_{z(B)}$  solution:

$$\lambda_B^\circ = t_B [C/z(B) \text{ M BY}_{z(B)}] \Lambda [C/z(B) \text{ M BY}_{z(B)}] \quad (20)$$

For the calculation of  $\lambda_{\text{Cd}}^{\circ}$ , the value of  $\Lambda \text{ Cd}(\text{ClO}_4)_2$  was measured by the author in a broad concentration range.<sup>2</sup> The transport number  $t_{\text{Cd}}$  can be determined with the help of an emf cell, as will be described in Ref. 7. Similarly, as a starting value for  $\lambda_{\text{H}}^{\text{tr}}$  we can take that which is valid in 3 M  $\text{HClO}_4$ . This can be calculated as  $\lambda_{\text{Cd}}^{\circ}$ . The necessary transport numbers and the molar conductivity of  $\text{HClO}_4$ , in broad concentration range, are given in Ref. 1.

Experimental details are given in Ref. 2.

## Discussion

Concerning the results obtained for  $\lambda_{\text{Na}}$ ,  $\lambda_{\text{Y}(3)}$ ,  $\lambda_{\text{Cd}}^{\text{tr}}$  and  $\lambda_{\text{H}}^{\text{tr}}$  in the two different mixtures studied, we can make the conclusions given below.

(a) The ionic molar conductivities are either constant or a linear function of  $c_{\text{H}}$  and  $c_{\text{Cd}}$ , respectively.

(b) The values of  $\lambda_{\text{Cd}}^{\text{tr}}$  and  $\lambda_{\text{H}}^{\text{tr}}$  are quite different in these mixtures and cannot be interchanged.

(c) In Mixture 1, the values of  $\lambda_{\text{Y}(3)}$  do not follow the additivity. Moreover,  $\lambda_{\text{Cd}}^{\text{tr}} = 0$  in this mixture. Obviously, at the experimental condition  $[\text{ClO}_4^-] = 3 \text{ M}$  constant, this constant ionic environment hinders the  $\text{Cd}^{2+}$  ions totally in the migration to the negatively charged electrode.

(d) In the nominator of the ideal diffusion potential term of the slope function  $\text{SL}(\text{H}, c_{\text{B}})$ , as given in eqns. (77) and (75) of Ref. 1,  $\lambda_{\text{Y}}$  does not appear. This very advantageous fact ensures the constancy of the ratios of the ionic molar conductivities in a broader concentration range than would be the case at  $[\text{A}^+] = C \text{ M}$  constant (cf. Ref. 2), and  $I = C \text{ M}$  constant (cf. Ref. 5).

After the determination of the ionic molar conductivities in Mixture 1 and Mixture 2, we can calculate the potential contribution of the  $\text{H}^+$  ions to  $E_{\text{OB}\alpha}$  [cf. eqn. (1c)] and of the  $\text{Cd}^{2+}$  ions to  $E_{\text{OH}\alpha}$  [cf. eqn. (1d)]. We obtain

$$gc_{\text{H}}d_2 = -0.63 \text{ mV}$$

$$E_{\text{OB}} = E_{\text{OB}\alpha} + 0.63 \text{ mV}$$

on the basis of eqn. (74) in Ref. 1.

Moreover,

$$gc_{\text{Cd}}d_3 = 0.56 \text{ mV}$$

$$E_{\text{OH}} = E_{\text{OH}\alpha} - 0.56 \text{ mV}$$

on the basis of eqns. (75) and (73) in Ref. 1.

According to these results, the constant  $E_{\text{OB}\alpha}$  has  $-0.63 \text{ mV}$  and  $E_{\text{OH}\alpha}$   $0.56 \text{ mV}$  systematic errors, if we do not correct for these effects.

The systematic error in the equilibrium constants,

$\log \beta_{p,q,r}$ , will be as follows for Mixture 1, due to the use of the conditional constant  $E_{\text{OB}\alpha}$ :

$$\begin{array}{cccc} E_{\text{OB}} + gd_2c_{\text{H}}/\text{mV} & p = 1 & p = 2 & p = 3 \\ E_{\text{OB}} - 0.50 & -0.017 & -0.034 & -0.050 \end{array}$$

according to Table 1 in Ref. 2. The composition of the species formed is  $\text{B}_p\text{H}_q\text{L}_r$ .

For Mixture 2 we obtain

$$\begin{array}{cccc} E_{\text{OH}} + gd_3c_{\text{B}}/\text{mV} & q = 1 & q = 2 & q = 3 \\ E_{\text{OH}} + 0.50 & 0.008 & 0.016 & 0.024 \end{array}$$

according to Table 2 in Ref. 2.

The real systematic error in  $\log \beta_{p,q,r}$  will be higher, because of the potential contributions of the ions of the equilibrium solution to the total cell emf, in cells with complex formation.

As is seen, at this experimental condition ( $[\text{Y}^-] = C \text{ M}$  constant) the systematic errors in  $E_{\text{OB}\alpha}$ ,  $E_{\text{OH}\alpha}$  and  $\log \beta_{p,q,r}$ , caused by the liquid junction potential, are smaller than in the case  $[\text{A}^+] = C \text{ M}$  constant.<sup>2</sup>

In Ref. 1, the potential contributions of the changing concentrations of the  $\text{Cd}^{2+}$  and  $\text{H}^+$  ions, respectively, to the total potential anomalies in the cells were calculated for the present experimental condition. The calculated and measured slopes (defined in Ref. 1) agree well.

It is important to know that the ionic molar conductivities, which have been determined in the mixtures of strong electrolytes, are not valid in emf cells with complex formation. The potential functions are different in these two different cells. This is so because in cells with complex formation the ion concentrations are determined by the mass action law (except for  $c_{\text{A}}$  and  $c_{\text{Y}}$ ). For cells containing mixtures of strong electrolytes, the ion concentrations are calculated by the mixing rule. Cells with complex formation will be described in Parts 5 and 6A, both to be published.

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