

# The Liquid Junction Potential in Potentiometric Titrations. 4. Determination of the Ionic Molar Conductivities in Mixtures of $\text{Cd}(\text{ClO}_4)_2 + \text{HClO}_4 + \text{NaClO}_4$ under the Experimental Condition that $I=3 \text{ M}$ is Kept Constant

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The ionic molar conductivities have been determined in the test solutions of some e.m.f. cells containing mixtures of  $\text{Cd}(\text{ClO}_4)_2 + \text{HClO}_4 + \text{NaClO}_4$  under the experimental condition that  $I$  (ionic strength) = 3 M is kept constant. It was found that the ionic molar conductivities are either constant or a linear function of the concentrations  $[\text{H}^+]$  or  $[\text{Cd}^{2+}]$ , respectively. The trace ionic molar conductivities of the  $\text{Cd}^{2+}$  ions ( $\lambda_{\text{Cd}}^{\text{tr}}$ ) and of 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  $E_{\text{OJ}}$  values of the Nernst equations could be calculated. These errors are:  $-0.71 \text{ mV}$  in  $E_{\text{OB}\alpha}$  and Mixture 1, where  $[\text{H}^+] = 0.025 \text{ mol dm}^{-3}$  was also kept constant, and  $-0.86 \text{ mV}$  in  $E_{\text{OH}\alpha}$  and Mixture 2, where the  $[\text{Cd}^{2+}] = 0.050 \text{ mol dm}^{-3}$  was also kept constant. The composition of the species formed in  $\text{B}_p\text{H}_q\text{L}_r$ , where B is the central metal ion and L is the ligand. The systematic errors in the equilibrium constants ( $\log \beta_{p,q,r}$ ) have been estimated caused by the systematic errors in  $E_{\text{OJ}}$ .

This work is Part 4 of a series. The earlier parts are presented in Refs. 1-3. In Ref. 1, potential functions were derived for the calculation of potentials across liquid junctions of constant ionic medium types, for e.m.f. cells<sup>1</sup> containing mixtures of strong electrolytes with the junction type  $\text{AY}|\text{AY} + \text{BY}_{z(\text{B})} + \text{HY}$  under the experimental conditions that  $[\text{A}^+] = C \text{ mol dm}^{-3}$  is constant,  $[\text{Y}^-] = C \text{ mol dm}^{-3}$  is constant and  $I = C \text{ mol dm}^{-3}$  is constant. 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.

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

In the present part, the ionic molar conductivities will be estimated in the electrolyte mixtures given above, under the experimental condition that  $I = C \text{ mol dm}^{-3}$  is

kept constant. The constants of the Nernst equation,  $E_{\text{OB}}$  and  $E_{\text{OH}}$ , are determined in e.m.f. cells containing these mixtures. The total cell e.m.f. for these cells studied can be given as

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

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<sup>1</sup> in the e.m.f. cells

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

in Mixture 1, as an intercept of the plot  $E_{\text{B}} - (g/z_{\text{B}}) \log c_{\text{B}}$  versus  $c_{\text{B}}$  at constant  $c_{\text{H}}$ . Moreover,

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

in Mixture 2, as an intercept of the plot<sup>1</sup>  $E_{\text{H}} - g \log c_{\text{H}}$  versus  $c_{\text{H}}$  at constant  $c_{\text{B}}$ . The composition of these mixtures is 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

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e.m.f. cells, the constants  $E_{0B}$  and  $E_{0H}$  are needed. Therefore, the systematic errors  $gc_H d_2$  and  $gc_B d_3$  must be determined.

The composition of the mixtures studied was as follows.

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 under the experimental condition that  $I = 3 \text{ mol dm}^{-3}$ , constant.

Mixture 2:  $c_B = 0.050 \text{ mol dm}^{-3}$ , is kept constant,  $c_H$  is varied within the range  $3 \times 10^{-3}-0.1 \text{ mol dm}^{-3}$ ,  $X' \text{ mol dm}^{-3}$  AY under the experimental condition that  $I = 3 \text{ mol dm}^{-3}$  is constant.

Here,  $B = \text{Cd}^{2+}$ ,  $Y^- = \text{ClO}_4^-$ ,  $A^+ = \text{Na}^+$  and  $c_H \equiv [\text{H}^+] = [\text{HClO}_4] \text{ mol dm}^{-3}$ ,  $c_B \equiv [\text{Cd}^{2+}] = [\text{Cd}(\text{ClO}_4)_2]_{\text{TOTAL}} \text{ mol dm}^{-3}$ .

The ionic strength in these mixtures can be given, with the concentration condition  $c_Y = z_B c_B + c_H + c_A$ , as

$$I = c_H + c_A + c_B(z_B^2 + z_B)/2 = C \text{ mol dm}^{-3} \quad (1e)$$

Moreover, for the ion concentrations  $c_A$  and  $c_Y$  we have

$$c_A = C - c_H - c_B(z_B^2 + z_B)/2 \text{ mol dm}^{-3} \text{ AY} \quad (2)$$

$$c_Y = C + z_B c_B - c_B(z_B^2 + z_B)/2 \quad (3)$$

### Estimation of the ionic molar conductivities

The conductivity measurements have been carried out as described in Ref. 2.

In this section, all molar conductivities ( $\lambda$  and  $\Lambda$ ) 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  $c_B$  is varied while  $c_H$  is kept constant.* The conductivity  $10^3 \kappa$  was measured in Mixture 1. These data have been interpreted in terms of the ionic molar conductivities  $\lambda_{\text{Cd}}^{\text{tr}}$ ,  $\lambda_{\text{H}}^{\text{tr}}$ ,  $\lambda_{\text{Na}}$  and  $\lambda_Y$ . The interpretation of the data was done with the help of several plots as presented below. A similar treatment has already been used in Ref. 2, where the same system was studied under the experimental condition that  $[\text{Na}^+] = 3 \text{ mol dm}^{-3}$  is constant. Here, tr denotes trace.

1.1. *The percentage deviations of the conductivity from additivity.* The data were plotted as  $10^2 (10^3 \kappa - 10^3 \kappa_{\text{add}}) / 10^3 \kappa$  versus  $c_B$ . 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 is seen, the deviation function is linear, positive and at around  $[\text{Cd}^{2+}] = 0.1 \text{ mol dm}^{-3}$  reaches 6%. This mixture shows the highest deviation from additivity among all the mixtures of  $\text{Cd}(\text{ClO}_4)_2 + \text{HClO}_4 + \text{NaClO}_4$  which were studied by the author.

1.2. *The plot  $10^3 \kappa$  versus  $[\text{Cd}^{2+}]$  at  $c_H = 0.025 \text{ mol dm}^{-3}$ , constant.* This plot is presented in Fig. 2 and gives the

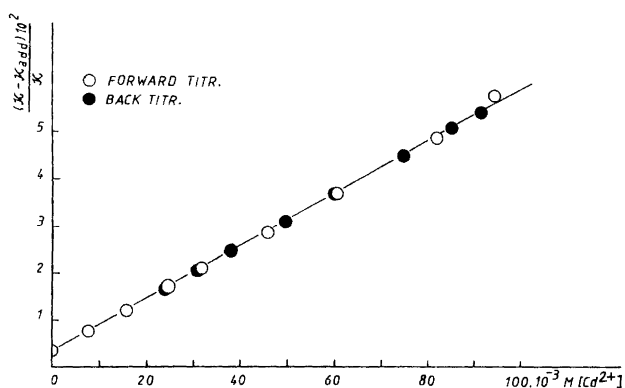


Fig. 1. The deviation of the measured conductivity ( $10^3 \kappa$ ) from additivity ( $10^3 \kappa_{\text{add}}$ ), in %, as a function of  $[\text{Cd}^{2+}]$ , in the system  $0.025 \text{ M HClO}_4$ ,  $0 \leq [\text{Cd}(\text{ClO}_4)_2] \leq 0.1 \text{ M}$  and  $X \text{ M NaClO}_4$ , using  $I = 3 \text{ M}$ , constant, at  $25.000 \pm 0.005^\circ \text{C}$ .

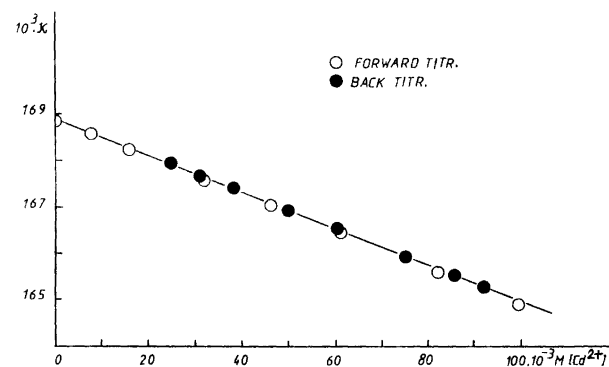


Fig. 2.  $10^3 \kappa$  versus  $[\text{Cd}^{2+}]$ , for the determination of the ionic molar conductivities in the system  $0.025 \text{ M HClO}_4$ ,  $0 \leq [\text{Cd}(\text{ClO}_4)_2] \leq 0.1 \text{ M}$  and  $X \text{ M NaClO}_4$ , using  $I = 3 \text{ M}$ , constant, at  $25.000 \pm 0.005^\circ \text{C}$ .

measured data without transformation. The fundamental equation, which is valid here, is

$$10^3 \kappa = z_B c_B \lambda_B^{\text{tr}} + c_H \lambda_H^{\text{tr}} + [Y^-] \lambda_Y + [A^+] \lambda_A \quad (4)$$

Here,  $\lambda_Y$  is the function of the composition of the test solution. For this plot

$$\text{the intercept} = c_H \lambda_H^{\text{tr}} + \lambda_{Y(2)} [Y^-] + \lambda_A [A^+]_2 \quad (5)$$

which is equal to 168.88 in experiment 1 and 169.33 in experiment 2. The intercept represents the conductivity of the two-component system  $0.025 \text{ M HClO}_4 + 2.975 \text{ M NaClO}_4$ . First, we can estimate the ionic molar conductivities valid in this system.

Here,  $\lambda_{\text{Na}}$  can be considered as constant, being equal to the value valid in  $3 \text{ M NaClO}_4$ . We assume that the ionic molar conductivity of the  $\text{ClO}_4^-$  ions in this two-component system,  $\lambda_{Y(2)}$ , can be calculated due to additivity [cf. eqn. (19) in Ref. 2] in terms of the ionic strength fractions. Therefore, we have

$$\lambda_{\text{Na}} = 0.43 \times 54.60 = 23.48$$

$$\lambda_{Y(2)} = [A^+] \lambda_Y (3 \text{ M NaClO}_4) / I + c_H \lambda_Y (3 \text{ M HClO}_4) / I = 31.19 \quad (6)$$

as

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

$$\lambda_Y (3 \text{ M HClO}_4) = 0.17 \times 233.1 = 39.6$$

Hence,  $\lambda_H^{\text{tr}}$  can be obtained from the intercept = 168.88

$$\lambda_{H(1)}^{\text{tr}} = 218.28$$

As is seen,  $\lambda_H^{\text{tr}}$  is slightly higher than its value in 3 M HClO<sub>4</sub>:  $\lambda_H (3 \text{ M HClO}_4) = 0.83 \times 233.1 = 193.5$ . This result is consistent with the positive intercept of the straight line obtained for the percentage deviation curve. Here, the transport numbers and the molar conductivities for 3 M NaClO<sub>4</sub> and 3 M HClO<sub>4</sub>, determined by Biedermann and Douh ret,<sup>4</sup> were taken from Ref. 1.

A small uncertainty in the position of the intercept strongly influence the value of  $\lambda_H^{\text{tr}}$ , as discussed in Ref. 2. In order to estimate the magnitude of this uncertainty, we shall consider the value of  $10^3 \kappa$ , measured in Mixture 1 and Mixture 2 (to be discussed in Section 2.2) at the common experimental point  $[H^+] = 0.025 \text{ M}$  and  $[Cd^{2+}] = 0.050 \text{ M}$ . These two values should be identical. At this composition we have

	Mixture 1	Mixture 2
$10^3 \kappa$	166.93 (in expt. 1)	
$10^3 \kappa$	167.27 (in expt. 2)	167.20

Here, expt. denotes experiment. According to this comparison,  $-0.27$  unit total uncertainty (0.18%) appears between the corresponding  $10^3 \kappa$  values for Mixture 1, expt. 1, and Mixture 2, due to some uncertainty in the position of the intercept in Fig. 2. Therefore, we choose expt. 2 as the correct one. Thus we take the intercept of expt. 2 ( $169.30 \pm 0.07$ ) for the calculation of the final value of  $\lambda_H^{\text{tr}}$ , from eqn. (5). Hence, we obtain

$$\lambda_{H(R)}^{\text{tr}} = 235.08 \pm 1.60$$

The uncertainty in this result is  $\pm 0.68\%$ . Here,  $R$  denotes result.

1.3. *The plot of  $10^3 \kappa - [Y^-] \lambda_{Y(3)}$  versus  $[Cd^{2+}]$ , at  $[HClO_4] = 0.025 \text{ M}$ , constant.* The value of  $\lambda_{Cd}^{\text{tr}}$  in this special mixture was estimated as follows. Inserting the special concentration condition given by eqn. (2) into eqn. (4) and forming the difference given in the title, we obtain

$$10^3 \kappa - [Y^-] \lambda_{Y(3)} = c_B [z_B \lambda_B^{\text{tr}} - \lambda_A (z_B^2 + z_B)/2] + c_H (\lambda_H^{\text{tr}} - \lambda_A) + C \lambda_A \quad (7)$$

Here,  $\lambda_{Y(3)}$  denotes the values valid in the three-component system and calculated according to the additivity

$$\lambda_{Y(3)} = c_A \lambda_Y (3 \text{ M NaClO}_4)/I + c_H \lambda_Y (3 \text{ M HClO}_4)/I + [c_B (z_B^2 + z_B)/2] \lambda_Y (1.5 \text{ M Cd(ClO}_4)_2)/I \quad (8)$$

The values obtained change linearly with composition, according to

$$\lambda_{Y(3)} = 31.19 - 15.03 [Cd^{2+}] \quad (9)$$

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  $t_{Cd} [1.5 \text{ M Cd(ClO}_4)_2] \cong t_{Zn} [1.5 \text{ M Zn(ClO}_4)_2] = 0.319$  was introduced. The plot in question is shown in Fig. 3. Here, the slope is equal to

$$z_B \lambda_B^{\text{tr}} - \lambda_A (z_B^2 + z_B)/2 = 35.10 \quad (10)$$

From this slope value we can calculate

$$\lambda_{Cd}^{\text{tr}} = 52.77$$

As is seen, the Cd<sup>2+</sup> ions are strongly accelerated in this mixture. Therefore, the deviations are positive in Fig. 1.

Having these results, we can check how the constancy of the ionic molar conductivities is fulfilled. As is seen,  $\lambda_{Cd}^{\text{tr}}$ ,  $\lambda_H^{\text{tr}}$  and  $\lambda_{Na}$  are constant.  $\lambda_{Y(3)}$  changes slightly with the composition of the test solution.

This mixture is generally used in  $E_0$  titrations where a B<sup>z(B)+</sup>-ion-sensitive indicator electrode is used. Here the potential function given below is valid.<sup>1</sup>

$$E_B \equiv E_B - (g/z_B) \log c_B = E_{0B} + g d_1 c_B + g d_2 c_H \quad (11)$$

The functions  $d_1$  and  $d_2$  are defined in Ref. 1 by eqns. (94) and (95). In this function,  $E_B'$ , ratios of the following ionic molar conductivities appear:

$$R(B^{z(B)+}) = - \frac{[\lambda_B - z_B \lambda_Y + (\lambda_Y - \lambda_A)(z_B^2 + z_B)/2]}{[2.303 C(\lambda_A + \lambda_Y)]} \quad (12)$$

$$R(H^+) = -(\lambda_H - \lambda_A)/[2.303 C(\lambda_A + \lambda_Y)] \quad (13)$$

Calculating these ratios at the beginning and at the end of the concentration range of the Cd<sup>2+</sup> ions studied, we obtain the uncertainties given in Table 1. As it is seen from this table, the ratios of the ionic molar conductivities in question are constant. However, the function obtained for the total cell e.m.f.  $E_B$ , is very sensitive to small changes in the ratios of the ionic molar conductivities. The uncertainties in  $E_B$ , which appear due to changes in  $\lambda_{Y(3)}$ , are 0.13 mV/M Cd<sup>2+</sup>, which gives 0.01 mV at 0.1 M [Cd<sup>2+</sup>], and 0.79 mV/M H<sup>+</sup>, which gives 0.02 mV

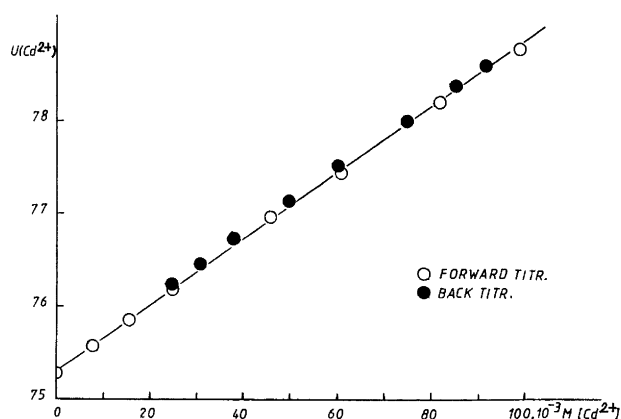


Fig. 3.  $U(Cd^{2+}) = 10^3 \kappa - [Y^-] \lambda_{Y(3)}$  versus  $[Cd^{2+}]$ , for the estimation of  $\lambda_{Cd}^{\text{tr}}$  in the system 0.025 M HClO<sub>4</sub>,  $0 \leq [Cd(ClO_4)_2] \leq 0.1 \text{ M}$  and  $X \text{ M NaClO}_4$ , at  $I = 3 \text{ M}$ , is kept constant.

Table 1. Estimation of the uncertainties  $|dE_B|$  in  $E_B$  [cf. eqn. (11)], in mV/M  $\text{Cd}^{2+}$  or  $\text{H}^+$ , caused by the change of  $\lambda_{Y(3)}$  with the composition.

$[\text{Cd}^{2+}]$ in M: $7.679 \times 10^{-3}$	$99.508 \times 10^{-3}$
$31.08 \geq \lambda_{Y(3)} \geq$	29.70
$-0.0356 \geq R(\text{B}^{2+}) \geq$	-0.0334
$-2.10 \geq 59.16 R(\text{B}^{2+}) \text{ mV L/mol Cd}^{2+} \geq$	-1.97
$ dE_B  \text{ mV L/mol Cd}^{2+} = 0.13$	
$-0.5158 \leq R(\text{H}^+) \leq$	-0.5292
$-30.52 \leq 59.16 R(\text{H}^+) \text{ mV L/mol H}^+ \leq$	-31.31
$ dE_B  \text{ mV L/mol H}^+ = 0.79$	

uncertainty at 0.025 M  $[\text{HClO}_4]$ . As is seen, the uncertainties are of the same order of magnitude as those of the most accurate e.m.f. measurements. Hence, the potential functions derived in Ref. 1 are valid for these mixtures.

2. Conductivity measurements in mixtures where  $c_H$  is varied and  $c_B$  is kept constant. The conductivity  $10^3 \kappa$  has been measured in Mixture 2. These data have been interpreted in terms of the ionic molar conductivities  $\lambda_{\text{Cd}}^{\text{tr}}$ ,  $\lambda_{\text{H}}^{\text{tr}}$ ,  $\lambda_{\text{Na}}$  and  $\lambda_{Y(3)}$ . The treatment of the data has been similar to that one used in Section 1.

2.1. The percentage deviations of the conductivity from additivity. The deviation function used in Section 1.1 is plotted as a function of  $[\text{H}^+]$  in Fig. 4. The deviations are positive, a linear function of  $[\text{H}^+]$  and decrease. At  $[\text{H}^+] = 0$  we have large positive deviation due to the increase of  $\lambda_{\text{Cd}}^{\text{tr}}$  in this mixture, too. The small and negative slope shows that  $\lambda_{\text{H}}^{\text{tr}}$  is slightly lower than in 3 M  $\text{HClO}_4$ .

2.2. The plot of  $10^3 \kappa$  versus  $[\text{H}^+]$  at  $[\text{Cd}(\text{ClO}_4)_2] = 0.050 \text{ M}$ , constant. This plot is presented in Fig. 5 which is a straight line and gives the measured data without transformation. According to eqn. (4), the intercept of

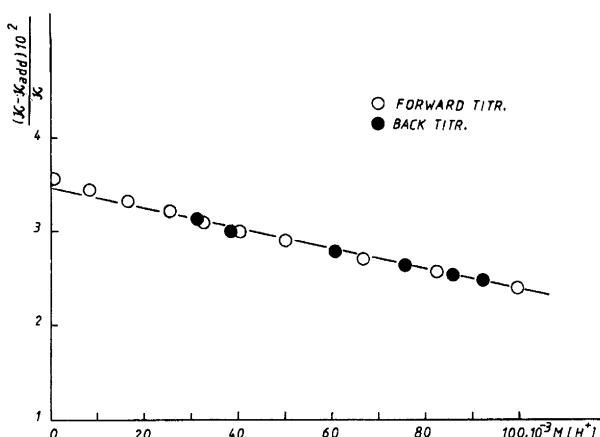


Fig. 4. The percentage deviation of the measured conductivity ( $10^3 \kappa$ ) from additivity ( $10^3 \kappa_{\text{add}}$ ) as a function of  $[\text{H}^+]$ , in the system 0.050 M  $\text{Cd}(\text{ClO}_4)_2$ ,  $\sim 2 \times 10^{-3} \leq [\text{HClO}_4] \leq 0.1 \text{ M}$  and  $X \text{ M NaClO}_4$ , at  $l = 3 \text{ M}$ , is kept constant, at  $25.000 \pm 0.005^\circ \text{C}$ .

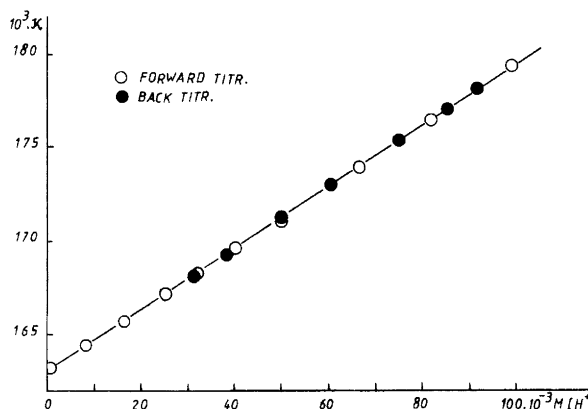


Fig. 5.  $10^3 \kappa$  versus  $[\text{H}^+]$ , for the determination of the ionic molar conductivities in the system 0.050 M  $\text{Cd}(\text{ClO}_4)_2$ ,  $\sim 2 \times 10^{-3} \leq [\text{HClO}_4] \leq 0.1 \text{ M}$  and  $X \text{ M NaClO}_4$ , using  $l = 3 \text{ M}$ , is kept constant, at  $25.000 \pm 0.005^\circ \text{C}$ .

this plot is

$$z_B c_B \lambda_B^{\text{tr}} + [\text{A}^+]_2 \lambda_A + \lambda_{Y(2)}^* [\text{Y}^-] = 163.1 \quad (14)$$

This equation describes the conductivity of the two-component system 0.050 M  $\text{Cd}(\text{ClO}_4)_2$ , is kept constant, and 2.850 M  $\text{NaClO}_4$ . The intercept can be used for the estimation of  $\lambda_{\text{Cd}}^{\text{tr}}$ ,  $\lambda_{Y(2)}^*$  and  $\lambda_A$ . We can assume, again, that  $\lambda_{\text{Na}}$  has the same value as in 3 M  $\text{NaClO}_4$ . Moreover,  $\lambda_{Y(2)}^*$  will be calculated as before. Hence, we have for this system  $\lambda_{\text{Na}} = 23.48$  and  $\lambda_{Y(2)}^* = 30.37$ . Thus, we can calculate from the intercept  $\lambda_{\text{Cd}(1)}^{\text{tr}} = 65.93$ .

Again, a small, possible uncertainty in the position of the intercept strongly influences the value of  $\lambda_{\text{Cd}}^{\text{tr}}$ . The uncertainty of the intercept in question was found to be  $\pm 0.04$  units. Hence, the following final result could be calculated:

$$\lambda_{\text{Cd}(R)} = 66.31 \pm 0.38$$

This corresponds to  $\pm 0.57\%$  uncertainty.

2.3. The plot of  $10^3 \kappa - [\text{Y}^-] \lambda_{Y(3)}^*$  versus  $[\text{H}^+]$  at  $[\text{Cd}(\text{ClO}_4)_2] = 0.050 \text{ M}$ , constant. The value of  $\lambda_{\text{H}}^{\text{tr}}$ , valid in this mixture, has been estimated with the help of the plot given in the title and is presented in Fig. 6. On the basis of this plot, and eqn. (7), the slope is given by

$$\lambda_{\text{H}}^{\text{tr}} - \lambda_{\text{Na}} = 156.43 \quad (15)$$

From this, we can calculate

$$\lambda_{\text{H}}^{\text{tr}} = 179.91$$

The values of  $\lambda_{Y(3)}^*$ , valid in the three-component system, have again been calculated due to the additivity. The values obtained can be described by the equation

$$\lambda_{Y(3)}^* = 30.37 + 2.83 [\text{H}^+] \quad (16)$$

The slight change in these values with  $[\text{H}^+]$  does not influence the constancy of the ratios  $R(\text{B}^{2+})$  and  $R(\text{H}^+)$  which appear in the total cell e.m.f.  $E_H$  [cf. eqns. (45), (95) and (96) in Ref. 1].

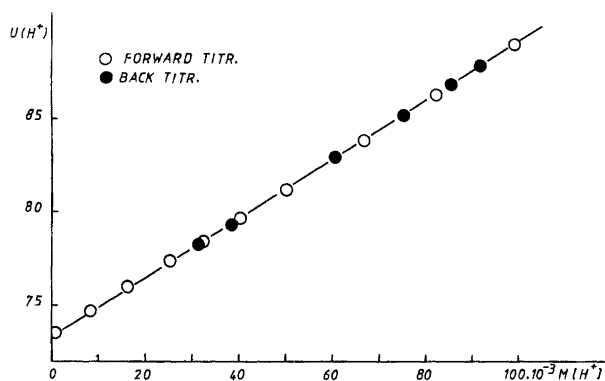


Fig. 6.  $U(\text{H}^+) = 10^3 \kappa - [\text{Y}_{(3)}] \lambda_{\text{Y}(3)}$  versus  $[\text{H}^+]$ , for the estimation of  $\lambda_{\text{H}}^{\text{tr}}$  in the system  $0.050 \text{ M Cd}(\text{ClO}_4)_2$ ,  $\sim 2 \times 10^{-3} \leq [\text{HClO}_4] \leq 0.1 \text{ M}$  and  $X \text{ M NaClO}_4$ , at  $l=3 \text{ M}$ , is kept constant.

3. *Conductivity measurements in mixtures where both  $c_{\text{B}}$  and  $c_{\text{H}}$  are varied.* If both  $E_{\text{OB}}$  and  $E_{\text{OH}}$  are to be determined within one titration, then both  $c_{\text{B}}$  and  $c_{\text{H}}$  should be varied. For the calculation of  $\Delta E_{\text{J}}$ , the relevant  $\lambda_{\text{J}}$  values must again be determined. The conductivity must be measured in a mixture of strong electrolytes, as suggested in Section 3 of Ref. 2. The measured conductivity data 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> This can be done in a similar way as suggested in Refs. 2 and 3. In this treatment of the data,  $\lambda_{\text{Y}(3)}$  can be used for the ionic molar conductivity of the  $\text{ClO}_4^-$  ions.

Expressing  $\lambda_{\text{Cd}}^{\text{tr}}$  in general as

$$\lambda_{\text{B}}^{\text{tr}} = f_1 + (\text{or } -) f_2 c_{\text{B}} \quad (17)$$

we can transform the data into the following form:

$$\begin{aligned} F_{\text{Oexp}} &\equiv 10^3 \kappa - [\text{Y}^-] \lambda_{\text{Y}(3)} - C \lambda_{\text{A}} \\ &= c_{\text{B}} \{ z_{\text{B}} [f_1 + (\text{or } -) f_2 c_{\text{B}}] - \lambda_{\text{A}} (z_{\text{B}}^2 + z_{\text{B}}) / 2 \} \\ &\quad + c_{\text{H}} (\lambda_{\text{H}}^{\text{tr}} - \lambda_{\text{A}}) \end{aligned} \quad (18)$$

on the basis of eqn. (7). Here, we can assume that  $\lambda_{\text{Na}}$  has the same value as in  $3 \text{ M NaClO}_4$ . Now, the function  $F_{\text{Ocalc}}$ , which consists of the right-hand side of eqn. (18), can be fitted to the data  $F_{\text{Oexp}}$  by adjusting  $f_1$ ,  $f_2$  and  $\lambda_{\text{H}}^{\text{tr}}$  as parameters. Here, we can use  $\lambda_{\text{Cd}}$  [ $1.5 \text{ M Cd}(\text{ClO}_4)_2$ ] as a starting value for  $f_1$ . The subscript calc stands for calculated. Experimental details are given in Ref. 2.

## Discussion

As is seen, the ionic molar conductivities (or some ratios of them) obtained here are constant. This was the most important condition of the deductions used for the calculations of the potential functions valid in e.m.f. cells with liquid junctions and contained mixtures of three strong electrolytes [cf. eqns. (1a) here and (40) and (45) in Ref. 1].

Having these results, we can estimate the systematic errors in the conditional constants  $E_{\text{OB}\alpha}$  and  $E_{\text{OH}\alpha}$ .

Considering eqn. (1c) here and eqn. (95) in Ref. 1, we can calculate the systematic error in  $E_{\text{OB}\alpha}$  and Mixture 1. We obtain

$$g c_{\text{H}} d_2 = -0.71 \text{ mV}$$

Hence, we have

$$E_{\text{OB}} = E_{\text{OB}\alpha} + 0.71 \text{ mV}$$

Considering eqn. (1d), here and eqn. (96) in Ref. 1, we can calculate the systematic error in  $E_{\text{OH}\alpha}$  and Mixture 2. We obtain

$$g c_{\text{B}} d_3 = -0.86 \text{ mV}$$

Hence, we have

$$E_{\text{OH}} = E_{\text{OH}\alpha} + 0.86 \text{ mV}$$

As is seen from these estimates, the systematic errors in  $E_{\text{OB}\alpha}$  and  $E_{\text{OH}\alpha}$  are not negligible if we use a curves fitting treatment for the e.m.f. titration data, and the accuracy of the fitted function should be  $0.01 \text{ mV}$ .

The systematic error  $g c_{\text{H}} d_2$  is a function of  $c_{\text{H}}$  and causes the variation of the equilibrium constants studied ( $\log \beta_{p,q,r}$ ) with  $c_{\text{H}}$ , as is seen from Table 1 in Ref. 2. If the complexes  $\text{B}_p \text{H}_q \text{L}_r$  are formed, we have the following systematic errors<sup>2</sup> in  $\log \beta_{p,q,r}$

For  $z(\text{B})=2$

$(E_{\text{OB}} + g c_{\text{H}} d_2) / \text{mV}$	$p=1$	$p=2$	$p=3$
$E_{\text{OB}} - 0.71$	-0.024	-0.048	-0.071

For  $z(\text{B})=3$

$(E_{\text{OB}} + g c_{\text{H}} d_2) / \text{mV}$	$p=1$	$p=2$	$p=3$
$E_{\text{OB}} - 0.71$	-0.036	-0.072	-0.106

The systematic error  $g c_{\text{B}} d_3$  is a function of  $c_{\text{B}}$  and it causes the variation of the equilibrium constants studied ( $\log \beta_{p,q,r}$ ) with  $c_{\text{B}}$ , as is seen from Table 2 of Ref. 2. Hence, in the present case, we have the following systematic errors<sup>2</sup> in  $\log \beta_{p,q,r}$

$(E_{\text{OH}} + g c_{\text{B}} d_3) / \text{mV}$	$q=1$	$q=2$	$q=3$
$E_{\text{OH}} - 0.86$	-0.014	-0.029	-0.043

The variation of  $\log \beta_{p,q,r}$  with  $c_{\text{H}}$  and  $c_{\text{B}}$ , respectively, can be interpreted as the formation of polynuclear complexes, if we do not take into account the systematic errors in question.

In Ref. 1, the potential contributions of the changing concentrations of the  $\text{Cd}^{2+}$  and  $\text{H}^+$  ions to the total potential anomalies in the cells were calculated, in order to prove the theory developed in Ref. 1. The calculated and measured slopes (defined in Ref. 1) agreed well.

Slope/ $\text{mV M}^{-1}$

	SL(H, $c_{\text{B}}$ )	SL(B, $c_{\text{B}}$ )	SL(H, $c_{\text{H}}$ )	SL(B, $c_{\text{H}}$ )
Calculated	-1.57	-2.75	-19.80	-19.80
Measured	1.6	$0 \pm 0.5$	-17.7	

Table 2. Estimation of the systematic errors in the formation constants  $\log \beta_{p,q,r}$  caused by the systematic errors in  $E_{0B}$  (cell B) and  $E_{0H}$  (cell H) under different experimental conditions.

Conditional constants/mV	Cell B Mixture 1: $c_H = 0.025 \text{ mol dm}^{-3}$ con- stant $E_{0B\alpha} = E_{0B} + gc_H d_2^1$			Cell H Mixture 2: $c_B = 0.050 \text{ mol dm}^{-3}$ con- stant $E_{0H\alpha} = E_{0H} + gc_B d_3^1$		
	Systematic errors in $\log \beta_{p,q,r}$					
Experimental conditions	$p=1$	$p=2$	$p=3$	$q=1$	$q=2$	$q=3$
$[\text{Na}^+] = 3 \text{ M}$ is kept constant: <sup>2</sup> Systematic error/mV $E_{0B}$ or $E_{0H}$ /mV $\Delta \log \beta_{p,q,r}$	in $E_{0B\alpha}$ : $gd_2^1 c_H = -0.17$ $E_{0B\alpha} + 0.17$ Negligible for $z(B) = 2$			in $E_{0H\alpha}$ : $gd_3^1 c_B = 1.99$ $E_{0H\alpha} - 1.99$ 0.034      0.067      0.102		
$[\text{ClO}_4^-] = 3 \text{ M}$ is kept constant: <sup>3</sup> Systematic error/mV $E_{0B}$ or $E_{0H}$ /mV $\Delta \log \beta_{p,q,r}$	in $E_{0B\alpha}$ : $gd_2^1 c_H = -0.63$ $E_{0B\alpha} + 0.63$ -0.017      -0.034      -0.050 for $z(B) = 2$			in $E_{0H\alpha}$ : $gd_3^1 c_B = 0.56$ $E_{0H\alpha} - 0.56$ 0.0084      0.016      0.024		
$I = 3 \text{ M}$ is kept constant: Systematic error/mV $E_{0B}$ or $E_{0H}$ /mV $\Delta \log \beta_{p,q,r}$	in $E_{0B\alpha}$ : $gd_2^1 c_H = -0.71$ $E_{0B\alpha} + 0.71$ -0.024      -0.048      -0.071 for $z(B) = 2$			in $E_{0H\alpha}$ : $gd_3^1 c_B = -0.86$ $E_{0H\alpha} + 0.86$ -0.014      -0.029      -0.043		

This means that both the developed equations<sup>1</sup> and the determined ionic molar conductivities are correct.

It should be pointed out that the real systematic errors in e.m.f. cells with complex formation will be higher than  $gc_H d_2$  and  $gc_B d_3$ , because the ions of the equilibrium solution will also contribute to the total potential anomalies in the cells [cf. eqns. (7) and (9) in Ref. 2 and Part 5<sup>7</sup>]. Moreover, the potential functions of the total cell e.m.f. are different in cells containing the mixtures of strong electrolytes and in those containing equilibrium solutions.

We can compare the systematic errors in the formation constants,  $\Delta \log \beta_{p,q,r}$ , in cells B and H, containing Mixtures 1 and 2, under the three different experimental conditions studied and caused by the systematic errors in  $E_{0B}$  and  $E_{0H}$ . These are presented in Table 2.

For cell B we obtained:

$$\begin{aligned} \Delta \log \beta_{p,q,r} &= \text{negligible for } z(B) = 2 \text{ at } [\text{Na}^+] \\ &= 3 \text{ M constant} < [\text{ClO}_4^-] = 3 \text{ M constant} < 1 \\ &= 3 \text{ M constant.} \end{aligned}$$

For cell H we obtained:

$$\Delta \log \beta_{p,q,r} = \text{smallest at } [\text{ClO}_4^-] = 3 \text{ M constant}$$

$$< I = 3 \text{ M constant} < [\text{Na}^+] = 3 \text{ M constant.}$$

At the experimental conditions  $[\text{ClO}_4^-] = 3 \text{ M}$  and  $I = 3 \text{ M}$ , both kept constant, the systematic error  $\Delta \log \beta_{p,q,r}$  is higher in cell B than in cell H.

If  $c_B$  and  $c_H$  are higher, the ionic molar conductivities should be measured again and  $\Delta \log \beta_{p,q,r}$  should be estimated again.

It is seen from this study too that the ionic molar conductivities change with the experimental conditions and cannot be interchanged.

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