The Liquid Junction Potential in Potentiometric Titrations. 2. Determination of Ionic Molar Conductivities in Mixtures of $Cd(ClO_4)_2 + HClO_4 + NaClO_4$ under the Experimental Condition that $[Na^+] = 3$ M is Kept Constant

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Néher-Neumann, E., 1998. The Liquid Junction Potential in Potentiometric Titrations. 2. Determination of Ionic Molar Conductivities in Mixtures of $Cd(ClO_4)_2 + HClO_4 + NaClO_4$ under the Experimental Condition that $[Na^+] = 3$ M is Kept Constant. – Acta Chem. Scand. 52: 873–882. © Acta Chemica Scandinavica 1998.

The molar conductivity of aqueous $Cd(ClO_4)_2$ solutions has been determined in the concentration range 0.75–1.5 mol dm^{-3}. The ionic molar conductivities were determined in the test solutions of some emf cells containing mixtures of $Cd(ClO_4)_2 + HClO_4 + NaClO_4$ under the experimental condition that $[Na^+] = 3$ M is kept constant.

In potentiometric titrations, emf cells containing equilibrium solutions, often with liquid junctions, are used for the determination of the equilibrium concentrations of the species and the formation constants $\log \beta_{p,q,r}$. Equilibrium studies, in the present practice, are interpreted by least-squares optimization programs[1] in which species are suggested until the theoretical and experimental titration data agree with 0.01 mV. The presence of the liquid junction in the cell causes a potential contribution of a magnitude of several mV at the boundary of the junction. This total potential anomaly is a function of the concentration of all ions present in the two terminal solutions. This has the result that a systematic error of several millivolts in the data will be interpreted as the formation of additional complexes, often polynuclear.

The goal of the present series is to develop correct equations for the calculation of potentials across liquid junctions, in order to reduce the systematic errors to around 0.1 mV and to avoid the suggestion of the formation of polynuclear species, dimers or trimers, which are artifacts. Moreover, the experimental condition which results in the smallest liquid junction potential will be identified.

The total cell emf in potentiometric studies can be defined as

$$E_J = E_{OJ} + (g/z_J) \log c_J f_{JTS2} + E_D + E_{Df} \qquad (1)$$

and the total potential anomalies as

$$\Delta E_J = (g/z_J) \log f_{JTS2} + E_D + E_{Df} \qquad (2)$$

Definitions and symbols used throughout this series are presented in Ref. 2.

In Ref. 2, potential functions were derived for the calculation of potentials across liquid junctions of constant ionic medium types, for emf cells containing mixtures of strong electrolytes: $BY_{z(B)} + HY + AY$ under the experimental conditions $[A^+] = C$ M constant, $[Y^-] = C$ M constant and $I = C$ M constant, respectively. This kind of cell is used for the determination of the experimental constants E_{OJ}. This study has shown that the determination of the constants of the Nernst equations, E_{OJ}, take place with systematic errors in the present practice. These errors cause the change of the equilibrium constants studied ($\log \beta_{p,q,r}$) with $[B^{z(B)+}]$ or $[H^+]$, respectively. Therefore, this phenomenon looks like the formation of polynuclear complexes, dimers, trimers, etc. The influence of this error on $\log \beta_{p,q,r}$ can be judged from the calculations given in Tables 1 and 2.

In the present practice, we determine[2] the conditional constants $E_{OB\alpha}$ and $E_{OH\alpha}$:

$$E_{OB\alpha} = E_{OB} + g c_H d_2 \qquad (3)$$

$$E_{OH\alpha} = E_{OH} + g c_B d_3 \qquad (4)$$

The terms d_2 and d_3 are the functions of some ionic molar conductivities and interaction coefficients.

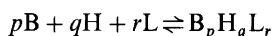In cells with complex formation, the following reaction

Table 1. The estimation of the systematic error in the formation constants $\log \beta_{p,q,r}$, caused by the neglected potential contribution of the H^+ ions to E_{OB}.

Cell B	$-p \, \Delta \log b = pgd_2 c_H z(B)/g$		
$E_{OB} + gd_2 c_H$/mV	$p = 1$	$p = 2$	$p = 3$
$z(B) = 2$			
$E_{OB} + 0.50$	0.017	0.034	0.050
$E_{OB} + 1.00$	0.034	0.067	0.101
$E_{OB} + 2.00$	0.067	0.135	0.203
$E_{OB} + 5.00$	0.169	0.338	0.507
$E_{OB} + 7.00$	0.236	0.473	0.710
$z(B) = 3$			
$E_{OB} + 0.20$	0.010	0.020	0.030
$E_{OB} + 0.50$	0.025	0.050	0.075
$E_{OB} + 1.00$	0.051	0.101	0.153
$E_{OB} + 2.00$	0.101	0.203	0.303
$E_{OB} + 5.00$	0.253	0.507	0.759
$E_{OB} + 7.00$	0.355	0.710	1.065

Table 2. The estimation of the systematic error in the formation constants $\log \beta_{p,q,r}$, caused by the neglected potential contribution of the $B^{+z(B)}$ ions to E_{OH}.

Cell H	$-q \, \Delta \log h = qgd_3 c_B / g$		
$E_{OH} + gd_3 c_B$/mV	$q = 1$	$q = 2$	$q = 3$
$E_{OH} + 0.5$	0.008	0.016	0.024
$E_{OH} + 1.00$	0.017	0.034	0.051
$E_{OH} + 2.00$	0.034	0.067	0.102
$E_{OH} + 5.00$	0.084	0.169	0.252
$E_{OH} + 7.00$	0.118	0.236	0.354
$E_{OH} + 10.00$	0.169	0.338	0.507

occurs

$$pB + qH + rL \rightleftharpoons B_p H_q L_r$$

The use of the conditional constant $E_{OB\alpha}$ in cells with complex formation will result in the following error in the equilibrium constant $\log \beta_{p,q,r}$

$$-p\Delta \log b = p(gd_2 c_H)z_B/g \tag{5}$$

in cell B, due to

$$\log \beta_{p,q,r} = \log [\text{complex}] - p \log b - q \log h - r \log l \tag{6}$$

and

$$\log b = (E_B - E_{OB} - gd_2 c_H)z_B/g + z_B^2[D(I) - D(C)]$$
$$- (z_B/g) \sum_V Q(B, V)V - \text{corr } z_B/g \tag{7}$$

These equations are valid for the preliminary data treatment. Here, $Q(B, V)$ denotes functions with constant values, in terms of some interaction coefficients and ionic molar conductivities (cf. Part 6A, to be published). V denotes the equilibrium concentrations $b = [B^{z(B)+}]$, $h = [H^+]$, $l = [L^{y-}]$ and the change of the composition of the ionic medium $\Delta c_A = c_A - C$ or $\Delta c_Y = c_Y - C$. Assuming values for the term $gd_2 c_H$ mV in eqns. (5) and (7), the

systematic error in $\log \beta_{p,q,r}$ can be estimated, as given in Table 1.

The use of the conditional constant $E_{OH\alpha}$ in cells with complex formation will result in the following error in $\log \beta_{p,q,r}$:

$$-q\Delta \log h = q(gd_3 c_B)/g \tag{8}$$

in cell H, due to

$$\log h = (E_H - E_{OH} - gd_3 c_B)/g + [D(I) - D(C)]$$
$$- (1/g) \sum_V Q(H, V)V - \text{corr}/g \tag{9}$$

where $Q(H, V)$ denotes constant functions, again. Assuming values for the term $gd_3 c_B$ mV in eqns. (8) and (9), the systematic error in $\log \beta_{p,q,r}$ can be estimated, as given in Table 2.

In order to calculate the correct total potential anomalies in the emf cells used, ΔE_B or ΔE_H,[2] we need the ionic molar conductivities in the transition layer (λ_j^*) for every mixture studied. In the present series it will be assumed that the ionic molar conductivities in the transition layer can be approximated by the λ_j values valid in the test solution.

In the present paper, the molar conductivity of aqueous $Cd(ClO_4)_2$ solutions was measured in concentrated and very dilute solutions.

Moreover, the ionic molar conductivities will be estimated from the measurements of the conductivity of the electrolyte mixtures $BY_{z(B)} + HY + AY$ with the composition given below. These mixtures were also investigated by emf measurements in Ref. 2.

Mixture 1: $c_H = 0.025$ mol dm^{-3}, is kept constant, $[AY] = 3$ mol dm^{-3}, is kept constant, c_B is varied within the range 0–0.180 mol dm^{-3}.

Mixture 2: $c_B = 0.050$ mol dm^{-3}, is kept constant, $[AY] = 3$ mol dm^{-3}, is kept constant, c_H is varied within the range 0.004–0.1 or 0.2 mol dm^{-3}. Here, $B = Cd^{2+}$, $Y^- = ClO_4^-$ and $c_H \equiv [H^+] = [HClO_4]$ mol dm^{-3}, $c_B \equiv [Cd^{2+}] = [Cd(ClO_4)_2]$ mol dm^{-3} and $[AY] \equiv [NaClO_4]$, the ionic medium used, in $C = 3$ mol dm^{-3} concentration.

Presentation of the conductivity measurements

1. Measurement of the molar conductivity of aqueous $Cd(ClO_4)_2$ solutions. In order to be able to calculate the deviations of conductivity from the additivity in the mixtures of aqueous $Cd(ClO_4)_2 + HClO_4 + NaClO_4$ solutions, we must know the molar conductivity and the transport numbers of the pure components. Therefore, conductivity measurements have been carried out in aqueous solutions of $Cd(ClO_4)_2$, in the concentrations range 0.76–1.5 mol dm^{-3} at $[H^+] = 8.891 \times 10^{-3}$ mol dm^{-3}, constant, and 25.000 ± 0.005 °C. The uncertainty of the resistance measurements was, in general, ca. 0.02%. The measurements have been carried out as forward and back titrations. The Λ value of $Cd(ClO_4)_2$ has also been checked in some points of low concentration.

In this publication, all molar conductivities (Λ and λ) are expressed in S cm^2 (g mol)$^{-1}$ and the conductivity (κ) in cm^{-1} S. These units are generally omitted in the text for simplicity.

1.1. Survey of the measurement of the molar conductivity in concentrated solutions of $Cd(ClO_4)_2$.

The conductivity of the test solution can be given according to eqn. (13) in Ref. 2 as

$$10^3 \kappa = z_B \lambda_B [B^{z(B)+}] + \lambda_Y [Y^-] + \lambda_H [H^+] \qquad (10)$$

Introducing the concentration condition

$$[Y^-] = z_B [B^{z(B)+}] + [H^+] \qquad (11)$$

we obtain

$$10^3 \kappa = z_B [B^{z(B)+}](\lambda_B + \lambda_Y) + [H^+][\lambda_H + \lambda_Y] \qquad (12)$$

Plotting $10^3 \kappa$ versus [Cd^{2+}], ($\lambda_{Cd} + \lambda_Y$) can be calculated from the slope. This plot is presented in Fig. 1. The function obtained could be divided into three regions, each of which could be described by a straight line. The results are given in Table 3.

As seen, we could obtain the quantity ($\lambda_{Cd} + \lambda_Y$) accurately. In these solutions, the conductivity of the ClO_4^- ions can slightly be influenced by the presence of $HClO_4$ at a constant level. This can be estimated as follows.

In these solutions, λ_Y may be estimated according to the additivity rule, in terms of the ionic strength fractions.
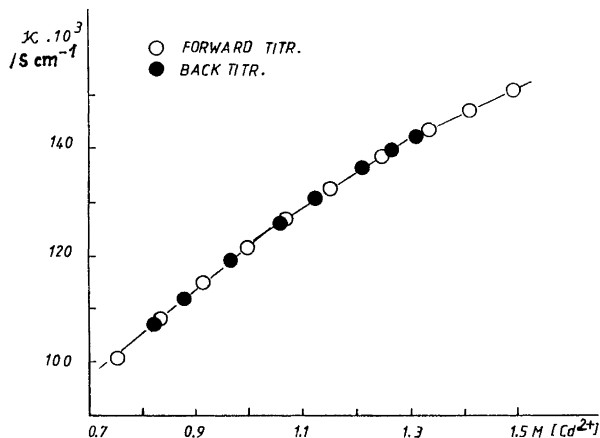

Fig. 1. Determination of the molar conductivity of the aqueous solutions of $Cd(ClO_4)_2$, $\Lambda_{Cd(ClO_4)_2}$, in the concentration range $0.75 \leqslant [Cd(ClO_4)_2] \leqslant 1.54$ mol dm^{-3} at $[HClO_4] = 8.891 \times 10^{-3}$ mol dm^{-3}, constant, and 25.000 ± 0.005 °C. $10^3 \kappa$ vs. [Cd^{2+}].

Table 3. Molar conductivity of the aqueous solutions of pure $Cd(ClO_4)_2$ in the concentration range 0.75–1.5 mol dm^{-3}.

$[Cd(ClO_4)_2] + 0.008891$ $HClO_4$ /mol dm^{-3}	$\Lambda Cd(ClO_4)_2$ /S cm^2 mol^{-1}
0.75–1.03	41.1
1.03–1.29	32.3
1.29–1.50	23.6

The ionic strength is

$$I = C + c_H + c_B(z_B^2 + z_B)/2 \qquad (13)$$

and therefore

$$\lambda_Y = [(z_B^2 + z_B)/2][B^{z(B)+}]\lambda_Y(BY_{z(B)})/I + [H^+]\lambda_Y(HY)/I \qquad (14)$$

where the values of λ_Y (component) refer to the ionic molar conductivity of the Y^- ions in the pure solution of the components of the mixture in question, at the actual level of $[Y^-]_T$.

The order of magnitude of the last term in the previous equation was estimated at 0.75 and 1.50 mol dm^{-3} concentrations of [Cd^{2+}] using the values λ_Y (1 mol dm^{-3} HY) = $329.3 \times 0.15 = 51.0$ and λ_Y (3 mol dm^{-3} HY) = $233.1 \times 0.17 = 39.6$. The result is λ_Y (HClO$_4$) [H$^+$]/I = 0.20 and 0.08, respectively. The molar conductivity of $HClO_4$ at 1 and 3 mol dm^{-3} levels and the corresponding transport numbers were taken from Ref. 2.

As is seen, the first decimal place of the value $(\lambda_{Cd} + \lambda_Y)_{exp}$ is influenced by the presence of 8.891×10^{-3} mol dm^{-3} $HClO_4$ in the solution studied. (Here, exp = experimental.) If we give the Λ [Cd(ClO$_4$)$_2$] values with one decimal place accuracy, no further correction is necessary.

If higher accuracy is required at a given concentration of, e.g., $Cd(ClO_4)_2$, then conductivity measurements should be carried out using a constant concentration for $Cd(ClO_4)_2$ and varying the concentration of $HClO_4$ slightly: e.g. $0.008 \leqslant [HClO_4] \leqslant 0.060$ mol dm^{-3}. Then extrapolation of a plot of $10^3 \kappa$ vs. [H$^+$] to [H$^+$] = 0 will give the correct value for ($\lambda_{Cd} + \lambda_Y$) on the basis of eqn. (12).

1.2. The molar conductivity of very dilute $Cd(ClO_4)_2$ solutions.

Matheson[3] has measured conductivities in dilute $Cd(ClO_4)_2$ solutions at 25 °C in the concentration range 0.001–0.1 N, where the test solutions had acidities pH = 4.8–5.0. He tried to make corrections for the hydrolysis of the Cd^{2+} ions. He considered only one hydrolysis process.[4]

$$Cd^{2+} + H_2O \rightleftharpoons CdOH^+ + H^+$$
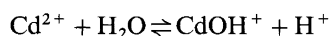
However, the hydrolysis of the Cd^{2+} ions is much more complex.[5]

For comparison, the molar conductivity of dilute $Cd(ClO_4)_2$ solutions was also measured in the present study, for some concentrations, in the presence of H$^+$ ions. The value of Λ [Cd(ClO$_4$)$_2$] was calculated through approximations of two steps.

1.2.1.

Considering eqn. (12), the conductivity of $Cd(ClO_4)_2$ solutions can be written as

$$z_B[B^{z(B)+}](\lambda_B + \lambda_Y) = 10^3 \kappa_{meas} - [H^+](\lambda_H + \lambda_Y) \qquad (15)$$

Here, meas = measured.

We assume that

$$\lambda_H = \lambda_H^\circ = 349.81$$

and

$$\lambda_Y = \lambda_Y^\circ = 67.37$$

both values at infinite dilution.[6a] Hence, the values presented in Table 4 could be calculated for $\lambda_{Cd} + \lambda_Y \equiv \Lambda$ [Cd(ClO$_4$)$_2$] from eqn. (15), as a first approximation.

1.2.2. We assume now, as a second step in the approximation, that Onsager's limiting law[6b] is valid for the value of $\lambda_H + \lambda_Y \equiv \Lambda$ (HClO$_4$) at the ionic strength in question

$$\Lambda(HClO_4) = \Lambda^\circ(HClO_4)$$

$$- \left(0.7852 \frac{q\Lambda^\circ(HClO_4)}{1 + \sqrt{q}} + 30.32(|z_1| + |z_2|) \right) \sqrt{I} \quad (16a)$$

where

$$q = \frac{|z_1 z_2|}{|z_1| + |z_2|} \times \frac{\lambda_1^\circ + \lambda_2^\circ}{|z_2|\lambda_1^\circ + |z_1|\lambda_2^\circ} \quad (16b)$$

Subscript 1 denotes the H$^+$ ion, 2 the ClO$_4^-$ ion. For $|z_1| = |z_2| = 1$, q is 1/2.

From eqns. (15), (16a) and (16b) the value of the second approximation could be calculated for Λ [Cd(ClO$_4$)$_2$], as presented in Table 4. As is seen, the results of the second approximation agree within ca. 1% with the values obtained by Matheson, although strictly, Onsager's limiting law is valid only if the concentration of the component is $\leqslant 0.001$ N.

2. Measurements of the ionic molar conductivities in the mixtures of Cd(ClO$_4$)$_2$ + HClO$_4$ + NaClO$_4$ at [Na$^+$] = 3 mol dm^{-3}. In order to calculate the different potential functions describing the total potential anomalies,[2] we must know the ionic molar conductivity values λ_H^{tr}, λ_{Cd}^{tr}, and also λ_Y and λ_{Na} in the actual mixtures. Here, tr denotes trace.

2.1. Conductivity measurements in mixtures where c$_{Cd}$ is varied while c$_H$ is kept constant. Conductivity measurements have been carried out for the determination of the λ_J values in question in Mixture 1 where [Cd(ClO$_4$)$_2$] was varied in the range 0–0.187 mol dm^{-3}. The conductivity of the mixtures, 10^3 κ, was calculated according to the definition given in Ref. 2. The conductivity data have been interpreted, in terms of the ionic molar conductivities, with the help of several plots as presented below.

2.1.1. The percentage deviations of the conductivity from additivity. First these deviations have been investigated through a plot of $10^2(10^3 \kappa - 10^3 \kappa_{add})/10^3 \kappa$ vs. [Cd^{2+}]. We assume that $\lambda_{Y,add}$ is valid and that it will change linearly with the composition. Here, $10^3 \kappa$ stands for the measured conductivity of the solution studied and $10^3 \kappa_{add}$ is calculated according to the additivity as

$$10^3 \kappa_{add} = [H^+]\lambda_H(C \text{ M HY}) + [Na^+]\lambda_A(C \text{ M AY})$$
$$+ [Y^-]_{Y,add} + z_B[B^{z(B)+}]\lambda_B(C/z_B \text{ M BY}_{z(B)}) \quad (17)$$

Here

$$\lambda_H(C \text{ M HY}) = t_H(C \text{ M HY})\Lambda(C \text{ M HY}) \quad (18a)$$

$$\lambda_B(C/z_B \text{ M BY}_{z(B)}) = t_B(C/z_B \text{ M BY}_{z(B)})\Lambda(C/z_B \text{ M BY}_{z(B)}) \quad (18b)$$

$$\lambda_A(C \text{ M AY}) = t_A(C \text{ M AY})\Lambda(C \text{ M AY}) \quad (18c)$$

$$\lambda_{Y,add} = [A^+]\lambda_Y(C \text{ M AY})/I + [H^+]\lambda_Y(C \text{ M HY})/I$$
$$+ [(z_B^2 + z_B)/2][B^{z(B)+}]\lambda_Y(C/z_B \text{ M BY}_{z(B)})/I \quad (19)$$

In the equations above. t_J stands for the transport number of the ion J and Λ is the molar conductivity of the electrolyte noted at $C/|z_J|$ mol dm^{-3} concentration, respectively. $\lambda_{Y,add}$ is calculated in terms of the ionic strength fractions. The necessary values of Λ and t can be found in Ref. 2 for NaClO$_4$ ionic medium. Moreover, the approximation t_{Cd} [1.5 mol dm^{-3} Cd(ClO$_4$)$_2$]$\approx t_{Zn}$ [1.5 mol dm^{-3} Zn(ClO$_4$)$_2$] = 0.319 was used, taken from Ref. 6c.

The plot in question is shown in Fig. 2. As is seen, the deviations from additivity are rather small, $\leqslant 1\%$, and
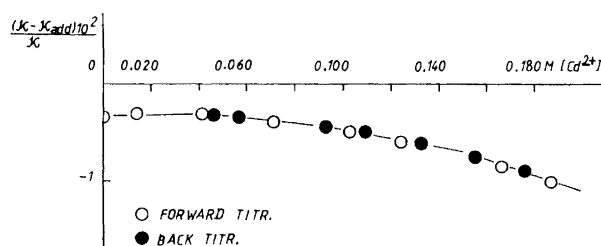

Fig. 2. Deviations of the measured conductivity (10^3 κ) from additivity (10^3 κ_{add}), in %, as a function of [Cd^{2+}], in the system 0.025 mol dm^{-3} HClO$_4$, 3 mol dm^{-3} NaClO$_4$, 0$\leqslant$[Cd(ClO$_4$)$_2$]$\leqslant$0.18 mol dm^{-3} at 25.000$\pm$0.005 °C.

Table 4. A survey of the molar conductivity of aqueous Cd(ClO$_4$)$_2$ solutions at some low concentrations and ionic strength (*I*/mol dm^{-3}): comparison is made with values from the literature.

[Cd^{2+}] /mmol dm^{-3}	[H$^+$] /mmol dm^{-3}	10^3 κ /S cm^{-1}	This work 1st approx. Λ[Cd(ClO$_4$)$_2$] /S cm^2 mol^{-1}	*I* /mol dm^{-3}	Λ(HClO$_4$) [cf. eqn. (16a)]	This work 2nd approx. Λ[Cd(ClO$_4$)$_2$] /S cm^2 mol^{-1}	Matheson's work[3] *I* /mol dm^{-3}	Λ[Cd(ClO$_4$)$_2$] /S cm^2 mol^{-1}
50.08	2.104	9.932	90.39	0.1523	367.20	91.45	0.1515	92.58
46.95	1.97	9.358	90.90	0.1428	368.79	91.92		
44.19	1.86	8.842	91.26	0.1344	370.24	92.25	0.1338	93.39

they are negative. They can be described with the help of two straight lines. As the deviations are a linear function of the $[Cd^{2+}]$, they can be interpreted as the result of the presence of the Cd^{2+} ions. Therefore, λ_{Cd}^{tr} will be smaller than its value in the pure solution of 1.5 mol dm^{-3} $Cd(ClO_4)_2$, and it changes its value at $[Cd^{2+}] \approx 0.090$ mol dm^{-3}. Moreover, the negative intercept is most probably due to the decrease of λ_H^{tr} value, compared to λ_H (3 mol dm^{-3} $HClO_4$).

2.1.2. The plot $10^3 \kappa$ vs. $[Cd^{2+}]$ at $[HClO_4] = 0.025$ mol dm^{-3}, constant. This plot is presented in Fig. 3. As is seen, the function has a break point around $[Cd^{2+}] \approx 0.090$ mol dm^{-3}. It is interpreted as the result of the change of λ_{Cd}. The linearity of this plot before and after the break point shows that the ionic molar conductivities in this system are either constant or a linear function of $[Cd^{2+}]$. The conductivity of these mixtures can be given as

$$10^3 \, \kappa_{calc} = z_B[B^{z(B)+}]\lambda_B^{tr} + [H^+]\lambda_H^{tr} + \lambda_{Y,add}[Y^-] + [A^+]\lambda_A \tag{20}$$

Here, the validity of $\lambda_{Y,add}$ was again assumed.
The intercept of this plot is

$$[H^+]\lambda_H^{tr} + [A^+]\lambda_A + [Y^-]\lambda_{Y,add(2)} = 169.15 \tag{21}$$

at $[Cd^{2+}] = 0$ mol dm^{-3}. This represents the ionic molar conductivities in the two-component system 0.025 mol dm^{-3} $HClO_4 + 3$ mol dm^{-3} $NaClO_4$. As these concentrations are kept constant, this mixture is functioning as a constant ionic medium in this system. This mixture will be termed 'actual medium'. Here, λ_{Na} can be considered as constant, being equal to the value in 3 mol dm^{-3} $NaClO_4$. The ionic molar conductivity of the ClO_4^- ions in this two-component system, $\lambda_{Y,add(2)} \equiv \lambda_Y^{MED}$, can be calculated due to the additivity [cf. eqn. (19)]. Therefore
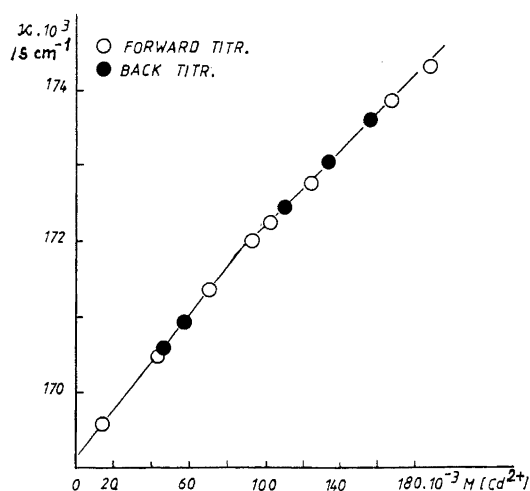

$$\kappa . 10^3 / S\ cm^{-1}$$

Fig. 3. $10^3 \kappa$ vs. $[Cd^{2+}]$, for the determination of the ionic molar conductivities in the system 0.025 mol dm^{-3} $HClO_4$, 3 mol dm^{-3} $NaClO_4$ and $0 \leqslant [Cd(ClO_4)_2] \leqslant 0.18$ mol dm^{-3}. (κ is the measured conductivity at $25.000 \pm 0.005\,°C$.)

we have

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

$$\lambda_Y^{MED} = 31.19$$

In this case λ_H^{tr} can be obtained from the intercept

$$\lambda_{H(1)}^{tr} = 174.40$$

As is seen, the H^+ ions are slowed down in this mixture, as their conductivity in 3 mol dm^{-3} $HClO_4$ is 233.1 $\times 0.83 = 193.5$.

The value of λ_H^{tr} cannot be obtained with a very high accuracy using eqn. (21). The reasons are as follows. (i) λ_H^{tr} is obtained as the result of a difference between two almost equal numbers, which then must be divided by a very small one. Therefore, a possible experimental uncertainty in the position of the intercept will be very much magnified. (ii) According to the author's experiences, gained in the conductivity measurements in question, the slopes of various plots such as Fig. 3, can always be reproduced very accurately. On the other hand, the starting points (intercepts) of two identical experiments can differ by around 0.1%. This uncertainty in the position of the intercept can result in much larger error in λ_H^{tr}. Accepting 0.1% uncertainty in the position of the intercept, the following alternative value can be calculated from eqn. (21):

$$\lambda_{H(2)}^{tr} = 166.01.$$

If we choose the average of the two values obtained, as the final result (denoted R), we have

$$\lambda_{H(R)}^{tr} = 170.20 \pm 4.20.$$

This result includes $\pm 2.46\%$ uncertainty. Now, only λ_{Cd}^{tr} is to be determined.

2.1.3. The plot of the deviation of λ_{Cd}^{tr} from λ_{Cd} [1.5 mol dm^{-3} $Cd(ClO_4)_2$] vs. $c_B = [Cd^{2+}]$. In order to investigate how much λ_{Cd}^{tr} deviates from its value in 1.5 mol dm^{-3} $Cd(ClO_4)_2$: λ_{Cd} [1.5 mol dm^{-3} $Cd(ClO_4)_2$] = $23.6 \times 0.319 = 7.5$, the deviation, defined as

$$\Delta(\lambda_B^{tr}) = 10^3 \, \kappa - [H^+]\lambda_{H(1)}^{tr} - [A^+]\lambda_A - \lambda_{Y,add(3)}[Y^-]$$

$$- z_B[B^{z(B)+}]\lambda_B(C/z_B \text{ M } BY_{z(B)}) = -z_B[B^{z(B)+}]r_1 \tag{22}$$

has been plotted as a function of $[Cd^{2+}]$. The subscript (3) refers to the three-component system. Here, those values of λ_{Na} and $\lambda_{H(1)}^{tr}$ should be used which have been determined in the previous section. This plot is shown in Fig. 4. Here, the break point is clearly visible at $[Cd^{2+}] = 0.086$ mol dm^{-3}, where the ionic molar conductivity of the Cd^{2+} ions changes. The deviation, r_1, could be calculated from the slopes. The results are presented in Table 5.

We can conclude from these results that the concentration of the Cd^{2+} ions should be $\leqslant 0.086$ mol dm^{-3} when this system is studied, in order to insure the constancy of λ_{Cd}^{tr}. It is seen from Fig. 3 and Table 5 that the individual values of λ_j and the ratios of some ionic molar
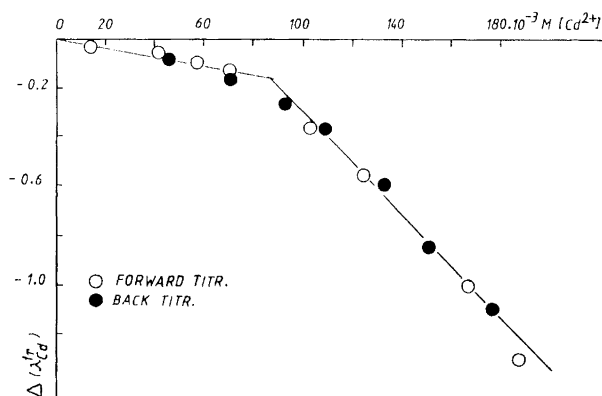
Fig. 4. The deviation of λ_{Cd}^{tr} from its value in 1.5 mol dm^{-3} Cd(ClO$_4$)$_2$, as a function of [Cd^{2+}], in the system 0.025 mol dm^{-3} HClO$_4$, 3 mol dm^{-3} NaClO$_4$, $0 \leqslant$ [Cd(ClO$_4$)$_2$] $\leqslant 0.18$ mol dm^{-3} at $25.000 \pm 0.005\,^\circ$C.

conductivities, which appear in the potential functions derived in Ref. 2 for the calculation of ΔE_j, are constant.

The data were also treated with the curve-fitting program MLAB.[7] Eqn. (23) was fitted to the data using the values λ_B^{tr}, λ_H^{tr} and λ_A as parameters.

$$F([B^{z(B)+}], [H^+]) \equiv 10^3 \, \kappa - \lambda_{Y,add(3)}[Y^-]$$

$$= z_B \lambda_B^{tr}[B^{z(B)+}] + \lambda_H^{tr}[H^+] + C\lambda_A \qquad (23)$$

The results are presented in Table 5. The author prefers the graphical result as the final one, which is based on the value $\lambda_{Na} = 23.48$, determined experimentally.

2.2. Conductivity measurements in mixtures where c_H is varied and c_{Cd} is kept constant at $[Na^+] = 3$ mol dm^{-3}, constant.

Conductivity measurements have been carried out for the determination of λ_H^{tr}, λ_{Na} and λ_Y in Mixture 2 where [HClO$_4$] have been varied in the range 0–0.1 mol dm^{-3}. The treatment of the data was similar to that used in section 2.1.

2.2.1. The percentage deviations of the conductivity from additivity.

The deviation function defined in section 2.1.1 has been plotted as a function of [H$^+$]. This plot is shown in Fig. 5. As is seen, the deviations are $\leqslant 3\%$. We have positive deviation at [H$^+$] $= 0$ mol dm^{-3}, due to the presence of the Cd^{2+} ions in 3 mol dm^{-3} NaClO$_4$. The presence of the H$^+$ ions causes negative deviations from additivity. The deviations are a linear function of [H$^+$]. This means that the ionic molar conductivities are either constant or a linear function of [H$^+$].

2.2.2. The plot $10^3 \kappa$ vs. $[H^+]$ at $[Cd(ClO_4)_2] = 0.050$ mol dm^{-3}, constant.

This plot is presented in Fig. 6, which is a complete straight line. Mathematically it is described by eqn. (20). For this plot we have

$$\text{Intercept} = [A^+]\lambda_A + z_B[B^{z(B)+}]\lambda_B^{tr} + \lambda_{Y,add(2)}[Y^-]$$

$$= 166.45 \qquad (24)$$

The intercept represents, again, the properties of the two-component system 0.050 mol dm^{-3} Cd(ClO$_4$)$_2$ + 3 mol dm^{-3} NaClO$_4$. As these concentrations are kept constant, this mixture can be considered as the actual medium used. Here, λ_{Na} can be considered to have the

Table 5. Survey of the values for ionic molar conductivities in S cm^2 mol^{-1} for the mixtures of 3 mol dm^{-3} NaClO$_4$, 0.025 mol dm^{-3} HClO$_4$, $0 \leqslant$ [Cd(ClO$_4$)$_2$] $\leqslant 0.187$ mol dm^{-3} at $25.000 \pm 0.005\,^\circ$C.[a]

Graphical analysis	$0.014\,127 \leqslant$ [Cd(ClO$_4$)$_2$] $\leqslant 0.080$/mol dm^{-3}
$\lambda_{Na} = 23.48$	
$\lambda_H^{tr} = 170.20 \pm 4.20$	$30.98 \leqslant \lambda_{Y,add(3)} \leqslant 30.08$
In the ranges	
$0 \leqslant$ [Cd(ClO$_4$)$_2$] $\leqslant 0.086$ mol dm^{-3}:	$0.57 \leqslant t_Y = \dfrac{\lambda_{Y,add(3)}}{\lambda_{Na} + \lambda_{Y,add(3)}} \leqslant 0.56$
$\lambda_{Cd}^{tr} = 7.54 - 0.90 = 6.64$	
$0.086 \leqslant$ [Cd(ClO$_4$)$_2$] $\leqslant 0.187$ mol dm^{-3}:	$0.43 \leqslant t_{Na} = \dfrac{\lambda_{Na}}{\lambda_{Na} + \lambda_{Y,add(3)}} \leqslant 0.44$
$\lambda_{Cd}^{tr} = 7.54 - 5.25 = 2.29$	$-0.15 \leqslant \dfrac{\lambda_{Cd} - z_{Cd}\lambda_{Y,add(3)}}{2.303\,C(\lambda_{Na} + \lambda_{Y,add(3)})} \leqslant -0.14$

Computer analysis
In the range $0 \leqslant$ [Cd(ClO$_4$)$_2$] $\leqslant 0.086$ mol dm^{-3}:
$\lambda_{Cd}^{tr} = 6.85$, $\lambda_H^{tr} = 167.85$, $\lambda_{Na} = 23.52$
In the range $0.086 \leqslant$ [Cd(ClO$_4$)$_2$] $\leqslant 0.187$ mol dm^{-3}:
$\lambda_{Cd}^{tr} = 2.23$, $\lambda_H^{tr} = 196.73$, $\lambda_{Na} = 23.55$

[a] Some quantities ($\lambda_{Y,add(3)}$, t_Y, t_{Na}, etc.) which appear in the potential functions are presented, Here, Y denotes ClO$_4^-$. The values of $\lambda_{Y,add(3)}$ change according to $\lambda_{Y,add(3)} = 31.19 - [Cd^{2+}] \times 13.87$.
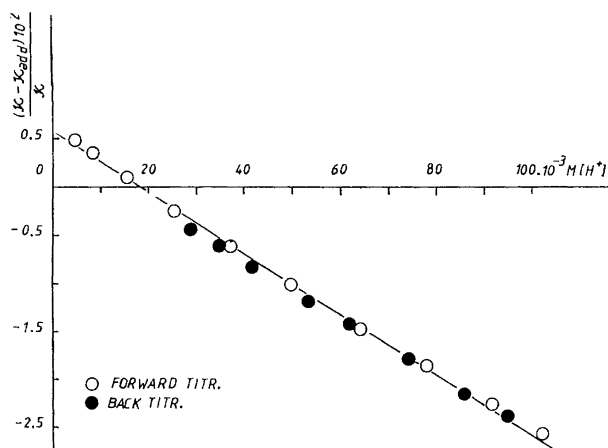
Fig. 5. Deviations of the measured conductivity (10^3 κ) from additivity (10^3 κ_{add}), in %, as a function of [H^+], in the system 0.050 mol dm^{-3} $Cd(ClO_4)_2$, 3 mol dm^{-3} $NaClO_4$, 0.005 $\leqslant$[$HClO_4$]$\leqslant$0.1 mol dm^{-3} at 25.000$\pm$0.005 °C.
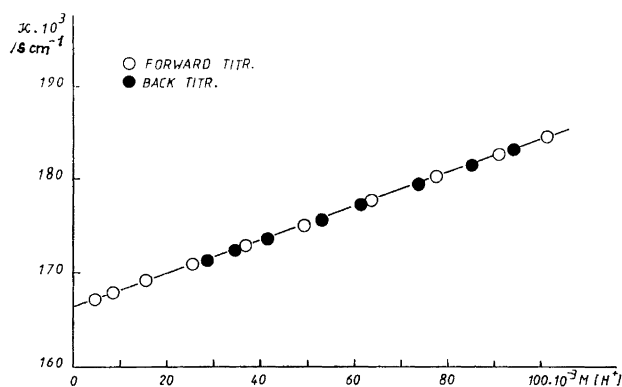

Fig. 6. 10^3 κ vs. [H^+] for the determination of the ionic molar conductivities in the system 0.050 mol dm^{-3} $Cd(ClO_4)_2$, 3 mol dm^{-3} $NaClO_4$ and 0.005$\leqslant$[$HClO_4$]$\leqslant$0.1 mol dm^{-3}, at 25.000$\pm$0.005 °C.

same value as in 3 mol dm^{-3} $NaClO_4$, again. $\lambda_{Y,add(2)} \equiv \lambda_Y^{MED}$ can be calculated in this two-component mixture according to eqn. (19). Then λ_{Cd}^{tr} can be obtained from the intercept. Hence, we have $\lambda_{Na} = 2.48$, $\lambda_Y^{MED} = 30.40$ and $\lambda_{Cd(1)}^{tr} = 17.57$.

Again, the value of λ_{Cd}^{tr} is strongly influenced by a possible small uncertainty in the position of the intercept. It was noticed in a second experiment that the intercept of Fig. 6 was 0.21 units higher: 166.66. With this value, we obtain an alternative result for λ_{Cd}^{tr}: $\lambda_{Cd(2)}^{tr} = 19.80$. Taking the average, as a final result, we have $\lambda_{Cd(R)}^{tr} = 18.68 \pm 1.12$. This corresponds to $\pm 6\%$ uncertainty, which is caused by 0.12% deviation in the position of the intercept.

Now, λ_H^{tr} should be estimated.

2.2.3. *Plot of the deviation of λ_H^{tr} from λ_H (3 mol dm^{-3} $HClO_4$) vs. $c_H = [H^+]$.* In order to investigate how much λ_H^{tr} deviates from its value in 3 mol dm^{-3} $HClO_4$ [λ_H^{tr} (3 mol dm^{-3} $HClO_4$) = 233.1 $\times$ 0.83 = 193.5], the devi-

ation, defined as

$$\Delta(\lambda_H^{tr}) = 10^3 \kappa - [A^+]\lambda_A - \lambda_Y[Y^-] - z_B[^{z(B)+}]\lambda_{B(1)}$$

$$- [H^+]\lambda_H^{tr}(C \text{ M HY}) = \pm[H^+]r_2 \qquad (25)$$

has been plotted as a function of [H^+]. Here, those values of λ_{Na} and $\lambda_{Cd(1)}^{tr}$ should be used which have been determined in the previous section. For the ionic molar conductivity of the ClO_4^- ions, both λ_Y^{MED}, constant, and $\lambda_{Y,add(3)}$, varying and calculated according to eqn. (19), have been tried.

2.2.3.1. The plot in question, using λ_Y^{MED}, is presented in Fig. 7. The slope of this straight line is identical with the deviation r_2:

$$r_2 = -48.41 \quad \text{and} \quad \lambda_H^{tr} = 193.5 - 48.41 = 145.0.$$

These results have been refined by using the curve-fitting program MLAB.[7] Substituting the concentration condition

$$[Y^-] = z_B[B^{z(B)+}] + [A^+] + [H^+] \qquad (26a)$$

into eqn.(20), we obtain, omitting the index MED,

$$10^3 \kappa_{calc} = z_B[B^{z(B)+}](\lambda_B^{tr} + \lambda_Y) + [H^+](\lambda_H^{tr} + \lambda_Y)$$

$$+ [A^+](\lambda_A + \lambda_Y) \qquad (26b)$$

with

$$\text{Slope} = \lambda_H^{tr} + \lambda_Y = 177.0 \qquad (26c)$$

Equation (26b) was fitted to the data by adjusting λ_H^{tr}, λ_Y, λ_B^{tr}, λ_A as parameters. The earlier results have been used as start values. The experimental slope [cf. eqn. (26c)] was given as a condition ('constraints') in the calculation. The results are presented in Table 6. As is seen, from the conductivity data of this table, the H^+ ions are strongly retarded in these mixtures.

2.2.3.2. The same plot can also be investigated using the assumption that the ionic molar conductivity of the ClO_4^- ions can be described by $\lambda_{Y,add(3)}$, valid for the three-component system and calculated according to eqn. (19). In this case, the results given in Table 7 have
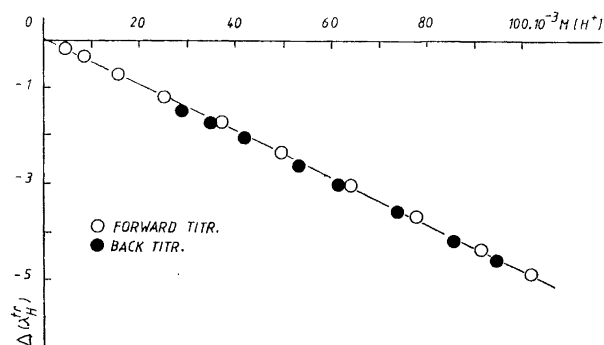

Fig. 7. The deviation of λ_H^{tr} from its value in 3 mol dm^{-3} $HClO_4$, as a function of [H^+], in the system 0.050 mol dm^{-3} $Cd(ClO_4)_2$, 3 mol dm^{-3} $NaClO_4$, 0.005$\leqslant$[$HClO_4$]$\leqslant$0.1 mol dm^{-3} at 25.000$\pm$0.005 °C.

Table 6. Survey of the values for ionic molar conductivities in $S cm^2 mol^{-1}$, valid in the mixtures of $3.00 mol dm^{-3}$ $NaClO_4$, $0.050 mol dm^{-3}$ $Cd(ClO_4)_2$, $0.0046 \leqslant [HClO_4]$ $\leqslant 0.100 mol dm^{-3}$ at $25.000 \pm 0.005 °C.$[a]

$\lambda_H^{tr} = 146.60$	$\Lambda_{CdY_2} = \lambda_{Cd}^{tr} + \lambda_Y = 47.83$
$\lambda_{Na} = 23.48$	$\Lambda_{NaY} = \lambda_{Na} + \lambda_Y = 53.88$
$\lambda_Y = 30.39_8$	$t_Y = \dfrac{\lambda_Y}{\lambda_{Na} + \lambda_Y} = 0.56$
$\lambda_{Cd}^{tr} = 17.43$	
$\Lambda_{HY} = \lambda_H^{tr} + \lambda_Y = 177.0$	$t_{Na} = \dfrac{\lambda_{Na}}{\lambda_{Na} + \lambda_Y} = 0.43$

[a] The molar conductivities Λ_{CdY_2}, Λ_{HY} and Λ_{NaY}, and also t_Y and t_{Na}, which appear in the potential functions, are presented. Equation (26b) was fitted to the experimental data using program MLAB.[7] The validity of λ_Y^{MED} was assumed, denoted λ_Y here.

been obtained. The data were also treated with the curve-fitting program MLAB.[7] Equation (23) was fitted to the data by using λ_H^{tr}, λ_{Cd}^{tr}, λ_{Na} as parameters. The results are shown in Table 7.

As at present we do not have any theory about how to interpret conductivity data in mixtures of concentrated electrolyte solutions, it is difficult to say which of these explanations is correct.

In sections 2.1 and 2.2 we have investigted two different types of mixture of $Cd(ClO_4)_2 + HClO_4 + 3 mol dm^{-3}$ $NaClO_4$. As is seen from the results presented in Tables 5–7, the ionic molar conductivities or the necessary ratios of them are constant in every special mixture. On the other hand, the individual values, especially λ_{Cd}^{tr} and λ_H^{tr}, differ greatly in the different mixtures, and they cannot be interchanged. Therefore, these ionic molar conductivities should be determined again, if both c_{Cd} and c_H

are varied durign the titration. This large variation of the values of λ_{Cd}^{tr} and λ_H^{tr} in the different mixtures of $Cd(ClO_4)_2 + HClO_4 + 3 mol dm^{-3}$ $NaClO_4$ has great importance for the determination of the constants of the Nernst equation, E_{OH} and E_{OB}.

3. Conductivity measurements in mixtures where both c_{Cd} and c_H are varied.

If both a H^+ and $B^{z(B)+}$ ion-sensitive indicator electrode is used in an emf titration, both E_{OH} and E_{OB} should be determined within one titration. In this case, both c_B and c_H should be varied. The ionic molar conductivities λ_H^{tr} and λ_B^{tr} will have new values which should be determined.

Conductivity measurements have to be carried out when the composition of the test solution is varied during the titration as $0.002 \leqslant [HClO_4] \leqslant 0.025 mol dm^{-3}$, $0 \leqslant [B(ClO_4)_2] \leqslant B_T(maximum) mol dm^{-3}$ and $NaClO_4$ ionic medium, when $[Na^+] = 3 mol dm^{-3}$, constant. Here, $B_T(maximum)$ is the highest value of the total concentration used for $BY_{z(B)}$ during the main titration in which complex formation is studied. As both c_{Cd} and c_H are varied in these mixtures, the graphical treatment used in sections 2.1.2 and 2.1.3, and 2.2.2 and 2.2.3, cannot be employed here. 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 program, e.g. MLAB.[7] This can be done by fitting eqn. (23) to the experimental data. λ_H^{tr}, λ_{Cd}^{tr} and λ_{Na} should be adjusted as parameters. The ionic molar conductivities of the pure components at the $C/|z_j| mol dm^{-3}$ concentration level can be used as start values for these parameters. These can be calculated in the same way as shown in section 2.1.1.

This procedure was tried on a mixture where both $[Cd(ClO_4)_2]$ and $[HClO_4]$ were varied equally (Mixture 3), in the range $0–0.110 mol dm^{-3}$, using $NaClO_4$ ionic

Table 7. Survey of the values for ionic molar conductivities in $S cm^2 mol^{-1}$, valid in the mixtures of $3.00 mol dm^{-3}$ $NaClO_4$, $0.050 mol dm^{-3}$ $Cd(ClO_4)_2$, $0.046 \leqslant [HClO_4] \leqslant 0.100 mol dm^{-3}$ at $25.000 \pm 0.005 °C.$[a]

Graphical analysis	$0.046 \leqslant [HClO_4] \leqslant 0.102/mol dm^{-3}$
$\lambda_H^{tr} = 137.78$	$30.42 \leqslant \lambda_{Y,add(3)} \leqslant 30.69$
$\lambda_{Cd}^{tr} = 18.68 \pm 1.12$	
$\lambda_{Na} = 23.48$	$0.56 \leqslant t_Y = \dfrac{\lambda_{Y,add(3)}}{\lambda_{Na} + \lambda_{Y,add(3)}} \leqslant 0.56$
	$0.43 \leqslant t_{Na} = \dfrac{\lambda_{Na}}{\lambda_{Na} + \lambda_{Y,add(3)}} \leqslant 0.43$
	$0.29 \leqslant \dfrac{\lambda_H - \lambda_{Y,add(3)}}{2.303 \, C(\lambda_{Na} + \lambda_{Y,add(3)})} \leqslant 0.29$

Computer analysis	
$\lambda_H^{tr} = 136.35$	
$\lambda_{Cd}^{tr} = 16.48$	
$\lambda_{Na} = 23.52$	

[a] The validity of $\lambda_{Y,add(3)}$ was assumed, describing the three-component system studied. Quantities like $\lambda_{Y,add(3)}$, t_Y, t_{Na}, etc., which appear in the potential functions, are presented. Y denotes ClO_4^-. Here, the values of $\lambda_{Y,add(3)}$ change according to $\lambda_{Y,add(3)} = 30.41 + 2.80[H^+]$.

medium under the experimental condition that $[Na^+] = 3$ mol dm^{-3}, constant. The results given below have been obtained.

For $0 \leqslant [Cd(ClO_4)_2] \leqslant 0.060$ mol dm^{-3}: $\lambda_{Cd}^{tr} = 16.11$, $\lambda_H^{tr} = 122.72$ and $\lambda_{Na} = 23.97$.

For $0.060 \leqslant [Cd(ClO_4)_2] \leqslant 0.109$ mol dm^{-3}; $\lambda_{Cd}^{tr} = 9.21$, $\lambda_H^{tr} = 117.52$ and $\lambda_{Na} = 24.32$.

Discussion

We can conclude that the ionic molar conductivities obtained are rather constant in the different mixtures studied. This constancy is valid for a given set of experimental conditions. The individual values of λ_{Cd} and λ_H differ greatly in the different mixtures. They cannot be interchanged. In the potential functions[2] ΔE_B and ΔE_H ratios of the ionic molar conductivities appear:

$$t_Y = \lambda_{Y,add}/(\lambda_A + \lambda_{Y,add}); \quad t_A = \lambda_A/(\lambda_A + \lambda_{Y,add})$$

$$(\lambda_B - z_B\lambda_{Y,add})/[2.303 C(\lambda_A + \lambda_{Y,add}]$$

$$(\lambda_H - \lambda_{Y,add})/[2.303 C(\lambda_A + \lambda_{Y,add}]$$

These ratios are rather constant. The uncertainty of these values, due to the slight change in $\lambda_{Y,add}$, does not exceed the uncertainty of the transport numbers and molar conductivities of $NaClO_4$ and $HClO_4$ solutions obtained from separate measurements.[8,9]

It is surprising that the ionic molar conductivities are so different in the three different mixtures studied. On the other hand, the actual ionic medium is quite different in these three types of mixtures. It means that the ions are migrating in quite different ionic environments in the different mixtures. It cannot be expected that the λ_j values are independent of the potential fields what the different actual mediums represent.

Obviously, this is the explanation to the fact that in the common point of Mixtures 1 and 2, with the composition $[H^+] = 0.025$ mol dm^{-3}, $[Cd^{2+}] = 0.050$ mol dm^{-3} and $[Na^+] = 3$ mol dm^{-3}, the values of λ_H and λ_{Cd} are different. In these points, the measured value of $10^3 \kappa$ is practically the same. This is also valid for λ_{Na} and $\lambda_{Y,add(3)}$. However, λ_{Cd} and λ_H cannot be determined from the conductivity of one point. We must examine the entire plots of $10^3 \kappa$ vs. $[Cd^{2+}]$ and $[H^+]$, respectively. In Mixture 1 the actual medium is 0.025 mol dm^{-3} $HClO_4 + 3$ mol dm^{-3} $NaClO_4$, both kept constant, with $[Cd^{2+}]$ as the independent variable. In Mixture 2 the actual medium is 0.050 mol dm^{-3} $Cd(ClO_4)_2 + 3$ mol dm^{-3} $NaClO_4$, both kept constant, with $[H^+]$ as the independent variable. The functions $10^3 \kappa$ vs. $[Cd^{2+}]$ and $10^3 \kappa$ vs. $[H^+]$ have different intercepts and slopes. These should be examined when we determine λ_{Cd} and λ_H, as we did here.

For these common points we have

$$10^3 \kappa - [A^+]\lambda_A - [Y^-]\lambda_{Y,add(3)}$$

$$= 2[Cd^{2+}]\lambda_{Cd(3)} + \lambda_{H(2)}[H^+]$$

$$= [H^+]\lambda_{H(3)} + 2[Cd^{2+}]\lambda_{Cd(2)} \qquad (27)$$

Here, $\lambda_{H(2)}[H^+] = 4.36$, valid in the two-component Mixture 1, and is determined by the intercept given in eqn. (21). $\lambda_{Cd(3)}$ is valid for the three-component Mixture 1 and can be calculated from the slope of Fig. 4 (6.64).

$2[Cd^{2+}]\lambda_{Cd(2)} = 1.77$, valid in the two-component Mixture 2, and is determined by the intercept given in eqn. (24). $\lambda_{H(3)}$ is valid for the three-component Mixture 2 and can be calculated from the plot 2.2.3.2 (137.78).

The value of function (27) is 5.02 for Mixture 1 and 5.21 for Mixture 2. This means that the values of $\lambda_{Cd(3)}$ and $\lambda_{H(3)}$ are correct.

After the determination of the ionic molar conductivities in Mixture 1 and Mixture 2, we can calculate the potential contribution of the H^+ ions to $E_{OB\alpha}$ [cf. eqn. (3)] and of the Cd^{2+} ions to $E_{OH\alpha}$ [cf. eqn. (4)]. We obtain $gc_Hd_2 = -0.17$ mV and $E_{OB} = E_{OB\alpha} + 0.17$ mV on the basis of eqn. (42) in Ref. 2. Moreover, $gc_{Cd}d_3 = 1.99$ mV and $E_{OH} = E_{OH\alpha} - 1.99$ mV on the basis of eqn. (46) in Ref. 2.

According to these results, the constants $E_{OB\alpha}$ has -0.17 mV and $E_{OH\alpha}$ has 1.99 mV systematic errors, if we do not correct for these effects. According to Table 2, 2 mV uncertainty in E_{OH} causes the following systematic errors in $\log \beta_{p,q,r}$:

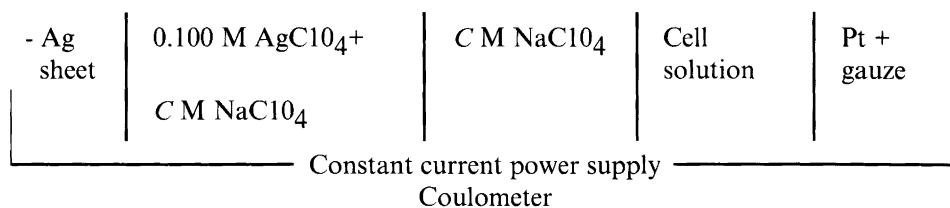| $q = 1$	$q = 2$	$q = 3$
0.034	0.067	0.102

at $[Cd^{2+}] = 0.050$ mol dm^{-3} kept constant during the determination of $E_{OH\alpha}$. If we have higher concentrations for the Cd^{2+} ions, this systematic error will increase and the uncertainty in $\log \beta_{p,q,r}$ will be higher. This also means that with the use of a least-squares optimization program, the real accuracy of the data should be used for the limitation of the fit, -0.17 and 2 mV here, instead of 0.01 mV, which is the accuracy of the readings of the potentiometer. However, 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 in cells with complex formation.

In Ref. 2 the potential contributions of the changing concentrations of the Cd^{2+} and H^+ ions, respectively, to the total potential anomalies in the cells were calculated, in order to prove the theory developed in Ref. 2. The calculated and measured slopes (defined in Ref. 2) agreed well. This means that both the developed equations and the determined ionic molar conductivities are correct.

No method can be found in the literature for the determination of the ionic molar conductivities in a junction of the type

$$AY \mid BY_{z(B)} + HY + AY$$
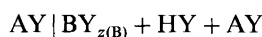
In earlier studies of simpler junctions, the values of the conductivities of the ions involved were used which were valid at infinite dilution. This is completely erroneous for liquid junctions of the constant ionic medium type.

| - Ag sheet | 0.100 M AgClO$_4$+

 C M NaClO$_4$ | C M NaClO$_4$ | Cell solution | Pt + gauze |

Constant current power supply
Coulometer

Scheme 1.

In some cases, λ_J values were used that were valid at the total concentration of the common anion (Y^-) involved.

For the concentration cell of the electrolyte MY and for junctions developed between two different electrolytes or mixtures of electrolytes, Harper[10] suggested a new calculation method. For these cases, it is supposed that for the ion J the values of λ_J and $\ln f_J$ in the mixture can be calculated as a linear combination of its values valid in all the pure binary components in which it participates, measured at the total ionic strength of the mixture, and weighted according to the ionic strength contribution of each component in the mixture. The use of this model is discussed at both moderate and higher concentrations. Harper's λ_J values vary with I. Harper has also developed a Fortran program for his calculations. The agreement between calculated and measured liquid junction values was good. The drawback of Harper's method is that the potential functions are rather complicated, even in the case of simple junctions.

Experimental

Reagents and solutions. Sodium perchlorate and dilute perchloric acid solutions were prepared and analyzed as usual in this laboratory.[11] The cadmium perchlorate stock solution was prepared and analyzed according to Ref. 5. The crystalline $Cd(NO_3)_2 \cdot 4H_2O$, Merck p.a. quality, did not contain any Cl^- impurity, so was used without purification. Gravimetric determinations of cadmium agreed to within 0.1 mass %.

The hydrogen ion concentration of the cadmium perchlorate stock solution was estimated by potentiometric titration. A weighed amount of the stock solution was added to 50 ml of 3 mol dm^{-3} NaClO$_4$ with a known hydrogen ion concentration in a titration vessel. Then H^+ ions were generated with the help of a coulometric circuit, in a titration procedure. The hydrogen ion content of the test solution was evaluated with the help of a Gran plot.[12]

Silver perchlorate stock solution was prepared by dissolving $Ag_2CO_3(s)$ in a slight access of perchloric acid. The silver content was determined gravimetrically as AgCl(s).

The experimental details of the emf measurements

are presented in Ref. 13. In the cell where $[Na^+]=$ 3 mol dm^{-3}, constant, a glass electrode (Beckman Co., type 40498) was used. The emf of the cell was measured with a Dynamco Ltd. digital voltmeter, type DM 2022. Stable emf values were obtained within a few minutes. A constant current power supply was used (Electronic Measurements, model C633).

The description of the coulometric circuit is given in Scheme 1 above for the generation of H^+ ions.

The conductivity measurements were carried out as described in Ref. 9. A dual-beam oscilloscope, type DM 64 from Telequipment, was used as a zero instrument, without amplification between the bridge output and the oscilloscope. During the conductivity measurements the temperature fluctuations in the bath were kept below $\pm 0.005\,^\circ\text{C}$.

The accuracy of conductivity measurements can be increased by using properly designed conductivity cells with large cell constants.

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Received October 24, 1997.