

Activities in the Systems $\text{Mg}^{2+} - \text{Na}^+ - \text{X}^- - \text{ClO}_4^-$ with $\text{X}^- = \text{Cl}^-, \text{Br}^-$ and SCN^- . The Possible Formation of MgX^+ Ion Pairs

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The changes in the activities of water and some positive and negative ions in 3 M (Na,Mg)ClO₄ when Na⁺ is replaced with Mg²⁺ have been studied by emf titrations and by vapor phase osmometry at 25°C. All data are consistent with eqn. (5) below, *i.e.* $z^{-1} \log y_1 = A + B[\text{Mg}^{2+}]$, when taking ion pair formation into account, where the two constants *A* and *B* are different for anions and cations and *z* is the charge of the ion studied. The following equilibrium constants are found for the formation of MgCl⁺ ($\log K_1 = -0.98 \pm 0.19$), MgBr⁺ ($\log K_1 = -1.45 (-1.01)$), MgSCN⁺ ($\log K_1 = -0.91 \pm 0.19$).

In a study of the equilibria between Mg(II) and phosphate¹ in 3 M (Na)ClO₄ it was sometimes necessary to replace as much as 600 mM of Na⁺ with Mg(II). Such a substantial change in the ionic medium might cause changes in the activity coefficients of the species involved and influence the description of the results obtained. In order to elucidate this point further some measurements have been performed in an attempt to evaluate the variation of the activity coefficients at about 3 M ionic strength ($\pm 10\%$) and 25°C in the systems $\text{Mg}^{2+} - \text{Na}^+ - \text{X}^- - \text{ClO}_4^-$ for $\text{X}^- = \text{Cl}^-, \text{Br}^-$ and SCN^- .

EXPERIMENTAL

Chemicals and solutions. NaCl (Merck, Suprapur) was used directly without further purification. NaBr (Merck, *p.a.*) was recrystallized twice from water. NaSCN (Mallinckrodt, anal.r.) was recrystallized three times from water.

Standard solutions of these salts were prepared from doubly distilled water. The concentration of NaX was determined by evaporating a known volume and drying in an oven at 120°C till constant weight, except for NaCl which was ignited at $\approx 300^\circ\text{C}$. The analyses were checked by precipitating the silver salts. The results obtained by the

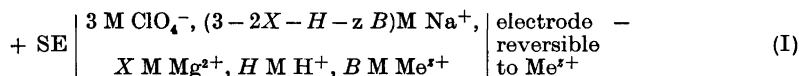
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two methods agreed to within 0.1 %. A stock solution of $\text{Cd}(\text{ClO}_4)_2$ was prepared as described by Hietanen *et al.*² and $\text{In}(\text{ClO}_4)_3$ as described by Biedermann and Wallin.³ The preparation of the other solutions, used in this paper, has been described elsewhere.¹

Apparatus. The emf titrations were performed in a paraffin oil thermostat at 25°C using the "Wilhelm" type bridge.⁴ The Ag,AgCl-electrodes in the reference half-cell were electrolytically prepared according to Brown.⁵ Ag,AgBr-electrodes were prepared from Ag,AgCl-electrodes by immersing in 0.1 M NaBr overnight, then carefully washing with distilled water, and equilibrating for a few days in 3 M NaClO_4 saturated with AgBr before use. Electrodes, electrolytically prepared according to Brown, gave the same results as those prepared by this method. Ag,AgSCN-electrodes were prepared by a slight modification of the method given by Wanderzee and Smith,⁶ *i.e.* by electrolyzing silver-coated Pt-electrodes in a solution containing 0.1 M NaSCN + 0.05 M HClO_4 for ~1 h at 0.2–0.5 mA. Cadmium and indium amalgam electrodes containing 0.01 % metal were prepared coulometrically *in situ*, using either Cd rod (99.99 % purity), In rod (99.99 % purity), or Ag-coated Pt plate as anode and a mercury pool as cathode. The emf of the glass electrodes used, Beckman, type 40498, was measured with a Metrohm compensator, type E388, with an accuracy of ± 0.2 mV. The emf of hydrogen (preparation given in Ref. 1) and Ag,AgX-electrodes was measured with a Cambridge Vernier potentiometer with an accuracy of ± 0.02 mV except for SCN^- , where the accuracy was ± 0.05 mV. The hydrogen electrode reached a stable potential within 20 min; it was stable to within ± 0.1 mV for 12 h.

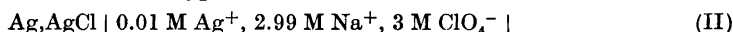
The vapor pressure measurements were made with a Hewlett-Packard Vapor Pressure Osmometer, Model 301A using an aqueous probe for 25°C.

The emf measurements. The investigation was carried out as a series of potentiometric titrations. The cell employed for studying positive ions can be described by



where $\text{Me}^{z+} = \text{Ag}^+, \text{Cd}^{2+}, \text{or In}^{3+}$.

The reference half-cell SE was of the type

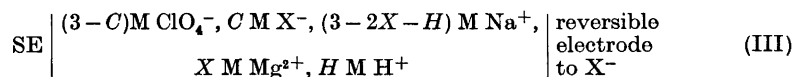


The emf of cell (I) can be expressed by

$$E = E_{0,\text{Me}} + 59.16 z^{-1} \log [\text{Me}^{z+}] + 59.16 z^{-1} \log y_{\text{Me}} + E_j \quad (\text{1})$$

where $E_{0,\text{Me}}$ is a constant, different for each kind of electrode; y_{Me} is the activity coefficient of Me^{z+} on the molarity scale and E_j the diffusion potential.

The cell employed for studying negative ions can be described by



where $\text{X}^- = \text{Cl}^-, \text{Br}^- \text{ or } \text{SCN}^-$.

The reference half-cell is that described by (II).

The emf of cell (III) can be expressed by

$$E = E_{0,\text{x}} - 59.16 \log [\text{X}^-] - 59.16 \log y_{\text{x}} + E_j \quad (\text{2})$$

where $E_{0,\text{x}}$ and y_{x} are defined analogously to $E_{0,\text{Me}}$ and y_{Me} , and E_j is the diffusion potential.

$E_{0,\text{Me}}$ and $E_{0,\text{x}}$ were determined from the first point of the titration, *i.e.* the point with no Mg^{2+} present, since the solution in the buret (T) always contained Mg^{2+} plus some H^+ , while the solution in the titrating vessel (S) contained a constant amount of the ion to which the measuring electrode was responding plus ionic media ions; *cf.* (I) and (III). Solution T also contained X^- or Me^{z+} at the same concentration as in S, so that $[\text{X}^-]_{\text{tot}}$ and $[\text{Me}^{z+}]_{\text{tot}}$ were kept constant during the titration. In this way the variation in E_j represents only the effects arising from the replacement of Na^+ with Mg^{2+} . All other contributions to E_j are constant during the titration and can be included in E_0 .

The standard state of the various species can conveniently be defined with reference to 3 M NaClO_4 , i.e. $y_i = 1$ when $C_i \rightarrow 0$ in that medium, where C_i is the concentration of species i . In this medium the water activity is 0.88 (= 21/23.74, cf. below).

The vapor pressure measurements. In the Mechrolab Osmometer the resistance difference (ΔR) corresponding to the steady-state temperature difference (ΔT) between two matched thermistors (one containing a drop of the solvent, the other a drop of the solution studied) is measured using a Wheatstone bridge. The quantity ΔR can be related to the vapor pressure of water, $p_{\text{H}_2\text{O}}$, by using standard solutions with known vapor pressure. At 25.0°C the standard solutions used were doubly distilled water ($p_{\text{H}_2\text{O}} = 23.74$ torr), 3 M NaClO_4 (21.0 torr)⁷ and 3 M HClO_4 (19.7 torr).⁷

RESULTS

The change of water activity. From the osmometric measurements the change in water activity when replacing Na^+ in 3 M $(\text{Na})\text{ClO}_4$ with Mg^{2+} can be estimated. In Fig. 1 p is plotted against ΔR for the solutions studied. A straight

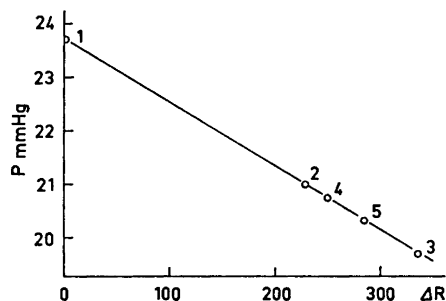


Fig. 1. The vapor pressure of water, $p_{\text{H}_2\text{O}}$ (mmHg), as a function of ΔR . 1, H_2O ; 2, 3 M NaClO_4 ; 3, 3 M HClO_4 ; 4, a mixture containing 0.60 M $\text{Mg}(\text{ClO}_4)_2$ and 1.80 M NaClO_4 ; 5, 1.5 M $\text{Mg}(\text{ClO}_4)_2$. Points 1, 2, and 3 were used for the definition of the straight line.

line can be fitted to the data and by interpolation it is found that by changing the concentration of Mg^{2+} from 0 to 600 mM the change in water activity is only = 1.3 % and to a good approximation negligible.

The emf measurements for positive ions. Using cell (I) emf titrations were performed such that the total concentrations of H^+ and Me^{z+} were kept constant during each titration except for a slight variation of the In^{3+} concentration, whilst the concentration of Mg^{2+} , $[\text{Mg}^{2+}]$, was varied. In Table 1 the data are collected on the form V (ml), $[\text{Mg}^{2+}]$ (mM), $E_{\text{gl(ass)}}$ (mV) $E_{\text{H(hydrogen)}}$ (m) or V , $[\text{Mg}^{2+}]$, E_{Me} . In Fig. 2 the quantity E'_j defined below, and easily obtained by a rearrangement of eqn. (1)

$$E'_{j,\text{Me}} = E_j + 59.16 z^{-1} \log y_{\text{Me}} = E - E_{0,\text{Me}} - 59.16 z^{-1} \log[\text{Me}^{z+}] \quad (3)$$

is plotted against $[\text{Mg}^{2+}]$ for all the cations studied. Not only do the curves have the same slope, but they all coincide, in the figure they have been shifted 1 mV in order not to crowd the data.

Rather high h -values (0.013 – 0.137) were used in order to permit accurate determination of the concentration of free H^+ , h , as well as to prevent hydrolysis of the cations. The h -values were determined by separate experiments. Two different h -values were used 114.8 mM and 59.0 mM. Measurements with

Table 1. The change of activities for some positive ions in 3 M (Na,Mg)ClO₄.

Measurements with glass and hydrogen electrodes.

Series 1: S: $H_0 = 114.76$ mM, $[Mg^{2+}]_{tot} = 0$.

T: $H_T = 114.76$ mM, $[Mg^{2+}]_{tot} = 1422.6$ mM; $V_0 = 40.04$ ml.

Experimental data (V , $[Mg^{2+}]$, E_{gl} , E_H (corrected for atm. pressure)):

0.00, 0.0, -24.6, -660.52; 0.50, 17.79, -24.3, -660.29; 1.00, 35.15, -24.05, -660.08; 2.50, 84.78, -23.4, -659.46; 5.00, 160.16, -22.4, -658.45; 10.50, 299.73, -20.45, -656.63; 20.00, 480.57, -18.0, -654.16; 40.00, 720.97, -14.7, -650.84.

Series 2: S: $H_0 = 58.95$ mM, $[Mg^{2+}]_{tot} = 0$.

T: $H_T = 58.95$ mM $[Mg^{2+}]_{tot} = 1470.5$ mM; $V_0 = 40.04$ ml.

0.00, 0.0, -41.0, -732.24; 2.48, 85.77, -39.85, -731.11; 5.00, 163.25, -38.9, -730.20; 10.00, 293.88, -37.1, -728.37; 20.00, 489.86, -34.2, -725.62; 45.03, 778.44, -30.00, -721.42.

Measurements with Ag,AgCl electrode.

$H_{tot} = 114.75$ mM and $[Ag^+]_{tot} = 10.06$ mM were kept constant throughout the titration.

S: $[Mg^{2+}]_{tot} = 0$; T: $[Mg^{2+}]_{tot} = 1437.6$ mM; $V_0 = 40.05$ ml. Experimental data (V , $[Mg^{2+}]$, E): 0.00, 0.0, -1.80; 2.50, 84.56, -0.77; 5.00, 159.73, 0.19; 10.00, 287.52, 1.83; 20.00, 479.20, 4.37; 45.04, 761.08, 8.27.

Measurements with Cd amalgam electrode.

$H_{tot} = 13.85$ mM and $[Cd^{2+}]_{tot} = 14.67$ mM were kept constant throughout the titration.

$V_0 = 40.05$ ml. Experimental data (V , $[Mg^{2+}]$, E (0.01 wt. % Cd amalgam used)): 0.00, 0.0, -989.85; 0.50, 18.25, -989.63; 1.00, 36.05, -989.43; 2.50, 86.94, -988.78; 5.01, 164.52, -987.83; 7.51, 233.66, -986.97; 10.01, 295.88, -986.175; 12.52, 335.19, -985.46; 15.02, 403.58, -984.78; 20.07, 493.98, -983.58; 25.07, 569.66, -982.50; 30.08, 634.68, -981.57; 40.09, 740.23, -980.07; 50.10, 822.34, -978.89; 60.05, 887.68, -977.90.

Measurements with In amalgam electrodes.

$H_{tot} = 136.96$ was kept constant throughout both series of titrations. Series 1: A silver anode and a Hg pool cathode were used when preparing the In amalgam electrodes.

S: $[Mg^{2+}]_{tot} = 0$ mM, $[Ag^+]_{tot} = 2.03$ mM, $[In^{3+}]_{tot} = 18.42$ mM T: $[Mg^{2+}]_{tot} = 1418.8$ mM, $[Ag^+]_{tot} = 0$ mM, $[In^{3+}]_{tot} = 19.10$ mM. Experimental data (V , $[Mg^{2+}]$, E): 0.0, 0.0, -915.8; 2.50, 109.11, -914.10; 5.01, 203.04, -913.02; 10.01, 354.89, -911.32; 20.02, 567.77, -909.41; 32.90, 742.01, -907.25.

Series 2: S: $[Mg^{2+}]_{tot} = 0.0$ mM, $[In^{3+}]_{tot} = 29.10$ mM.

T: $[Mg^{2+}]_{tot} = 1418.8$ mM, $[In^{3+}]_{tot} = 19.10$ mM; $V_0 = 40.04$ ml.

Experimental data (V , $[Mg^{2+}]$, E): 0.00, 0.0, -934.19; 0.50, 17.50, -934.03; 1.00, 34.57, -933.85; 2.50, 83.38, -933.31; 5.01, 157.50, -932.52; 10.01, 283.76, -931.12; 15.02, 387.04, -929.90; 20.02, 472.93, -928.93; 40.04, 709.40, -926.17; 60.06, 851.27, -924.25.

Table 2. The change of activities of some negative ions.

1. The change of chloride ion activity during Na⁺ - Mg²⁺ replacement.

Series 1: $[Cl^-]_{tot} = 1.00$ mM was constant throughout the series, S: $[Mg^{2+}]_{tot} = 0.0$ mM; T: $[Mg^{2+}]_{tot} = 1499.5$ mM; $V_0 = 50.09$ ml. Experimental data (V (ml), $[Mg^{2+}]$ (mM), $E_{Ag,AgCl}$ (mV)): 0.0, 0.0, -276.34; 0.25, 7.45, -276.29; 0.50, 14.82, -276.26; 1.00, 29.35, -276.12; 2.51, 71.55, -275.74; 5.01, 136.34, -275.10; 10.01, 249.74, -274.07; 15.02, 345.90, -273.19; 20.02, 428.17, -272.46; 25.03, 499.62, -271.81; 30.03, 562.02, -271.23; 40.04, 666.13, -270.17.

Series 2: $[Cl^-]_{tot} = 20.02$ mM, S: $[Mg^{2+}]_{tot} = 0.0$ mM; T: $[Mg^{2+}]_{tot} = 1490.0$ mM; $V_0 = 40.05$ ml. Experimental data: 0.0, 0.0, -352.86; 0.25, 9.24, -352.79; 0.50, 18.37, -352.70; 1.00, 36.30, -352.53; 2.51, 87.87, -352.04; 5.01, 165.67, -351.29; 7.51, 235.28, -350.62; 10.01, 297.94, -350.07; 12.51, 354.64, -349.50; 15.02, 406.39, -349.01; 20.02, 496.58, -348.17; 30.03, 638.48, -346.86; 40.04, 744.91, -345.88.

Table 2. Continued.

Series 3: $[\text{Cl}^-]_{\text{tot}} = 50.18$ mM, S: $[\text{Mg}^{2+}]_{\text{tot}} = 0.0$ mM; T: $[\text{Mg}^{2+}]_{\text{tot}} = 1474.9$ mM; $V_0 = 40.05$ ml. Experimental data: 0.0, 0.0, -376.47; 0.25, 9.15, -376.38; 0.55, 19.98, -376.29; 1.00, 35.93, -376.12; 2.51, 86.98, -375.64; 5.01, 163.99, -374.91; 7.51, 232.90, -374.22; 10.01, 294.92, -373.64; 15.01, 402.08, -372.65; 20.01, 491.39, -371.82; 30.00, 631.65, -370.52; 39.99, 736.90, -369.53.

Series 4: $[\text{Cl}^-]_{\text{tot}} = 199.85$ mM, S: $[\text{Mg}^{2+}]_{\text{tot}} = 0.0$ mM; T: $[\text{Mg}^{2+}]_{\text{tot}} = 1400.1$ mM; $V_0 = 40.05$ ml. Experimental data: 0.0, 0.0, -411.42; 0.25, 8.69, -411.36; 0.50, 17.26, -411.27; 1.00, 34.11, -411.13; 2.51, 82.57, -410.67; 5.01, 155.67, -410.01; 10.01, 279.96, -408.85; 15.01, 381.68, -407.93; 17.52, 426.08, -407.52; 20.02, 466.61, -407.16; 30.01, 599.72, -405.95; 40.00, 699.60, -405.05; 49.99, 777.32, -404.31.

2. The change of bromide ion activity.

Series 1: $[\text{Br}^-]_{\text{tot}} = 24.83$ mM, S: $[\text{Mg}^{2+}]_{\text{tot}} = 0.0$ mM; T: $[\text{Mg}^{2+}]_{\text{tot}} = 1487.6$ mM; $V_0 = 40.05$ ml. Experimental data ($V(\text{ml})$, $[\text{Mg}^{2+}]$ (mM), $E_{\text{Ag,AgBr}}(\text{mV})$): 0.0, 0.0, -512.67; 0.26, 9.59, -512.60; 0.50, 18.34, -512.53; 1.00, 36.24, -512.39; 2.51, 87.73, -512.02; 5.02, 165.69, -511.45; 7.51, 234.90, -510.96; 10.01, 297.46, -510.51; 15.01, 405.53, -509.75; 20.02, 495.78, -509.11; 22.53, 535.56, -508.84; 22.05, 572.41, -508.57; 30.03, 637.45, -508.11; 35.03, 694.06, -507.68; 40.06, 743.89, -507.28.

Series 2: $[\text{Br}^-]_{\text{tot}} = 49.66$ mM, S: $[\text{Mg}^{2+}]_{\text{tot}} = 0.0$ mM; T: $[\text{Mg}^{2+}]_{\text{tot}} = 1475.2$ mM; $V_0 = 40.05$ ml. Experimental data: 0.0, 0.0, -530.43; 0.26, 9.51, -530.37; 0.51, 18.55, -530.29; 1.00, 35.94, -530.14; 2.51, 87.00, -529.77; 5.01, 164.02, -529.21; 7.51, 232.94, -528.71; 10.01, 294.97, -528.27; 12.51, 351.11, -527.86; 15.02, 402.34, -527.48; 20.02, 491.64, -526.84; 25.03, 567.36, -526.29; 30.03, 632.13, -525.83; 32.53, 661.16, -525.60; 35.03, 688.27, -525.40; 40.06, 737.68, -525.03.

Series 3: $[\text{Br}^-]_{\text{tot}} = 197.60$ mM, S: $[\text{Mg}^{2+}]_{\text{tot}} = 0.0$ mM; T: $[\text{Mg}^{2+}]_{\text{tot}} = 1401.2$ mM; $V_0 = 40.05$ ml. Experimental data: 0.0, 0.0, -565.74; 0.25, 8.69, -565.69; 0.50, 17.28, -565.65; 1.00, 34.13, -565.53; 2.52, 82.95, -565.20; 5.01, 155.79, -564.69; 7.51, 221.26, -564.22; 10.01, 280.18, -563.79; 15.02, 382.17, -563.06; 17.52, 426.42, -562.74; 20.02, 466.99, -562.44; 25.03, 538.91, -561.91; 30.03, 600.43, -561.49; 35.03, 653.76, -561.08; 40.04, 700.51, -560.74.

3. The change of thiocyanate ion activity.

Series 1: $[\text{SCN}^-]_{\text{tot}} = 217.93$ mM, S: $[\text{Mg}^{2+}]_{\text{tot}} = 0.0$ mM; T: $[\text{Mg}^{2+}]_{\text{tot}} = 1391.0$ mM; $V_0 = 40.05$ ml. Experimental data ($V(\text{ml})$, $[\text{Mg}^{2+}]$ (mM), $E_{\text{Ag,AgSCN}}(\text{mV})$): 0.0, 0.0, -547.28; 0.25, 8.63, -547.20; 0.50, 17.15, -547.15; 1.00, 33.89, -546.99; 2.51, 82.04, -546.57; 5.01, 154.66, -545.93; 7.51, 219.65, -545.36; 10.02, 278.37, -544.85; 12.51, 331.08, -544.39; 15.02, 379.39, -543.97; 20.02, 463.60, -543.23; 25.04, 535.13, -542.64; 30.03, 596.07, -542.11; 35.04, 649.11, -541.63; 40.04, 695.43, -541.22; 50.04, 772.64, -540.52; 60.05, 834.48, -539.95.

Series 2: $[\text{SCN}^-]_{\text{tot}} = 145.08$ mM, S: $[\text{Mg}^{2+}]_{\text{tot}} = 0.0$ mM; T: $[\text{Mg}^{2+}]_{\text{tot}} = 1427.5$ mM; $V_0 = 40.05$ ml. Experimental data: 0.0, 0.0, -537.96; 0.25, 8.86, -537.51; 0.50, 17.60, -537.41; 1.00, 34.77, -537.27; 2.50, 83.87, -536.77; 5.01, 158.71, -536.08; 7.51, 225.40, -535.48; 10.01, 285.43, -534.94; 15.02, 389.33, -534.05; 20.02, 475.74, -533.23; 25.01, 548.74, -532.63; 30.03, 611.68, -532.11; 35.04, 666.11, -531.70; 40.04, 713.64, -531.30; 50.06, 793.02, -530.62; 60.06, 856.39, -530.02.

Series 3: $[\text{SCN}^-]_{\text{tot}} = 36.46$ mM, S: $[\text{Mg}^{2+}]_{\text{tot}} = 0.0$ mM; T: $[\text{Mg}^{2+}]_{\text{tot}} = 1481.8$ mM; $V_0 = 40.05$ ml. Experimental data: 0.0, 0.0, -502.85; 0.25, 9.19, -502.62; 0.50, 18.27, -502.50; 1.00, 36.10, -502.31; 2.50, 87.06, -501.80; 5.01, 164.75, -501.04; 7.51, 233.98, -500.39; 10.01, 296.29, -499.81; 12.51, 352.68, -499.28; 15.02, 404.14, -498.76; 20.02, 493.84, -497.95; 25.02, 569.75, -497.23; 30.02, 634.83, -496.64; 35.54, 696.68, -496.06; 40.04, 740.79, -495.57; 50.05, 823.11, -494.86.

both glass and hydrogen electrodes agreed within the limits of experimental accuracy.

The emf measurements for negative ions. Titrations were performed at several rather low C -levels for each anion and these were kept constant in each titra-

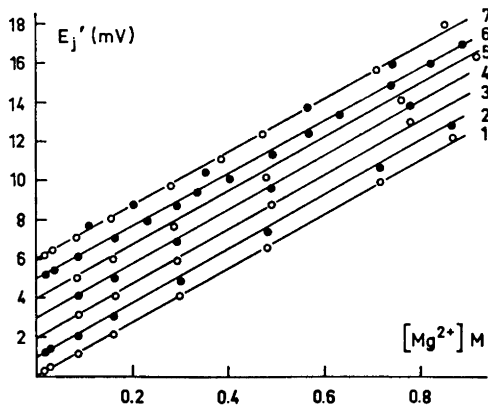


Fig. 2. The change of $E'_{j,Me}$, [cf. eqn. (3)] with $[Mg^{2+}]$ for some positive ions. 1, glass electrode, $H = 114.76$ mM; 2, hydrogen electrode, $H = 114.76$ mM; 3, glass electrode, $H = 58.95$ mM; 4, hydrogen electrode, $H = 58.95$ mM; 5, Ag,AgCl electrode, $H = 114.75$ mM, $[Ag^+]_{tot} = 10.06$ mM; 6, Cd amalgam electrode, $H = 13.85$ mM, $[Cd^{2+}]_{tot} = 14.67$ mM; 7, In amalgam electrode, $H = 136.96$ mM, open circles $[In^{3+}] = 18.42 - 19.10$ mM, dots $[In^{3+}] = 19.10 - 29.10$ mM. The full drawn lines correspond to the slope (13.568 ± 0.002) mV mol^{-1} and they are shifted stepwise by 1.00 mV for the sake of clarity.

tion. The hydrogen ion concentration, h , was also kept constant at ≈ 2.5 mM. For SCN^- the solutions were saturated with AgSCN in order to ensure stable potentials. The results of measurements with cell (III) are collected in Table 2.

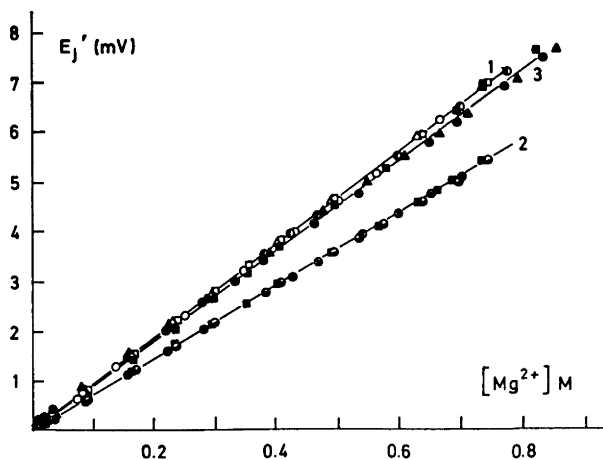


Fig. 3. The change of $E'_{j,x}$ [cf. eqn. (11)] with $[Mg^{2+}]$ in 3 M $(Na^+, Mg^{2+})ClO_4$ for some negative ions. 1, Ag,AgCl electrode: 1.00 mM, 20.0 mM, 50.18 mM, 199.85 mM Cl^- ; 2, Ag,AgBr electrode: 24.83 mM, 49.66 mM, and 197.60 mM Br^- ; 3, Ag,AgSCN electrode: 36.46 mM, 145.08 mM, and 217.93 mM SCN^- . The straight lines through the experimental points are those obtained using LETAGROP, assuming $E'_{j,x}$ to be a linear function of $[Mg^{2+}]$ and neglecting any complex formation. The slopes are: 9.29 ± 0.02 , 7.26 ± 0.02 , and 9.05 ± 0.07 mV mol^{-1} for Cl^- (1), Br^- (2) and SCN^- (3).

In Fig. 3 the quantity $E'_{j,X}$ defined analogously to $E'_{j,Me}$ in eqn. (3) is plotted against $[Mg^{2+}]$ for the anions studied. In this case three separate straight lines are obtained, one for each anion.

TREATMENT OF DATA

Positive ions. The data in Fig. 2, were fitted to a straight line, employing a least squares computer program, giving

$$E'_j = E_j + 59.16 z^{-1} \log y_{Me} = (13.568 \pm 0.002)[Mg^{2+}] \quad (4)$$

Results^{3,8} similar to (4) have been obtained for the replacement of Na^+ in 3 M $NaClO_4$ with In^{3+} . Biedermann and Wallin³ found $\log y_{Ag^3}/y_{In} = 0.20[In^{3+}]$ while Ferri⁸ obtained $\log y_{H^3}/y_{In} = 0.52[In^{3+}]$. The influence of changes in ionic medium has recently been studied by Byé *et al.*⁹ They suggest that the activity coefficient for an ion in a system at constant ionic strength (I), but varying composition, can be described by

$$\log y_i = F_i(I) + \sum a_{ij} C_j \quad (5)$$

where $F_i(I)$ corresponds to the Debye-Hückel term and the second term to a Setchenow salting-out term where C_j is the concentration of species j . They report several systems which follow eqn. (5). It is easily seen that expression (4) is of the same type as (5). According to (5) there is one term for each ion, whose concentration varies during the experiment. In the present study $[H^+]$ and $[Me^{2+}]$ were kept constant at rather low values so that only $[Mg^{2+}]$ and $[Na^+]$ varied. To a first approximation, however,

$$2[Mg^{2+}] + [Na^+] \sim 3.0 \pm 0.4 \quad (6)$$

and it is possible to express the variation of $\log y_{Me}$ as a function of $[Mg^{2+}]$ only. If we denote the salting-out terms for Mg^{2+} and Na^+ by $a_{Me,Mg}$ and $a_{Me,Na}$ we get

$$\log y_i = F_i(I) + 3a_{Me,Na} + (a_{Me,Mg} - 2a_{Me,Na})[Mg^{2+}] \quad (7)$$

By comparing (4) with (7) we get

$$\frac{-zE'_j}{59.16} = F_i(I) + 3a_{Me,Na} \quad (8a,b)$$

and

$$(a_{Me,Mg} - 2a_{Me,Na}) = \frac{13.568}{59.16} z$$

According to eqn. (8a) $-E'_j$ must be constant and the difference $a_{Me,Mg} - 2a_{Me,Na}$ must depend only on z , which seems somewhat surprising. It is hardly to be expected, however, that E'_j is constant during the exchange of Na^+ for Mg^{2+} . It has recently been shown by Österberg and Sjöberg¹⁰ that changes in sodium ion concentration are reflected in changes in E'_j .

A correct estimate of E'_j is difficult to make. The conditions for which the Henderson¹¹ and Planck^{12,13} equations are derived are practically impossible to fulfil.¹⁴ These equations can therefore only be used as rough guides when

Table 3. Treatment of the data for the Ag,AgCl electrode by the program LETAGROP ETITR.

Run No.	Variable parameters	$k(E_j')$ mV mol ⁻¹	K_1	E_0 mV	U	$\sigma(E)$ mV
1	k	9.29 ± 0.02	—	— 453.83 — 453.35 — 453.34 — 452.79	0.163	0.06
2	k, E_0	9.29 ± 0.02	—	— 453.86 \pm 0.01 — 453.31 \pm 0.01 — 453.29 \pm 0.01 — 452.84 \pm 0.01	0.068	0.04
3	k, K_1	8.11 ± 0.44	0.048 ± 0.018	— 452.84 \pm 0.01	0.059	0.04
4	k, K_1, E_0	6.74 ± 0.36	0.106 ± 0.016 $\log K_1 =$ -0.98 ± 0.19	— 453.89 \pm 0.02 — 453.33 \pm 0.01 — 453.30 \pm 0.01 — 452.81 \pm 0.00 ₄	0.048	0.03
5	$k, K_1, E_0, \delta B$ $\delta B =$ -25.92 ± 7.54 mM -11.70 ± 2.10 $+18.63 \pm 2.83$ $+0.48 \pm 1.73$	6.36 ± 0.70	0.122 ± 0.031 $\log K_1 =$ -0.914 ± 0.056	— 453.85 \pm 0.02 — 453.35 \pm 0.01 — 453.33 \pm 0.01 — 452.80 \pm 0.01	0.019	0.02

Table 4. Treatment of the data for the Ag,AgBr electrode by the program LETAGROP ETITR.

Run No.	Variable parameters	$k(E_j')$ mV mol ⁻¹	K_1	E_0 mV	U	$\sigma(E)$ mV
1	k	7.21 ± 0.02	—	— 607.62 — 607.57 — 607.40	0.086	0.04
2	k, E_0	7.21 ± 0.01	—	— 607.62 \pm 0.01 — 607.53 \pm 0.01 — 607.45 \pm 0.01	0.022	0.02
3	k, K_1, E_0	6.33 ± 0.52	0.035 ± 0.021 $\log K_1 =$ -1.45 (max. — 1.01)	— 607.62 \pm 0.01 — 607.53 \pm 0.01 — 607.44 \pm 0.01	0.021	0.02

Table 5. Treatment of the data for the Ag,AgSCN electrode by the program LETAGROP ETITR.

Run No.	Variable parameters	$k(E_j')$ mV mol ⁻¹	K_1	E_0 mV	U	$\sigma(E)$ mV
1	k	9.36 ± 0.09	—	— 586.42 — 587.55 — 587.93	3.65	0.28
2	k, E_0	9.05 ± 0.07	—	— 586.54 \pm 0.02 — 587.23 \pm 0.03 — 587.58 \pm 0.04	0.75	0.12
3	K_1	—	0.430 ± 0.003	»	1.84	0.19
4	K_1, E_0	—	0.420 ± 0.003	— 586.54 \pm 0.02 — 587.28 \pm 0.02 — 587.75 \pm 0.03	0.37	0.09
5	k, K_1, E_0	6.10 ± 1.10	0.123 ± 0.045 $\log K_1 =$ -0.91 ± 0.19	— 586.50 \pm 0.03 — 587.19 \pm 0.02 — 587.58 \pm 0.05	0.32	0.07

applied to real systems. Nevertheless, Henderson's equation has been used to estimate E_j using some different assumptions.

$$E_j = \frac{\sum u_j/z_j(C_{j,2} - C_{j,1})}{\sum u_j(C_{j,2} - C_{j,1})} + \frac{RT}{F} \ln \frac{\sum u_j C_{j,2}}{\sum u_j C_{j,1}} \quad (9)$$

$C_{j,1}$ and $C_{j,2}$ are ionic concentrations in the two solutions I and II. z_j is the ionic charge and u_j the ionic mobility. Inserting the ionic conductivities ($l_i (= u_i F)$) at infinite dilution ($l_{Na} = 50.11$, $l_{ClO_4} = 67.32$ and $\frac{1}{2}l_{Mg} = 53.06$ ohm⁻¹ cm²)¹⁵ we get $E_j = 5.07$ mV. On the other hand if we use $\sum u_j C_{j,2} / \sum u_j C_{j,1} = \kappa_2 / \kappa_1$ where κ_2 (54.50) is the conductivity of 3 M NaClO₄ and κ_1 that of 1.5 M MgClO₄¹⁷ (65.0 as obtained by interpolation) we get $E_j = 36.18$ mV. From the slope of eqn. (4) we get 20.35 mV, which is somewhere between the calculated values. It is tempting to assume that the whole variation in E_j is due rather to E_j than to y_{Mc} , in agreement with the findings of Biedermann and Sillén⁷ who found that when replacing Na⁺ with H⁺ up to 600 mM in 3 M (Na)ClO₄ no change in the activity coefficients of the cations could be observed. However, from the present information it cannot be determined whether both E_j and y_{Mc} vary or only E_j .

Negative ions. (a) *The slope.* The data in Fig. 3 have been treated in the same way as those in Fig. 2 and best straight lines evaluated by a least squares computer method. The results are given in Tables 3–5 as run No. 1. In the treatment of these data the program LETAGROP was used and besides the evaluation of the slope k_j in the expression

$$E'_{j,x} = k_j[Mg^{2+}] \quad (10)$$

$E_{0,x}$ in the expression

$$E_{j,x^-} = E_j - 59.16 \log y_x = E - E_{0,x^-} + 59.16 \log[X^-] \quad (11)$$

was evaluated as well. The results of these calculations are given as run No. 2 in Tables 3–5. As seen, the E_{0,x^-} -values obtained are within a few hundredths of a millivolt of the directly measured values, except for the less accurate data for SCN⁻ where the difference in some cases amounts to 0.2–0.3 mV. The straight lines in Fig. 3 have been drawn using the results of run No. 2 in Tables 3–5.

(b) *The ion pair formation constant.* On considering eqns. (5) and (11) it can be surmised that the different slopes obtained for the three anions can only be due to y_{x^-} varying differently for each anion, since E_j must be the same in all three cases. In their study Biedermann and Sillén⁷ found that the activity coefficients of anions varied, but all in the same way. It is thus tempting to try to interpret the differences in the slopes of the three anions studied as being due to ion pair formation. The species MgCl⁺^{18–22} has been suggested by several investigators and it is thus not unreasonable to attribute the difference in slopes to ion pair formation.

An estimate of the equilibrium constant K_1 of the reaction



was obtained by neglecting the activity coefficient term in the relation:

$$\log K_1 = \log [\text{MgX}^+][\text{Mg}^{2+}]^{-1}[\text{X}^-]^{-1} + \log \frac{y_{\text{MgX}^+}}{y_{\text{Mg}^{2+}}y_{\text{X}^-}} \quad (13)$$

In the activity coefficient expression in eqn. (13) the ratio $y_{\text{MgX}^+}/y_{\text{Mg}^{2+}}$ might be constant if the findings of Biedermann and Sillén⁷ can be applied to the systems investigated in this study, while y_{X^-} can be expected to vary. By neglecting the activity coefficient term only a first approximation to K_1 is obtained.

By means of the computer program LETAGROP ETITR developed by Sillén *et al.*²³ besides K_1 the values of $E_{0,x}$ and k_i (cf. eqn. (10)) were varied either one at a time or simultaneously. The results are given in Tables 3–5 as runs Nos. 3–5. In addition for Cl^- a correction to the Mg^{2+} -concentration δB in the burette was also varied (run No. 5). From Table 3 we find that run No. 5 gives the best fit to the data as measured by the error squares sum (U) defined by

$$U = \sum_1^N (E_{\text{obs}} - E_{\text{calc}})^2 \quad (14)$$

where the summation is taken over all experimental points (N). As well as this the standard deviation in the measured emf values $\sigma(E)$ is smallest for run No. 5. However, in this run the correction δB obtained is larger (max. 1.85 %) than the experimental uncertainty (~ 0.5 %). For this reason this run has been discarded and the best fit obtained with run No. 4.

For Br^- the best results were obtained with run No. 3 and for SCN^- with run No. 5. In all cases, however, the improvement of the fit to the experimental data on the introduction of K_1 is only very slight, the low K_1 -values found indicate only a very slight ion pair formation. It is interesting to note, however, that the quantity k_i becomes practically the same (6.33, 6.33, and 6.10 for Cl^- , Br^- , and SCN^-) after the correction for ion pair formation. This is what is to be expected when supposing that both E_i and perhaps also y_{X^-} (cf. Ref. 7) might be the same for all anions.

DISCUSSION

Activity coefficients. From the information presently available it is difficult to ascertain whether or how much the activity coefficients of cations and anions change during the exchange of Na^+ for Mg^{2+} . If they vary, they change linearly with $[\text{Mg}^{2+}]$ in agreement with eqn. (5). On the other hand activity coefficient quotients like that in eqn. (13) may stay nearly constant so that the evaluation of stability constants may be quite accurate.

Ion pair formation. Table 6 gives the currently known estimates of K_1 together with the results of the present study. From Table 6 is evident that the consistency between the various investigations is poor. The estimates obtained by extrapolation from solvent-water mixtures to pure water seem too high, while the values obtained in water show a poor agreement. As recently discussed by Bjerrum²⁶ equilibrium constants < 10 are difficult to estimate with any reasonable certainty as illustrated by, *e.g.*, the case of the formation

Table 6. $\log K_1$ for reaction (12) and $\text{X}^- = \text{Cl}^-$, Br^- , SCN^- .

Anion	Temp. °C	Medium	$\log K_1$	Ref.
Cl^-	35	20 % dioxane	1.3	19
	35	30 % dioxane	1.7	19
	35	0 % dioxane	0.5	This work/20
	0	sat. KClO_4	0.62	20
	0	sat. KClO_3	0.08	20
	0	$\rightarrow 0$	0.91	20
	-40	$\text{C}_2\text{H}_5\text{OH}, \rightarrow 0$	3.22	24, 25
	-20	$\text{C}_2\text{H}_5\text{OH}, \rightarrow 0$	3.40	24, 25
	0	$\text{C}_2\text{H}_5\text{OH}, \rightarrow 0$	3.67	24, 25
	20	$\text{C}_2\text{H}_5\text{OH}, \rightarrow 0$	3.79	24, 25
	25	$\sim 3 \text{ M}(\text{Na})\text{ClO}_4$	-0.98 ± 0.19	This work
Br^-	20	$\text{C}_2\text{H}_5\text{OH}, \rightarrow 0$	3.38	25
	25	$\sim 3 \text{ M}(\text{Na})\text{ClO}_4$	$-1.41(-1.01)$	This work
SCN^-	25	$\sim 3 \text{ M}(\text{Na})\text{ClO}_4$	-0.91 ± 0.19	This work

of outer-sphere complexes. The low values obtained in the present study indicate weak interactions indeed and it seems highly probable that the MgX^+ -species discussed can be regarded as Bjerrum's ion pairs rather than complexes in the ordinary sense of the word. The use of Bjerrum's theory and some simplifying assumptions lead to ion pair formation constants about 10 and below. Experimentally, however, it has been found that many 1:2 electrolytes give equilibrium constants of the same order of magnitude as found in this paper.²⁷ Instead of introducing ion pair formation constants, the results in the present paper can equally well be rationalized in terms of α -coefficients according to Harned's rule²⁸ and extensions thereof.²⁹ This approach, however, is only a way of representing experimental data and of less interest in the present context, although its applicability emphasizes the difficulty in obtaining unique descriptions, when weak interactions are concerned.

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