# Ion Activities of Alkaline-earth Chlorides in Aqueous Solution

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Determinations are made of convenient single-ion activity data for alkaline-earth chlorides in 0.1–4.0 molal aqueous single-salt solutions at 25 °C. Comparisons are made to corresponding data for the alkali-metal chlorides. The results are discussed on the basis of current theories of electrolyte solutions. Support is found for the convenient activity scale used being close to an absolute one.

In a previous paper,[1] a convenient scale for single-ion activities is described and applied to alkali-metal and ammonium chlorides in aqueous solution. The results indicate that this scale is very close (perhaps equal) to the absolute one. This makes further studies and applications of it desirable. The present work pursues this to aqueous solutions of alkaline-earth chlorides at 25 °C. A major aim is to assist in elucidating ionic interactions in concentrated electrolyte solutions.[2,3]

## ACTIVITY DETERMINATIONS

Convenient ($\gamma_z'$) and absolute ($\gamma_z$) molal bare-ion activity coefficients of an ionic species are interrelated by the scale definition:[1]

$$\gamma_z' = r^{-z/2}\gamma_z \tag{1}$$

where $z$ is the charge number (with sign) of the ion concerned, and $r$ is the activity ratio $\gamma_+/\gamma_-$ for potassium chloride in pure, saturated solution at the temperature concerned. This definition makes the convenient activity coefficient of an ionic species in a test solution determinable from the potential $vs.$ SCE ($E_z'$) of an electrode reversible to the ion, provided the liquid-junction potential difference ($\phi_t - \phi_r$) between test and reference (saturated KCl) solution can be estimated accurately enough.[1] At 25 °C, the determining equation is:[1]

$$\gamma_z' = (m°/m_z)\exp[(zF/RT)\times$$
$$(E_z' - (\phi_t - \phi_r) - E_z° + 0.241 \text{ V})] \tag{2}$$

where $m°$, $m_z$ and $E_z°$ are the standard molality (1 mol kg$^{-1}$), the actual molality of the ion concerned and the standard hydrogen-scale potential of the reversible test electrode applied, respectively.

In the present work, eqn. (2) is applied to the chloride ion ($z = -1$) in 0.1–4.0 molal aqueous single-salt solutions of alkaline-earth chlorides at 25 °C. This is done by measuring the liquid-junction-containing reversible potential ($E_-'$) of the Ag/AgCl electrode ($E_-° = 0.222$ V (NHE))[2] in the test solutions against a saturated calomel electrode, and estimating the liquid-junction potential difference involved ($\phi_t - \phi_r$) by means of the Henderson equation[4] and mobility data.[2] From (1) and the definition ($\gamma_\pm^3 = \gamma_{2+}\gamma_-^2$) of the mean-ion activity coefficient for 2:1 valency type electrolytes, one easily deduces that the equation

$$\gamma_{2+}' = \gamma_\pm^3(\gamma_-')^{-2} \tag{3}$$

should apply to single-salt solutions of alkaline-earth chlorides. This equation is presently applied to obtain convenient cation data from corresponding anion data (present work) and conventional mean-ion data (tabulated by Robinson and Stokes[2]).

## EXPERIMENTAL

Solutions were made from $p.a.$ quality salts (Merck) and twice distilled water. They were deoxygenated with purified and premoistened nitrogen and kept under nitrogen atmosphere during measurements. The measurements were performed with procedures and equipment exactly as recently described[1] for corresponding studies on aqueous solutions of alkali-metal chlorides. All measurements apply to solutions and electrodes at 25 °C.

## RESULTS

The intermediate and final results of the present activity determinations are given in Tables 1 and 2, respectively. These results yield the specificities and concentration dependences shown for $\gamma'_{2+}$ and $\gamma'_-$ in Figs. 1 and 2, respectively. Clearly, with increasing concentration, the activity sequence

$$BaCl_2 < SrCl_2 < CaCl_2 < MgCl_2 \qquad (4)$$

*Table 1.* Ag/AgCl reversible potentials measured *vs.* SCE ($E'_-$) and liquid-junction potentials estimated ($\Delta\phi = \phi_t - \phi_r$) for $x$ molal aqueous single-salt solutions of alkaline-earth chlorides at 25 °C.

| $x =$ | 0.1 | 0.2 | 0.5 | 1 | 2 | 3 | 4 |
|---|---|---|---|---|---|---|---|
| **MgCl$_2$** | | | | | | | |
| $E'_-$/mV | 31.5 | 17.0 | −2.2 | −17.7 | −37.1 | −50.8 | −61.3 |
| $\Delta\phi$/mV | −0.3 | 0.9 | 3.1 | 5.4 | 8.4 | 10.5 | 12.2 |
| **CaCl$_2$** | | | | | | | |
| $E'_-$/mV | 31.4 | 16.9 | −2.3 | −18.0 | −36.8 | −50.1 | −60.6 |
| $\Delta\phi$/mV | −0.4 | 0.7 | 2.8 | 4.9 | 7.7 | 9.6 | 11.1 |
| **SrCl$_2$** | | | | | | | |
| $E'_-$/mV | 31.8 | 17.3 | −1.6 | −16.7 | −34.1 | −46.6 | |
| $\Delta\phi$/mV | −0.4 | 0.7 | 2.8 | 4.9 | 7.7 | 9.6 | |
| **BaCl$_2$** | | | | | | | |
| $E'_-$/mV | 31.4 | 17.1 | −1.5 | −16.2 | −28.2[a] | | |
| $\Delta\phi$/mV | −0.4 | 0.6 | 2.6 | 4.6 | 6.8[a] | | |

[a] At $x = 1.8$.

*Table 2.* Molal bare-ion activity coefficients for alkaline-earth chlorides in $x$ molal aqueous single-salt solutions at 25 °C.

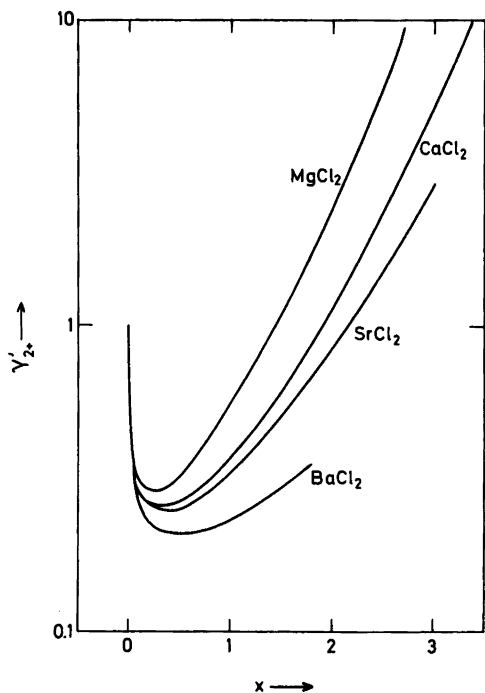| $x =$ | 0.1 | 0.2 | 0.5 | 1 | 2 | 3 | 4 |
|---|---|---|---|---|---|---|---|
| **MgCl$_2$** | | | | | | | |
| $\gamma'_+$ | 0.31 | 0.29 | 0.32 | 0.54 | 2.36 | 16.7 | 155 |
| $\gamma'_-$ | 0.69 | 0.64 | 0.59 | 0.59 | 0.70 | 0.87 | 1.04 |
| $\gamma_\pm$ | 0.528 | 0.488 | 0.480 | 0.569 | 1.051 | 2.32 | 5.53 |
| **CaCl$_2$** | | | | | | | |
| $\gamma'_+$ | 0.29 | 0.26 | 0.27 | 0.37 | 1.09 | 4.93 | 26.6 |
| $\gamma'_-$ | 0.69 | 0.63 | 0.58 | 0.58 | 0.67 | 0.81 | 0.97 |
| $\gamma_\pm$ | 0.518 | 0.472 | 0.448 | 0.500 | 0.792 | 1.483 | 2.93 |
| **SrCl$_2$** | | | | | | | |
| $\gamma'_+$ | 0.29 | 0.26 | 0.25 | 0.33 | 0.83 | 2.90 | |
| $\gamma'_-$ | 0.68 | 0.62$_5$ | 0.57 | 0.55 | 0.61 | 0.71 | |
| $\gamma_\pm$ | 0.515 | 0.466 | 0.433 | 0.465 | 0.675 | 1.135 | |
| **BaCl$_2$** | | | | | | | |
| $\gamma'_+$ | 0.27 | 0.23 | 0.21 | 0.23 | 0.35[a] | | |
| $\gamma'_-$ | 0.69 | 0.63 | 0.56 | 0.53 | 0.52[a] | | |
| $\gamma_\pm$ | 0.508 | 0.450 | 0.403 | 0.401 | 0.455[a] | | |

[a] At $x = 1.8$.

Fig. 1. The convenient molal bare-ion activity coefficient ($\gamma'_{2+}$) for the cations of alkaline-earth chlorides in $x$ molal aqueous single-salt solutions at 25 °C.
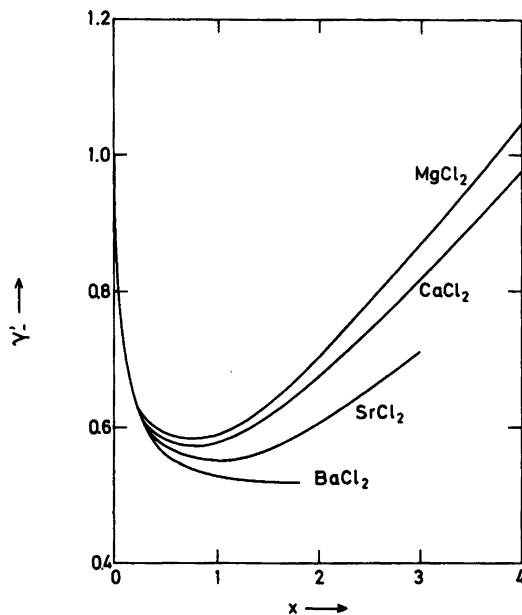


Fig. 2. The convenient molal bare-ion activity coefficient ($\gamma'_-$) for the chloride ion in $x$ molal aqueous single-salt solutions of alkaline-earth chlorides at 25 °C.

is developed and steadily strengthened both for the cations (Fig. 1) and for the common anion (Fig. 2) of the single-salt solutions studied. This occurs much more strongly for the cations than for the anion, however.

The ratio $\gamma'_{2+}/(\gamma'_-)^4 = r^{-3}\gamma_{2+}/\gamma_-{}^4$ is interesting, since the Debye-Hückel value of $\gamma_{2+}/\gamma_-{}^4$ is unity and hence gives the former ratio a low-concentration limiting value of $r^{-3}$. A semilogarithmic plot of presently obtained values for this ratio $vs.$ solution molality is given in Fig. 3. These results support previous findings [1] of $r$ being close to unity, but do not allow a more exact determination of this important parameter.

## DISCUSSION

The present results on alkaline-earth chlorides add to previous results [1] on alkali-metal and ammonium chlorides both in elucidating the convenient scale chosen for single-ion activities and in building

up a bank of such data for ions in aqueous single-salt solutions. Important is that these results all agree that the chosen convenient scale be close to the absolute one (by $r$ being close to 1). This makes the convenient single-ion activity data determined most useful. These data, however, to some extent depend on estimations of liquid-junction potential differences involved in their determination.

The mean-ion activity of alkali-metal and alkaline-earth chlorides in aqueous single-salt solutions [2] mostly decreases both with increasing cation size (except at very low concentration) and with increasing cation charge (except at very high concentration). The single-ion data show that these changes are carried mostly by the cations themselves and only to a small extent by the anion. The effects of size and charge on the cations of such solutions are illustrated in Fig. 4 (by the pairs $Li^+/K^+$ and $Mg^{2+}/Ba^{2+}$ of equally charged ions and the pairs $Li^+/Mg^{2+}$ and $K^+/Ba^{2+}$ of nearly equally sized ions).
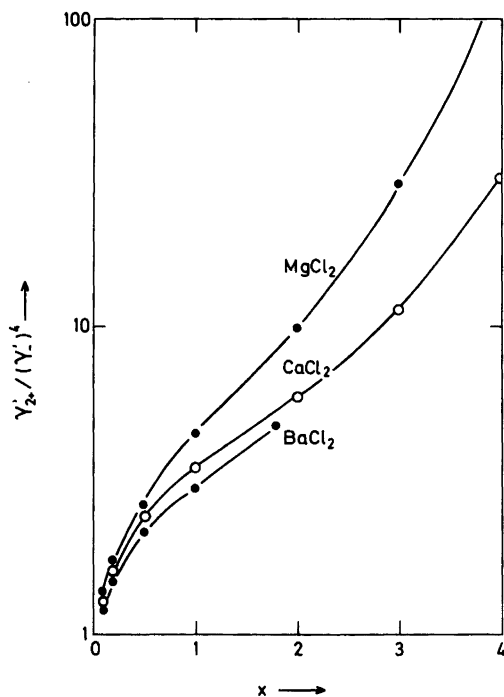
Fig. 3. The ratio $\gamma'_{2+}/(\gamma'_-)^4$ for alkaline-earth chlorides in $x$ molal aqueous single-salt solutions at 25 °C.



Fig. 4. An activity comparison of pairs of equally charged ions ($Li^+/K^+$ and $Mg^{2+}/Ba^{2+}$) and of nearly equally sized ions ($Li^+/Mg^{2+}$ and $K^+/Ba^{2+}$) in aqueous single-salt solutions of chlorides at 25 °C.

With increasing concentration, the mean-ion activity coefficient of a noncomplexing salt[2] generally goes towards or through a minimum. This reflects a gradual change in dominance from stabilization by ion-ion interactions (at low concentration) to destabilization by loss in ion-water interactions (at high concentration). The latter may be described as hydration energy loss by overlap of hydration cospheres.[3] Also the single-ion data show this behaviour and clearly reveal that the destabilization by hydration energy loss for alkalimetal[1] and alkaline-earth ions is stronger the smaller is the ion and the larger is its charge (Figs. 1 and 4). This follows the same trends as does the ion hydration energy itself.[5]

In hydration energy, the chloride ion is closer to the sodium ion than to the potassium ion.[5] In activity behaviour, however, the opposite is the case.[1] Referring to the two-state cosphere model for ions in water,[3] this could mean that the outer cosphere of the chloride ion be energetically closer to the one of the potassium ion than to the one of the sodium ion.
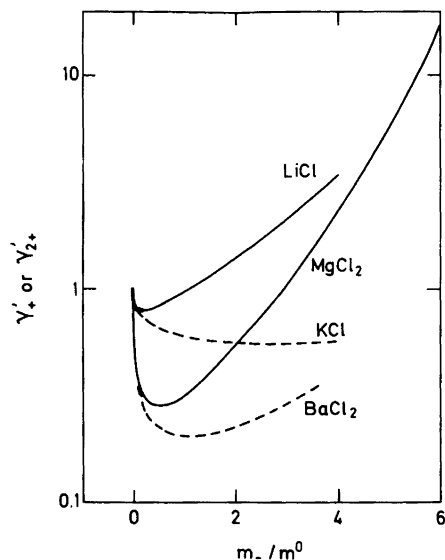
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