INDIVIDUAL ACTIVITY OF CALCIUM IONS IN PURE SOLUTIONS OF $CaCl_2$ AND IN MIXTURES

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ABSTRACT Individual ion activities were calculated for Ca^{2+} in pure solutions of $CaCl_2$ and in mixtures of $CaCl_2$ with $MgCl_2$ and with NaCl, using different conventions to obtain $\gamma_{Ca^{2+}}$. The results were compared with potentiometric measurements, using calcium specific electrodes. It is found that significant differences should be obtained for emf's using the different conventions, when ionic strength is greater than 0.5. The experimental results obtained for ionic strengths up to 0.2 favor slightly the direct use of $\gamma_{\pm CaCl_2}$, but are fairly consistent also with the use of the Guggenheim and the MacInnes conventions.

INTRODUCTION

In a recent paper (1) the activity of Ca^{2+} ions in mixed solutions was discussed. The activity was measured with electrodes assumed to be specific to Ca^{2+} (2, 3) so that the emf measured against an inert reference electrode was taken as due to the individual ion activity $a_{Ca^{2+}}$, i.e.

$$E = E^0 - \frac{RT}{2F} \ln C_{Ca^{2+}} \gamma_{Ca^{2+}} . \qquad (1)$$

In some investigations on the specificity of calcium electrodes (2–4) the assumption was made that $\gamma_{Ca^{2+}}$ was directly proportional to $\gamma_{\pm CaCl_2}$, and the emf was plotted against $C_{CaCl_2}\gamma_{\pm}$. The same assumption was used in other calculations which required the individual ion activity $a_{Ca^{2+}}$, e.g. the use of dissociation constants (5) or the calculation of ion exchange equilibria (6). Any assumption as to the single ion activity of Ca^{2+} in pure $CaCl_2$ solutions should conform to the convention that

$$a_{CaCl_2} = \gamma_{Ca^{2+}} C_{Ca^{2+}} (\gamma_{Cl^-} C_{Cl^-})^2 = 4\, C^3_{CaCl_2} (\gamma_{\pm CaCl_2})^3 . \qquad (2)$$

It can be seen that the above use of $\gamma_{\pm}$ is consistent with equation 2. However it may be preferable to assign to $\gamma_{Ca^{2+}}$ and to γ_{Cl^-} values which are not directly proportional to $\gamma_{\pm}$ but conform to equation 2, using for instance the Guggenheim convention [where $\gamma_{Ca^{2+}} = (\gamma_{\pm CaCl_2})^2$ and $\gamma_{Cl^-} = \sqrt{\gamma_{\pm CaCl_2}}$] or the MacInnes convention [where $\gamma_{Ca^{2+}} = (\gamma_{\pm CaCl_2})^3/(\gamma_{\pm KCl})^2$]. The consistence of the above conventions with some experimental results is discussed by Kortüm (7), who favors the Guggenheim convention.

In a recent paper Kohn and Furda (8) calculated $\gamma_{Ca^{2+}}$ by three different methods (two based on the use of the theory of Debye-Hückel and one using the MacInnes convention) for $C_{CaCl_2} \simeq 3.3 \times 10^{-3}$ m to $\simeq 5 \times 10^{-2}$ m. The values obtained by the use of the three methods are almost identical (± 1 %). The experimental results obtained by Kohn and Furda are more consistent with such $\gamma_{Ca^{2+}}$ than with the use of $\gamma_{\pm}$ as employed by Raaflaub (5). Similar calculations were carried out by Garrels (9) up to a concentration of $C_{CaCl_2} \simeq 1.3$ m. It would be of interest to extend the examination of our potentiometric results (1) by using the various γ's discussed above to obtain the activity of Ca^{2+}.

RESULTS AND DISCUSSION

The experimental setup has been described in previous publications (1–3).

In Fig. 1 we plot the different $\gamma_{Ca^{2+}}$ for pure $CaCl_2$ against the ionic strength I (using molalities). The values of $\gamma_{Ca^{2+}}$ obtained by using the MacInnes convention

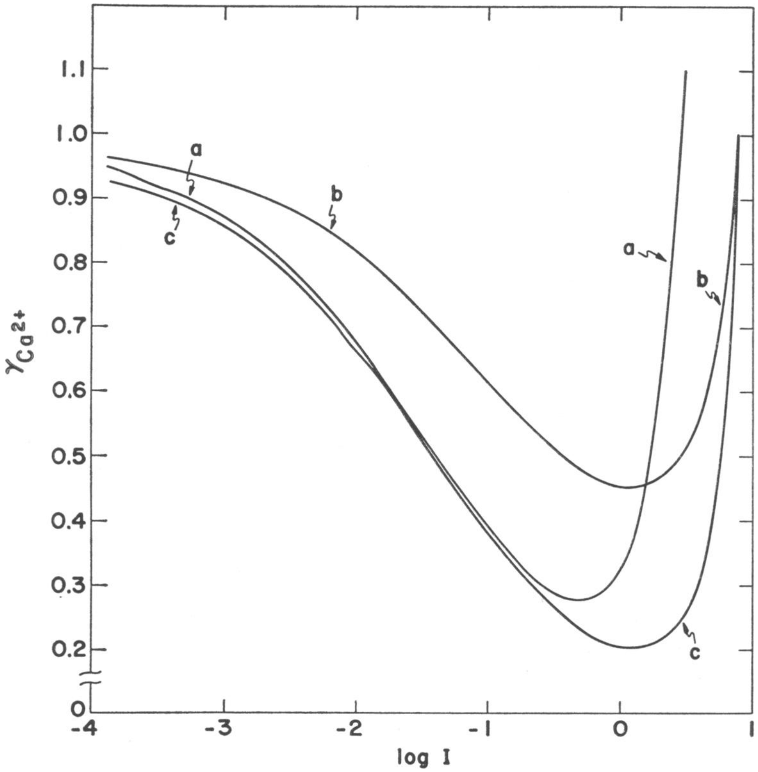

FIGURE 1 Activity coefficients of Ca^{2+} as function of the ionic strength. *a*—using the MacInnes convention (Garrels); *b*—$\gamma_{\pm}$; *c*—using the Guggenheim convention ($\gamma_{\pm}^2$).

were taken from Garrels (9). $\gamma_{\pm CaCl_2}$ was taken from interpolation of values given in the literature (10, 11). $\gamma_{\pm CaCl_2}$ calculated by the Glueckauf equation and discussed in a previous paper (1), reduces to $\gamma_{\pm CaCl_2}$ in the absence of other components in the solution.

It can be seen that for $I < 10^{-4}$, the different $\gamma_{Ca^{2+}}$ almost coincide. In the range of $I < 10^{-1}$, the Guggenheim convention and the MacInnes convention yield practically the same values for $\gamma_{Ca^{2+}}$, while the use of $\gamma_{\pm}$ would give activities higher by some 30%. In the range of $I > 10^{-1}$, the three values differ considerably, though at $I \simeq 1.5$, the MacInnes convention gives a coefficient approaching $\gamma_{\pm}$, and at $I \simeq 7.5$, the Guggenheim γ approaches $\gamma_{\pm}$.

Fig. 2 presents the emf's obtained in pure solutions of $CaCl_2$, using a solid polymer membrane at two concentrations of the reference $CaCl_2$ solutions (parts I and II), and using the liquid ion exchange (Orion) electrode (Calcium Activity Electrode, Model 92-20, Orion Research, Inc., Cambridge, Mass.) (part III).

The experimental emf's are plotted against $a_{Ca^{2+}}$ obtained through the use of $\gamma_{\pm}$ (curves *a*), $\gamma_{\pm}^2$ (Guggenheim convention, curves *b*), and $\gamma_{Ca^{2+}}$ (MacInnes convention, curves *c*). In all the curves, at $4 \times 10^{-4} < a_{Ca^{2+}} < 2 \times 10^{-2}$ the slopes are constant. The values of the constant slopes (the Nernst value being 29 mv/log $a_{Ca^{2+}}$) are summarized in Table I.

It can be seen that the use of the MacInnes convention would yield (in the range of concentrations discussed up to now) a good approximation to the Nernstian slope; the use of $\gamma_{\pm}$ would yield a slightly smaller slope, and the use of the Guggenheim convention would yield a value slightly too high.

At activities above 2×10^{-2} m, the use of the MacInnes convention leads to a marked deviation from linearity, and to slopes smaller than Nernstian ($\simeq$25 mv/log *a*). Use of $\gamma_{\pm}$ maintains the linearity at 28 mv/log *a* to activity of $\simeq 10^{-1}$ m. At higher concentrations, the slope given by $\gamma_{\pm}$ increases up to about 35 mv/log *a* at the limit of our experiments. Use of the Guggenheim convention gives slightly better results than the use of $\gamma_{\pm}$, particularly at high concentrations. In all the above considerations we have ignored the liquid junction potential between the saturated calomel electrode and the varying solutions of $CaCl_2$. In the case of the solid polymer membrane there is also a liquid junction potential between a saturated calomel electrode and the reference solution. In the Orion electrode the reference solution is in contact with an Ag/AgCl electrode. Use of Ag/AgCl as reference electrodes would eliminate some of the difficulties owing to the changing liquid junction potential. However such a reference electrode would be affected by the chloride ions of the NaCl and $MgCl_2$ added in great excess in the experiments with mixtures, and so mask the contribution of the calcium electrode to the final emf. Furthermore the activity of the anions would also be affected by the specific interactions with the mixed cations, and the interpretation of the results would be problematic. Possible improvements in the use of reference electrodes are now being investigated.

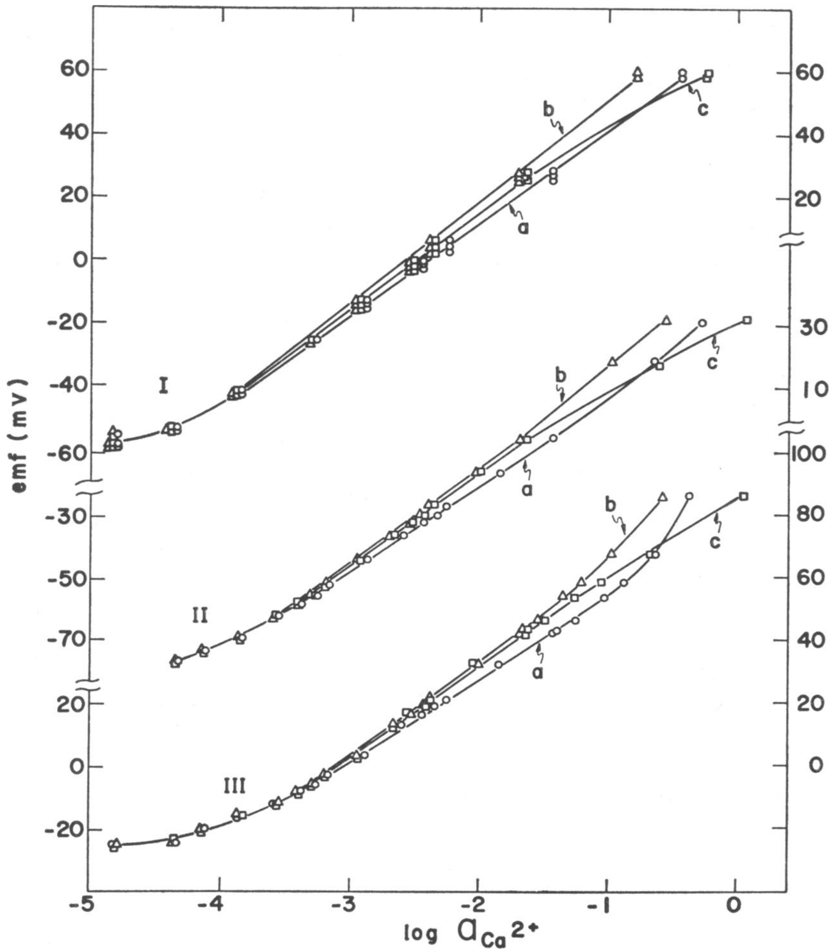

FIGURE 2 Experimental emf vs. activity of Ca^{2+}, using different $\gamma_{Ca^{2+}}$. I. Solid polymer membrane, reference solution 6.03 × 10^{-3} m $CaCl_2$. II. Solid polymer membrane, reference solution 1.10 × 10^{-1} m $CaCl_2$. III. Orion electrode. Curves *a* (○)—using $\gamma_\pm$; Curves *b* (△)—using the Guggenheim convention; Curves *c* (□)—using the MacInnes convention.

TABLE I

THE SLOPE OF *d* emf/*d* log $a_{Ca^{2+}}$ IN THE LINEAR RANGE OF FIG. 2

	For $\gamma_\pm$	For $\gamma_\pm^2$ (Guggenheim)	For $\gamma_{Ca^{2+}}$ (MacInnes)
Solid polymer membrane, reference solution 6 × 10^{-3} m	29.5	32.0	31.5
Solid polymer membrane, reference solution 1.1 × 10^{-1} m	27.0	29.5	28.5
Orion electrode	27.0	30	29

It appears that the results of the measurements in pure $CaCl_2$ solutions are inconclusive, and improvement of technique would not change them significantly. However, it might be possible to obtain more significant results from the study of mixtures.

Fig. 3 summarizes experiments conducted with the aid of the Orion electrode. In part I we plot the emf's obtained upon introducing varying amounts of $MgCl_2$ into a 3.80×10^{-3} m solution of $CaCl_2$. The theoretical curves were obtained by using the various γ's of Fig. 1 for the given ionic strength, applying them to C_{CaCl_2}, and obtaining the corresponding emf from Fig. 2. The $(\gamma_\pm)^2$ obtained through the use of Glueckauf's equation (12) was applied to the curves in Fig. 2 corresponding to $\gamma_\pm{}^2{}_{CaCl_2}$, as explained above.

Such a method of calculating the expected emf's is based on two assumptions: first, that the electrode is completely specific to calcium; and second, that the change of the activity of calcium is due solely to the change in the ionic strength (13).

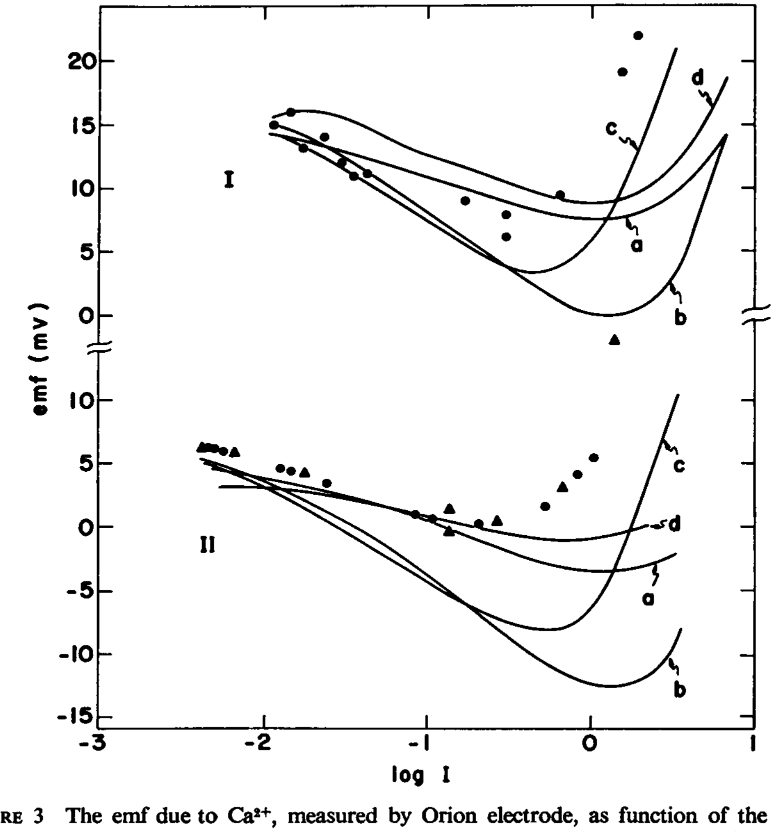

FIGURE 3 The emf due to Ca^{2+}, measured by Orion electrode, as function of the ionic strength. I. 3.80×10^{-3} m $CaCl_2$ in $MgCl_2$ (●). II. 1.52×10^{-3} m $CaCl_2$ in NaCl (●) and in NaCl + $MgCl_2$ (▲). Curves—theoretical. *a*—using $\gamma_\pm$; *b*—using $\gamma_\pm{}^2$ (Guggenheim); *c*—using $\gamma_{Ca^{2+}}$ (MacInnes); *d*—using $\gamma^2_{Glueckauf}$ (Guggenheim).

The first assumption depends on the quality of the electrode and can be justified, at least within some specified range, when the specificity-ratio towards calcium is high enough. The second assumption ignores the specific interactions between ions, such as those considered in Harned's rule (reference 11, chapter 14), which states that in a mixture at a constant ionic strength the logarithm of the activity coefficient of one electrolyte is linearily dependent on the concentration of this electrolyte, i.e. it is *not* constant. Unfortunately Harned's rule in its simple form does not hold for all mixtures (reference 10, chapter 15); and even where it does hold, its use in systems whose ionic strength is not constant (as in ours) would present considerable difficulties. Rudimentary attempts to obtain the activity coefficients of calcium in

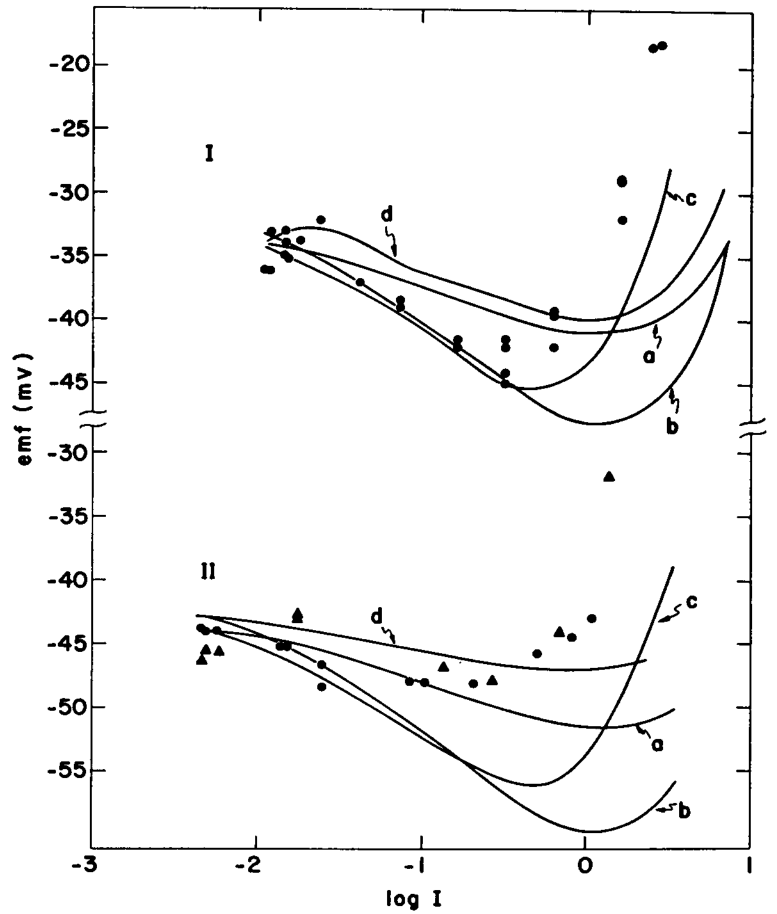

FIGURE 4 The emf due to Ca^{2+}, measured by solid polymer membrane, as function of the ionic strength. I. 3.80 × 10^{-3} m $CaCl_2$ in $MgCl_2$ (●). II. 1.52 × 10^{-3} m $CaCl_2$ in NaCl (●) and in NaCl + $MgCl_2$ (▲). Curves—theoretical. *a*—using $\gamma_{\pm}$; *b*—using $\gamma_{\pm}^{2}$ (Guggenheim) *c*—using $\gamma_{Ca^{2+}}$ (MacInnes); *d*—using $\gamma^{2}_{Glueckauf}$ (Guggenheim).

mixtures, using ion-specific electrodes, have already been made (1). More elaborate methods are now being investigated. In the consideration of the calculated curves in Figs. 3 and 4, the above limitations should be kept in mind.

If the electrode is assumed to be ion specific up to $I < 3 \times 10^{-1}$, then the experimental values are consistent with all the three activities mentioned above, slightly favoring the use of $C\gamma_{\pm}$.

Part II of Fig. 3 presents the behavior of 1.52×10^{-3} m $CaCl_2$ in a mixture with NaCl, and in a mixture of both NaCl and $MgCl_2$ in the molar ratio of 9 to 1. The results are consistent with $C\gamma_{\pm}$, and also with the use of Glueckauf's $\gamma_{\pm}$ adopting the Guggenheim convention.

Fig. 4 summarizes the results obtained with the aid of the solid polymer membrane, in experiments similar to those described in Fig. 3. Here the results in the presence of $MgCl_2$ are more consistent with the MacInnes and the Guggenheim conventions, as applied to $\gamma_{\pm CaCl_2}$. For mixtures of NaCl and of NaCl with $MgCl_2$, the results are consistent with all three activities described above.

It will be noted that the results obtained with the two calcium electrodes are not the same. As the errors owing to the neglect of specific interactions in mixtures and to the use of liquid junction reference electrodes affect equally the calculated curves in Figs. 3 and 4, the difference in the divergence of the experimental values from the calculated curves in Figs. 3 and 4 is probably due to the different specificity ratios of the two electrodes. From the practical point of view, however, both electrodes may be considered as calcium specific in the biological range (3), within the experimental error of ±1 mv, as shown by the scattering of data in Figs. 2–4. These errors are not due to the accuracy of measurement, which is reliable within ±0.2 mv, but to the difficulty in obtaining reproducible results from the same electrode after a lapse of a few days.

It can be seen in Figs. 3 and 4 that at ionic strengths higher than 0.5 the results predicted by the various conventions vary greatly, so that the investigation of mixtures could perhaps serve as a good test for the consistency of the various conventions. Unfortunately, the specificity ratio of the available membrane electrodes does not allow their use at the required ionic strength. It is to be expected, however, that better membranes will soon be available (more specific and yielding more reproducible readings), so that the present investigation can be extended.

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