Spectrophotometric determination of the activity of strontium and calcium ions by metal-indicator method

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Tetramethylmurexide as metallochromic indicator has been used for spectrophotometric determination of the activity of Sr^{2+} ions. Single-ion activity coefficients $\gamma_{Sr^{2+}}$ as determined in mixed solutions of $SrCl_2$ and KCl ($I \leq 0.05$), are in a very good agreement with those calculated according to Debye and Hückel equation ($\Delta\gamma_{Sr^{2+}} < +0.005$); at a higher ionic strength I 0.10 to 0.15, $\Delta\gamma_{Sr^{2+}} = +0.02$. This method is suitable for determination of the activity $a_{Sr^{2+}}$ within 0.1×10^{-3} to 2.0×10^{-3} range. The effect of some simple salts on the determination of the Sr^{2+} and Ca^{2+} activity has been described. The use of Debye and Hückel equation and MacInnes' convention for the calculation of single-ion activity coefficients $\gamma_{Sr^{2+}}$ and $\gamma_{Ca^{2+}}$ in dilute solutions of $SrCl_2$ ($I \leq 0.05$) and $CaCl_2$ ($I \leq 0.15$) has been substantiated.

The metal-indicator method is well suited for the determination of cations *concentration* of various metals [1—11]. (For the survey of literature see [1].) *Kohn* and *Furda* [12] have shown that the *Raaflaub*'s method [3, 4] could directly be used for the determination of the activity of calcium ions in dilute solutions of calcium salts; the activity of calcium ions in solutions of calcium pectinates and some calcium oligo- and polyuronates [12—14] has been determined.

The principle of this method is of general applicability and it could therefore be also used to determine activity of other metal cations providing that there exists a convenient metallochromic indicator. This paper refers to spectrophotometric determination of strontium ions activity in dilute solutions of strontium salts, tetramethylmurexide being the metallochromic indicator, and to the effect of some simple salts on the determination of strontium and calcium ions activity.

Experimental

Chemicals

Tetramethylmurexide was prepared from coffeine *via* tetramethylalloxanthine [15, 16]. Its characteristic data were reported earlier [12].

All chemicals were of anal. grade. Dilute $MgCl_2$ and $Mg(NO_3)_2$ solutions were prepared by neutralization of MgO with the appropriate acid; the unchanged portion of MgO was filtered off and the pH of the filtrate was set to 6.5—7.0. Dilute CH_3COOK, $SrCl_2$, and $Sr(NO_3)_2$ solutions were obtained by neutralization of the corresponding acids with either carbonate-free 0.5 N-KOH or 0.1 N-Sr(OH)$_2$ under potentiometric indication. Redistilled water of specific conductivity 2×10^{-6} ohm^{-1} cm^{-1} was used.

Analytical methods

The concentration of calcium and magnesium salts was determined chelatometrically. The concentration of dilute potassium acetate, strontium chloride, and strontium nitrate solutions was calculated from the consumption of hydroxides upon titration of acids.

Determination of activity of Sr^{2+} and Ca^{2+} ions

The principle of this method was published in one of our previous papers [12]. The stock solution of tetramethylmurexide (ammonium salt, 4×10^{-4} mol l^{-1}) was freshly prepared before each series of measurements. Absorbances A were determined in solutions containing $0-3.5 \times 10^{-3}$ M-[Me^{2+}] and 4×10^{-5} M tetramethylmurexide in 1 liter at $23-25°C$. The ionic strength of solution I was adjusted by addition of neutral salts within the 0.01 to 0.15 range. Absorbances for the activity determination of strontium ions were measured at 500 nm (A_1) and 550 nm (A_2), those of Ca^{2+} at 490 nm (A_1) and 530 nm (A_2) in 1-cm cells using UVISPEC-Hilger compensation spectrophotometer; accuracy ± 0.001. Reference solutions were the corresponding solutions of pure salts without metallochromic indicator. For further details concerning the exact determination of the quotient $\varphi = A_1/A_2$, the stability of tetramethylmurexide solution, *etc.* see [1]. The calibration curve $\varphi = f(a_{Me^{2+}})$ was estimated for each series of measurements separately.

Single-ion activity coefficients $\gamma_{Me^{2+}}$ were calculated on the basis of the theory of strong electrolytes according to Debye and Hückel for 25°C [17, 12]; the effective diameters of hydrated Sr^{2+} ions $a_i' = 5$ A, Ca^{2+}, $a_i' = 6$ A.

Determination of the single-ion activity coefficients $\gamma_{Sr^{2+}}$ in mixed (SrCl$_2$ + KCl) solutions

A series of mixed (SrCl$_2$ + KCl) solutions of Sr^{2+} concentration ranging from 0 to 3×10^{-3} mol l^{-1} and ionic strength I 0.01, 0.02, 0.05, 0.10, and 0.15 was prepared. Quotients φ were determined. For the lowest ionic strength I 0.01 the reference calibration curve $\varphi = f(a_{Sr^{2+}})$ was constructed employing the single-ion activity coefficient $\gamma_{Sr^{2+}} = 0.670$ as calculated according to Debye and Hückel equation. Curves showing the relation of the quotient φ upon the SrCl$_2$ concentration in solution were constructed for ionic strengths I 0.02, 0.05, 0.10, and 0.15; $\varphi = f(c_{Sr^{2+}})$. The activities $a_{Sr^{2+}}$ for φ 1.0, 1.05, 1.10, 1.15, and 1.20 were read on the reference calibration curve $\varphi = f(a_{Sr^{2+}})$, whereas the corresponding concentrations of SrCl$_2$ for each ionic strength I on curves $\varphi = f(c_{Sr^{2+}})$. These experimental data served for calculation of single-ion activity coefficients $\gamma_{Sr^{2+}} = a_{Sr^{2+}}/c_{Sr^{2+}}$. The resulting activity coefficients $\gamma_{Sr^{2+}}$ are the average values determined for the φ 1.0—1.2 range, what corresponds to activities $a_{Sr^{2+}}$ 0.3×10^{-3} to 1.2×10^{-3}.

Results and discussion

Tetramethylmurexide (ammonium tetramethyl 5,5'-nitrilodibarbiturate) forms with Sr^{2+} ions a coloured complex Sr(TMM)$^+$, the absorption curve of which is plotted in the low [Sr^{2+}] concentration range in Fig. 1 (curves *1* and *2*).

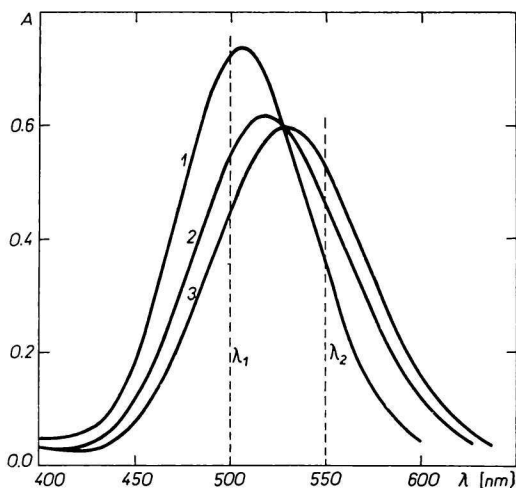*Fig. 1.* Absorption curves of tetramethylmurexide in dilute SrCl₂ solutions.
A — absorbance; tetramethylmurexide: 4×10^{-5} mol l⁻¹; SrCl₂: *1.* 0.050; *2.* 0.002; *3.* 0.000 mol l⁻¹.

Curve *3* shows the absorption curve of the anionic form (TMM)⁻ of this metallochromic indicator. The formation of the complex tetramethylmurexide with metal cations does not depend on the pH of the solution in the 4.8 to 8.1 range in contrast to murexide, which is strongly pH dependent [4].

The theoretical basis of this method was described in detail in our previous paper [12]. Activities of Sr^{2+} ions were determined by means of a calibration curve, which shows the relation between the colour of the metallochromic indicator and the activity of Sr^{2+} ions in calibration solutions. The application of the metal-indicator method is limited, in comparison with other methods, to a certain region of activities of cations given by the value of the stability constant of the proper complex. The stability constant K of the complex of murexide with Sr^{2+} ions, as well as that of tetramethylmurexide complex $Sr(TMM)^+$ equals 280 [18]. The activity of Sr^{2+} ions could be, therefore, best determined with solutions having the activity $a_{Sr^{2+}}$ roughly 10^{-3}. This activity region is convenient for the determination of activities $a_{Sr^{2+}}$ in biological systems, when studying the strontium binding to natural and synthetic polyelectrolytes, *etc.*

Calibration curve $\varphi = f(a_{Sr^{2+}})$

The colour of the metallochromic indicator is given by the quotient φ [5, 1]. The absorption curve of tetramethylmurexide in solution of concentration [Sr^{2+}] 2×10^{-3} mol l⁻¹ (Fig. 1, curve *2*) is considerably close to that of anionic form of tetramethylmurexide (TMM)⁻ (curve *3*). Even though it is possible to obtain also in this low concentration region a sufficiently steep calibration curve, if absorbances A_1 and A_2 were determined at wavelengths adjacent to both sides of absorbance maxima, *i.e.* at $\lambda_1 = 500$ nm and $\lambda_2 = 550$ nm.

Strontium chloride solutions of concentration 0 to 3×10^{-3} mol l⁻¹ without addition of further electrolyte were used for calibration purposes. The ionic strength I was
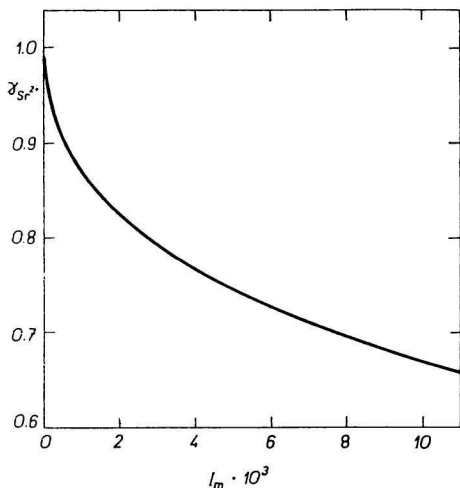
Fig. 2. Dependence of single-ion activity coefficient $\gamma_{Sr^{2+}}$ on the ionic strength of the solution.

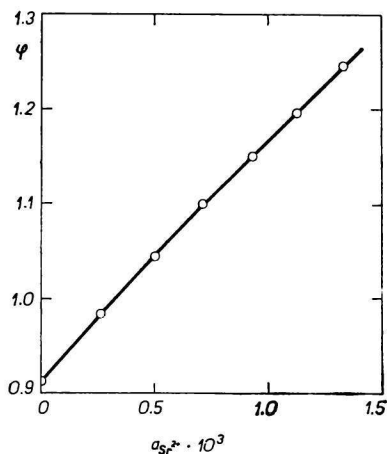I_m — ionic strength · of the solution of molality m.

Fig. 3. Calibration curve for determination of single-ion activities of Sr^{2+} ions.
$$\varphi = A_{500}/A_{550}.$$

calculated for each calibration solution and employing the function $\gamma_{Sr^{2+}} = f(I)$ shown in Fig. 2 the particular single-ion activity coefficient $\gamma_{Sr^{2+}}$ was read and the activity of Sr^{2+} ions calculated. The calibration curve $\varphi = f(a_{Sr^{2+}})$ was constructed from quotients φ (cf. Fig. 3).

Mixed solutions ($SrCl_2 + KCl$)

As it follows from the theoretical basis of this method [12], the activity of Sr^{2+} ions in calibration solutions has to be calculated employing the single-ion activity coefficient $\gamma_{Sr^{2+}}$. The single-ion acivity coefficients $\gamma_{Ca^{2+}}$, calculated for dilute solutions $CaCl_2$ ($I \leq 0.15$) according to Debye and Hückel equation were earlier shown to be virtually identical [12] with those obtained from the mean activity coefficients $\gamma_{\pm CaCl_2}$ and $\gamma_{\pm KCl}$ using MacInnes' convention

$$\gamma_{K^+} = \gamma_{Cl^-} = \gamma_{\pm KCl}.$$

Single-ion activity coefficients $\gamma_{Sr^{2+}}$ were therefore calculated by analogy according to Debye and Hückel equation [17, 12].

To verify the validity of the method for determination of Sr^{2+} ions activity, it was necessary to prove that all theoretical assumptions afford results, which are in accordance with experimental data. The procedure was the same as for the system ($CaCl_2 + KCl$) [12] excepting that instead of activities $a_{Sr^{2+}}$ single-ion activity coefficients $\gamma_{Sr^{2+}}$ were calculated. In mixed solutions ($SrCl_2 + KCl$) of ionic strength I 0.01 to 0.15 quotients φ were determined. By the procedure described in experimental part the single-ion activity coefficients $\gamma_{Sr^{2+}}$ were calculated from experimental data for individual ionic strengths and compared with theoretical values $\gamma_{Sr^{2+}}$ obtained from Debye and Hückel

Table 1

Single-ion activity coefficients $\gamma_{Sr^{2+}}$ in mixed solutions (SrCl$_2$ + KCl)

Ionic strength I	$\gamma_{Sr^{2+}}$ (according to D and H)	$\gamma_{Sr^{2+}}$ (experimental)	$\Delta\gamma_{Sr^{2+}}$
0.01	0.670	(0.670)*	
0.02	0.586	0.590±0.002	+0.004
0.05	0.467	0.470±0.001	+0.003
0.10	0.379	0.399±0.002	+0.020
0.15	0.332	0.355±0.004	+0.023

* Reference value.

Table 2

Quotient φ in dilute SrCl$_2$ and Sr(NO$_3$)$_2$ solutions

[Sr^{2+}] 10^{-3} mol l^{-1}	φ_{SrCl_2}	$\varphi_{Sr(NO_3)_2}$
0.00	0.912	0.913
0.30	0.983	0.986
0.60	1.044	1.041
0.90	1.101	1.101
1.20	1.149	1.149
1.50	1.194	1.195
1.80	1.246	1.243

equation [17, 12]. Results are listed in Table 1. The $\gamma_{Sr^{2+}}$ are average values of 6 measurements. A very good agreement has been found with both these activity coefficients $\gamma_{Sr^{2+}}$ in solutions of ionic strength I 0.02 and 0.05. Higher ionic strength I 0.10 and 0.15 is associated with a little higher experimental values of activity coefficients $\gamma_{Sr^{2+}}$ when compared with theoretical ones ($\Delta\gamma_{Sr^{2+}} = +0.02$).

Also quotients φ determined in pure dilute solutions of SrCl$_2$ and Sr(NO$_3$)$_2$ were compared. Results listed in Table 2 show that quotients φ and thereby the activities $a_{Sr^{2+}}$ in corresponding solutions of both strontium salts are equal regardless of the anion of strontium salt (Cl$^-$, NO$_3^-$). Differences $\Delta\varphi = \pm 0.003$ are within the experimental error range.

As it follows from our results, solutions for calibration of Sr^{2+} ions activity can be either pure solutions of SrCl$_2$ and Sr(NO$_3$)$_2$ without addition of further electrolyte, or mixed solutions (SrCl$_2$ + KCl) the ionic strength I of which does not exceed the value 0.05. Under these conditions a very good accordance between theoretical values $\gamma_{Sr^{2+}}$ calculated according to the theory of Debye and Hückel and those determined experimentally has been achieved.

The effect of some simple salts on the determination of the activity of Sr^{2+} ions and the error of this method

The aim of this method was to determine activities $a_{Sr^{2+}}$ preponderantly in pure solutions of strontium salts of organic acids without addition of further electrolyte (uronic and polyuronic acids). The described method could, however, be applied to all

systems, which, besides strontium salt, do not contain further cations reacting with tetramethylmurexide (for details see [19]). Indifferent were shown to be potassium salts KCl, KNO$_3$, and potassium acetate the first two of which could be used to adjust the ionic strength of solutions under study. Similarly, the presence of MgCl$_2$ and Mg(NO$_3$)$_2$ in solutions up to ionic strength I 0.15 does not influence the absorbance of metallochromic indicator. A significant hypsochromic effect of Mg^{2+} ions on the absorption curves of tetramethylmurexide is seen at higher concentrations of magnesium salt only [19]. On the other hand, Na$^+$ ions do react with tetramethylmurexide, although in a relatively low extent. The stability constant of the Na complex [4] is roughly 500 times lower than that of the Sr complex. The presence of NaCl in concentration lower than 0.01 mol l^{-1} in the solution does not influence the determination of activity $a_{Sr^{2+}}$. The deviation of quotient φ caused by the presence of a greater amount of NaCl in the solution would be possible to compensate using calibration solutions of the same NaCl concentration. The determination of activity $a_{Sr^{2+}}$ in those systems has not been experimentally investigated.

Absorbances A_1 and A_2 were determined in the wavelength range, where the absorption curve is steep (Fig. 1). When the conditions for an exact determination of quotient φ described earlier in [1] are satisfied, the quotient φ could be estimated quite precisely $\Delta\varphi = \pm 0.0025$. The relative error of Sr^{2+} activity determination is given by the slope of the calibration curve for the particular activity $a_{Sr^{2+}}$ and the error of quotient φ determination. Table 3 shows errors of activities determination in the range $a_{Sr^{2+}}$ 0.10 $\times$ $\times$ 10^{-3} to 2.00 $\times$ 10^{-3} calculated for $\Delta\varphi$ ± 0.0025 constant for all measurements. The calculated errors are in accordance with those found in numerous experiments when measuring activities $a_{Sr^{2+}}$ in solutions of strontium oligouronates [20].

Table 3

The error of activity $a_{Sr^{2+}}$ determination

$a_{Sr^{2+}} \cdot 10^3$	Relative error [$\pm$ %]
0.100$\pm$0.009	9.0
0.200$\pm$0.009	4.5
0.500$\pm$0.010	2.0
1.000$\pm$0.010	1.0
1.500$\pm$0.010	0.7
2.000$\pm$0.011	0.6

The determination of activity $a_{Sr^{2+}}$ described in this paper was first of all intended for solutions of the lowest concentration of strontium salts. As evidenced by the course of the calibration curve in Fig. 3, it is possible to determine the activity of Sr^{2+} ions also in solutions of substantially higher concentration of strontium salt. The exact analysis requires, however, the ionic strength I of the calibration solution not to exceed 0.05.

Single-ion activity coefficient $\gamma_{Ca^{2+}}$ in mixed solutions of calcium chloride and some simple salts

This paper appends some so far unpublished results concerning the single-ion activity coefficient $\gamma_{Ca^{2+}}$ determined in mixed solutions of calcium salts.

The presence of potassium and magnesium salts in the solution under investigation $(I \leq 0.15)$ does not, as mentioned, influence the absorbance of tetramethylmurexide. It remains to answer whether mixed solutions, containing in addition to $CaCl_2$ a further electrolyte, could be used as calibration solutions for activity $a_{Ca^{2+}}$ determination. In other words, whether the single-ion activity coefficient $\gamma_{Ca^{2+}}$ is in all mixed solutions a function of sole ionic strength of the solution I, independently of the kind of electrolyte added.

To a series of $CaCl_2$ solutions of concentration Ca^{2+} 0 to 3×10^{-3} mol l^{-1} salts: KCl, KNO_3, CH_3COOK, $MgCl_2$, and $Mg(NO_3)_2$ were added so as the final ionic strength I was 0.01, 0.02, 0.05, 0.10, and 0.15. Quotients φ were determined and the results were evaluated in the same way as with $\gamma_{Sr^{2+}}$ determination in mixed solutions ($SrCl_2$ + KCl). Since absorbances of mixed solutions of the lowest ionic strength I 0.01 differed in the range close to experimental errors independently of the kind of electrolyte added, only the same activity coefficient $\gamma_{Ca^{2+}}$ 0.675 was employed as reference value for all solutions [17, 12].

Results of this measurement are listed in Table 4 and seen in Fig. 4. The $\gamma_{Ca^{2+}}$ are average values of three estimations. The full line represents theoretical values $\gamma_{Ca^{2+}}$ as

Table 4

Single-ion activity coefficient $\gamma_{Ca^{2+}}$ in mixed solutions of $CaCl_2$ and some simple electrolytes

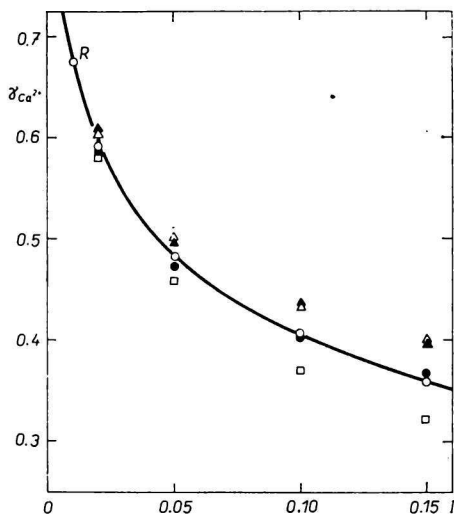| Ionic strength I	$\gamma_{Ca^{2+}}$ (according to D and H)	$\gamma_{Ca^{2+}}$ (experimental) electrolyte added				
		KCl	KNO_3	CH_3COOK	$MgCl_2$	$Mg(NO_3)_2$
0.01	0.675	(0.675)*	(0.675)	(0.675)	(0.675)	(0.675)
0.02	0.596	0.591	0.589	0.581	0.605	0.606
0.05	0.485	0.483	0.476	0.459	0.501	0.496
0.10	0.405	0.407	0.403	0.370	0.434	0.438
0.15	0.359	0.360	0.369	0.321	0.399	0.398

* Reference value.

Fig. 4. Single-ion activity coefficient $\gamma_{Ca^{2+}}$ in mixed solutions of $CaCl_2$ and some simple electrolytes.
Electrolyte added: ○ KCl; ● KNO_3; □ CH_3COOK; △ $MgCl_2$; ▲ $Mg(NO_3)_2$.
I — ionic strength of the solution; R — reference value.

calculated according to Debye and Hückel equation. In mixed solutions ($CaCl_2$ + KCl) a full agreement between theoretical values $\gamma_{Ca^{2+}}$ and those determined experimentally has been found. The deviation $\Delta\gamma_{Ca^{2+}}$ is in most cases less than ± 0.005. The results completely entitle to use the Debye and Hückel equation [17, 12] and also MacInnes' convention for calculation of single-ion activity coefficients $\gamma_{Ca^{2+}}$ in $CaCl_2$ solutions. The same conclusion has been reported by *Shatkay* [21], who determined the single-ion activity coefficients $\gamma_{Ca^{2+}}$ in pure $CaCl_2$ solutions employing a specific Ca electrode.

A similar accordance of results has been found in mixed solutions ($CaCl_2$ + KNO_3); $\Delta\gamma_{Ca^{2+}} = \pm 0.010$. In the presence of acetate anion lower $\gamma_{Ca^{2+}}$ values than the theoretical ones were found. The negative deviation $\Delta\gamma_{Ca^{2+}}$ increases with the increasing ionic strength (Fig. 4). On the contrary, the presence of magnesium salts results in a positive deviation $\Delta\gamma_{Ca^{2+}}$, which also increases with the increasing ionic strength of the solution. As evidenced by results, in the presence of Mg^{2+} and CH_3COO^- ions the single-ion activity coefficient $\gamma_{Ca^{2+}}$ is no more a function of sole ionic strength, but depends also on the kind of the electrolyte added.

Moreover, quotients φ were estimated in pure $CaCl_2$ and $Ca(NO_3)_2$ solutions of concentration Ca^{2+} 0 to 1.8×10^{-3} mol l^{-1} without addition of further electrolyte. Quotients φ as well as the activities $a_{Ca^{2+}}$ of the corresponding solutions of both calcium salts were identical, independently of the calcium salt anion (Cl^-, NO_3^-).

From the results presented it could be deduced that for calibration purposes either pure $CaCl_2$ and $Ca(NO_3)_2$, or combined solutions containing in addition to Ca^{2+} ions also K^+, Cl^-, and NO_3^- ($I \leq 0.15$) could be used. The same conclusion holds also for calibration solutions of strontium salts ($I \leq 0.05$).

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