Short communication

Thin-layer chromatographic behavior and separation of alkaline earth metals on silica gel in aqueous sodium perchlorate solution

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Abstract

The thin-layer chromatographic behavior of alkaline earth metal ions (Mg^{2+}, Ca^{2+}, Sr^{2+}, and Ba^{2+}) in aqueous sodium perchlorate solutions on silica gel thin-layers impregnated with sodium hydroxide has been surveyed as a function of salt concentration. At salt concentrations above $2\,mol\,l^{-1}$, the selectivity of the metals increased with a decrease in the crystal ionic radii; with further increases in salt concentration, the selectivity differences among the metals expanded remarkably. In the present systems, it was supposed that the cation exchange, the surface complexation, and the salting-out effect participate simultaneously in the adsorption of the metals on silica gel. Typical chromatograms for the mutual separation of the alkaline earth metals are presented.
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Keywords: Alkaline earth metals; Silica gel; Aqueous sodium perchlorate solution

1. Introduction

High-performance liquid chromatography (HPLC) has increasingly been used for the separation of metal ions; recent advances in this area have been reviewed by Sarzanini [1]. Alkaline earth metals can be separated by cation [2–7] or anion [8] exchange chromatography and chelation ion chromatography [9–12], using suitable eluents. Cation exchange systems are the most commonly used for the separation of alkaline earth metals; in the stationary phases, they generally provide a selectivity sequence of Mg < Ca < Sr < Ba corresponding to an increase in ionic radii, almost regardless of the kinds of functional groups. A partial change in the selectivity of the metals has been found to occur in some cases in cation exchange chromatography and chelation ion chromatography, depending on the kinds of the ligands in the stationary and/or mobile phase and various other factors, such as the pH

and ionic strength of an eluant. However, reverse selectivity is obtained only in anion exchange systems involving strong complexing agents, such as ethylenediaminetetraacetic acid (EDTA) in an eluent.

We used thin-layer chromatography (TLC) to survey the adsorption behaviors of alkaline earth metals on silica gel impregnated with sodium hydroxide in various concentrations of aqueous sodium perchlorate solutions, and found that the selectivity of the metal was quite opposite the general order in cation exchange chromatography. On the other hand, separation of alkaline earth metals has been achieved in many TLC systems over the past years. It is known that ion exchange systems using cation exchange resins are effective in TLC [13] as well as in HPLC. Partition TLC also is successful in separating the metals from each other and has confirmed the general selectivity of (Be) < Mg < Ca < Sr < Ba, on various support materials, such as alumina [14], silica gel [14,15], microcrystalline cellulose [16,17] in mixed solvents of alcohols or ketones and hydrochloric or nitric acids.

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Little information is available about the chromatographic systems in which the selectivity of alkaline earth metals increase with a decrease of their ionic radii without using complexing agents that may prevent detection after the separation, either in TLC or in HPLC.

2. Experimental

2.1. Materials

Stock solutions of four alkaline earth metals (Mg, Ca, Sr, and Ba) were prepared by dissolving sufficient amounts of metal chlorides (99.0% or higher purity) in $0.1 \, mol \, l^{-1}$ hydrochloric acid to give a $1 \, mol \, l^{-1}$ metal solution. Test and sample solutions were prepared by diluting the stock solutions with hydrochloric acid of the same concentration and by mixing all of the stock solutions, respectively, followed by dilution to give a $0.05 \, mol \, l^{-1}$ for each metal. Polyvinylalcohol (Polyvinylalcohol 1000; average number of polymerizations: 900–1000; Saponification degree: >96.0%; Wako, Japan) was utilized as a binder of the silica gel thin-layer plates. All the chemicals were of analytical-reagent grade.

2.2. Preparation of thin layers

A 48-g portion of silica gel (Wako gel B–0, Wako, Japan) was mixed with 100 ml of a $3 \, mol \, l^{-1}$ hydrochloric acid-3% (w/v) hydrogen peroxide solution in order to dissolve and remove impurities, such as alkali metals, alkaline earth metals, aluminum, iron, manganese, and titanium. The silica gel was filtered through a filter paper (12 cm in diameter, No.5A, Toyo, Japan) with suction and was washed with three 50-ml portions of $1 \, mol \, l^{-1}$ hydrochloric acid, six 60-ml portions of water, and three 60-ml portions of ethanol. The purified silica gel was then dried at $110 \, °C$ for 1 h in a constant-temperature oven. After cooling, the gel was stored in a sealed bottle.

A 12-g portion of purified silica gel was mechanically homogenized for 2 min with 1% (w/v) polyvinylalcohol solution of an ethanol–water (2:3, v/v) mixture, and then the slurry was mixed thoroughly with 2.0 ml of a $3 \, mol \, l^{-1}$ aqueous sodium hydroxide solution. With an applicator, the slurry was spread to a thickness of $250 \, \mu m$ on glass plates (20 cm × 15 cm). The plates were dried in cool air blown for 10 min and then were allowed to stand at $100 \, °C$ for 1 h in a constant-temperature oven. They were stored in a sealed box containing a saturated $CaCl_2$ solution until ready for use.

2.3. Procedure

The test solution (0.3 μl) was applied to the TLC plate by means of a micropipette (Pipetman, P2, Gilson, France) at a point 2.5 cm from one edge, and the spots were allowed to stand for 5 min in a desiccator containing saturated $CaCl_2$ solution. The plate was placed in a chromatographic chamber (22 cm × 10 cm × 22 cm) equipped with a tank (21 cm

× 3 cm × 2.5 cm), containing 15 ml of a developing solvent, and then developed up to 10 cm from the starting point by the ascending technique at $25 \, °C$. After the development, the plate was dried on a hot plate at ca. $60 \, °C$. The metals were visualized by spraying with a 0.1% aqueous Alizarin S solution and then with a $3 \, mol \, l^{-1}$ aqueous ammonia solution, followed by gentle heating. The spot of Mg^{2+} showed up in red, and other metal ions were detected as purple spots on a yellow background.

3. Results and discussion

3.1. Effect of impregnation of silica gel thin layers with sodium hydroxide

It has been well known that adsorption of metal ions on silica usually increases in aqueous solutions of higher pH [18]. In our preliminary work, a development on a thin layer of silica gel with an aqueous sodium perchlorate solution adjusted pH by sodium hydroxide resulted in demixing of the solvent during chromatography, because probably of specifically high selectivity of hydroxide ions on silica gel. All the metals tested always lay on the first solvent front regardless of the concentrations of sodium hydroxide in the solvent. On the other hand, it has been revealed that the pretreatment of silica gel with aqueous solution of weakly basic amine and diluted hydrochloric acid makes it possible to arbitrarily regulate the adsorbability of trivalent cations of rare earths in TLC [19]. However, by this pretreatment, it was difficult to obtain the silica gel that indicated sufficiently high activity for divalent cations of alkaline earth metals. Therefore, we inspected the effect of the impregnation of silica gel with sodium hydroxide on TLC behaviors of the metals in a $0.2 \, mol \, l^{-1}$ sodium perchlorate solution. It was found that the adsorbability of the metals increased remarkably with an increase of sodium hydroxide added into a thin-layer and that all the metals gave reproducible R_F-values and compact spots without tailings given the impregnation with 0.0625–0.75 mmol sodium hydroxide per gram of silica gel. On the basis of these results, we decided to add 0.5 mmol of sodium hydroxide per gram of silica gel in preparing the TLC plates, on which the metals indicate moderate R_F-values adequate for measurement.

3.2. Adsorption behavior

Table 1 summarizes the R_F-values (×100) of the alkaline earth metals on silica gel in various concentrations of sodium perchlorate solutions. For example, in the $1 \, mol \, l^{-1}$ sodium perchlorate solution, the R_F-values of the metals increased in the order of $Mg^{2+} < Ca^{2+} < Ba^{2+} \sim Sr^{2+}$, though the differences were small. On the other hand, the aqueous $8–9 \, mol \, l^{-1}$ sodium perchlorate solution made a great difference in the R_F-values of the metals, which increased in the order of $Mg^{2+} < Ca^{2+} < Sr^{2+} < Ba^{2+}$. This selectivity was quite opposite the general order in many systems, such as

Table 1
R_F-values ($\times 100$) of alkaline earth metals on silica gel in aqueous sodium perchlorate solutions

Concentration of NaClO$_4$ (mol l^{-1})	$R_F \times 100$							
	Mg		Ca		Sr		Ba	
	Rear	Front	Rear	Front	Rear	Front	Rear	Front
0.2	2	8	3	10	5	13	4	12
0.5	11	20	16	27	24	36	21	32
1.0	27	37	36	48	47	60	45	58
2.0	37	48	52	62	64	76	65	77
3.0	38	49	57	66	69	80	74	84
4.0	30	43	51	63	68	80	74	86
5.0	22	35	46	57	65	78	75	87
6.0	14	25	36	48	62	74	74	88
7.0	7	17	24	38	55	70	73	86
8.0	2	10	15	27	48	63	70	84
9.0	0	7	7	18	39	55	68	83

partition TLC [14–17] and cation exchange TLC [13]/HPLC [2–4], as well as HPLC using unmodified silica gel columns [5–7]. The selectivity of the metals in the present system was similar to that of lanthanoids in TLC systems composed of aqueous salt solutions and silica gel [19–21]. That is, the selectivity of lanthanoids on silica gel increased as their ionic radii decreased as a result of the lanthanoid contraction from the cation exchange and the inner-sphere complexation with silanol groups on silica gel. In general, perchlorates, which were the solvent anions in the present system, are among the anions forming the weakest complexes with metal ions. It therefore seems reasonable to conclude that the surface complexation between alkaline earth metals and silanol groups on silica gel plays a very important role in determining the selectivity of the metals at higher salt concentrations in the present systems.

3.3. Effect of salt concentration

The variations in the R_M-values [$\log(R_F^{-1} - 1)$] of the alkaline earth metals are shown as a function of salt concentrations in Fig. 1. On the whole, the R_M-value of each metal at first decreased with an increasing concentration of sodium perchlorate, then reached broad minimums at concentrations of 2–3 mol l^{-1} for Mg, 3 mol l^{-1} for Ca, 3–4 mol l^{-1} for Sr and 5–6 mol l^{-1} for Ba, and finally increased with further increases in the salt concentration. Similar trends in the variation of R_M-values have been observed in the TLC behaviors of rare earths on silica gel in aqueous salt solutions [20,21]. Consequently, it is supposed that the R_M-lowering at lower salt concentrations is attributable mainly to competitive cation exchange between the hydrate solvent cations and the hydrated alkaline earth metal ions for silanol groups on silica gel, and that in higher concentrations of salt solutions, the R_M-values of the metals increase based on the salting-out effect.

As evidenced in Fig. 1, the R_M-lowering at lower salt concentrations appeared, at somewhat remarkable levels, with the heavier alkaline earth metals, while the increases in R_M-values at higher salt concentrations were greater with the lighter alkaline earth metals. As a result of these variations, the order of the R_M-values of Sr^{2+} and Ba^{2+} varied in an opposite manner at higher salt concentrations, i.e., more than 2 mol l^{-1}. The differences in the R_M-values of the four metals expanded markedly as the salt concentrations increased further.

3.4. Separations

The knowledge obtained from the adsorption behavior described above suggests that the differences in the R_F-values of the four alkaline earth metals are large enough for them to be clearly resolved in salt concentrations above 6 mol l^{-1}.
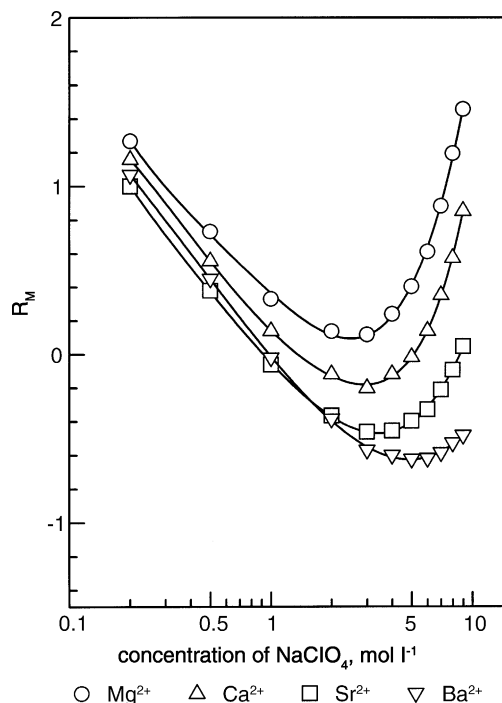

Fig. 1. Variation of R_M-values of alkaline earth metals with salt concentration in aqueous sodium perchlorate solution.
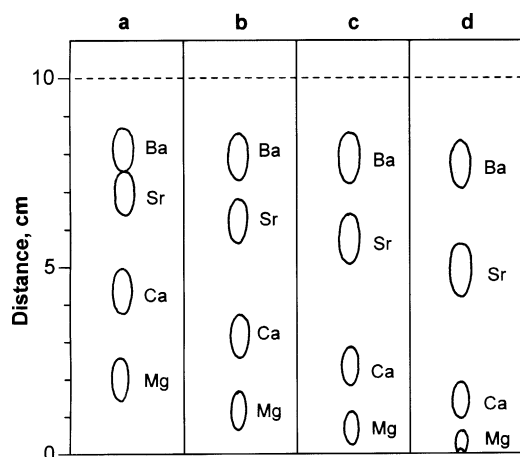
Fig. 2. Separation of quaternary component mixture of alkaline earth metals in aqueous sodium perchlorate solutions of various concentrations. (a) $6.0 \, \text{mol} \, l^{-1}$, (b) $7.0 \, \text{mol} \, l^{-1}$, (c) $8.0 \, \text{mol} \, l^{-1}$, and (d) $9.0 \, \text{mol} \, l^{-1}$, solvent front: (----).

Fig. 2 shows typical thin-layer chromatograms developed in aqueous sodium perchlorate solutions at several concentrations for the separation of quaternary component mixtures of the alkaline earth metals. The 6 and $9 \, \text{mol} \, l^{-1}$ sodium perchlorate solutions provided good resolution, especially for Mg^{2+}–Ca^{2+}–Sr^{2+} and Ca^{2+}–Sr^{2+}–Ba^{2+}, respectively. The best resolution for all metals was obtained in 7–$8 \, \text{mol} \, l^{-1}$ sodium chlorate solutions.

4. Conclusions

In this work, the TLC behavior of the alkaline earth metals on silica gel thin layers impregnated with sodium hydroxide in aqueous sodium perchlorate solutions was investigated as a function of salt concentration. The results showed that in the present TLC systems, the selectivity of the alkaline earth metals for silica gel at higher salt concentrations increased as the ionic radii of the metals decreased, and that differences in R_F-values large enough to separate the metals from each other were obtained at salt concentrations above $6 \, \text{mol} \, l^{-1}$.

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