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Separation of Some Post-Transition Metal Ions by Thin-Layer Chromatography in Molten Salts

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Summary

A method is described for the use of molten salts as an eluent for thin-layer chromatography of inorganic ions. The separation of some post-transition metal ions can be successfully accomplished through the use of alkali metal nitrate eutectic melts. The mechanism of separation appears to be one of cation exchange with the silica gel used as the adsorbent. By appropriate use of the various alkali metal cations of the nitrate eutectics and the using of complexing anions, such as chloride, cyanide, and thiocyanate, most mixtures of these metal ions could be resolved. A possible application of the technique could be in the separation and identification of chemical species that are unstable at room temperature but are stable in molten salts or at higher temperatures.

Thin-layer chromatographic separation of ionic substances has been one of the less thoroughly investigated aspects of this recently developed analytical method (*12*). To date, the solvents and systems of electrolytes separated by thin-layer chromatography have been quite conventional, yet modern inorganic chemistry has been venturing more and more into unconventional experimental techniques.

One recent field of interest has been the use of molten salts as a high-temperature solvent and medium for metathesis. With the expanding use of molten electrolytes, it would seem natural that analytical techniques be devised for use in molten salt solvent systems. Already several types of electroanalytical procedures have been adapted for

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use in molten salts (*10*). The development of chromatographic procedures which rely on molten salts has been quite limited, however. Gruen (*8*) reported the use of molten $LiNO_3$–KNO_3 eutectic to separate several transition metal ions on an alumina column. More recently, Alberti, Grassini, and Trucco (*1,2*) have reported separations of inorganic ions by chromatography on glass fiber paper, using molten $LiNO_3$–KNO_3 eutectic and LiCl–KCl eutectic.

Thin-layer chromatography with conventional solvents represents one of the faster and more sensitive methods of separation. The use of molten salts could extend this procedure to higher temperatures where it might be of help in identifying chemical species that would otherwise not be observed at room temperature for thermodynamic reasons. In a previous note (*6*), the successful separation of a few ions on silica gel using molten $NaNO_3$–KNO_3 eutectic was reported. This paper represents a more detailed investigation of some of the variables that affect the separation of certain post-transition metal ions.

EXPERIMENTAL

The chromatographic chamber consisted of a welded stainless steel tank, 8¾ × 2⅞ × 9 in. (Standard X-Ray Sales Company, Newark, N.J.) immersed 6–7 in. in a molten $NaNO_3$–KNO_3 eutectic (50:50 by weight). The salt bath which served as the constant temperature regulator was contained in a large porcelainized metal diaper pail wrapped with several layers of asbestos sheet for insulation. An external Chromalux Type-A ring heater with a three-heat switch provided most of the heat for the bath. Close temperature control of the bath was obtained by using a small glass-shielded, Nichrome spiral regulated by a Barber-Coleman Amplitrol pyrometer controller. A mechanical stainless steel stirrer agitated the liquid. The bath temperature could be regulated to ±1°. Unfortunately, because of the large exposed surface at the top of the chamber, a temperature gradient of about 30° over 10 cm usually existed within the chromatographic chamber. A glass lid was placed over the chamber. Although the $NaNO_3$–KNO_3 eutectic has a melting point of 226°C, the lowest safe operating limit was found to be about 250° to 260°C, due to the thermal gradient. The upper limit was defined by the decomposition of the molten nitrate, in air, at 400°C. The temperatures reported are for the solvent in the bottom of the chamber.

Pyrex plates, 200 × 200 mm were coated with a slurry of silica gel "N-HR" (Brinkmann Instruments, Westbury, N.Y.) using a Research

Specialties spreading apparatus, to a thickness of 250 μ. The silica gel "N-HR" is free of detectable amounts of foreign cations and contains no binder. After air-drying the plates for 1 hr, they were activated by heating at 115° for at least 1 hr, and stored until used over $CaCl_2$. Prolonged heating of the plates was found to have an adverse effect on the subsequent mobility and reproducibility of results.

The salts used in the preparation of the solvent and those used for standard solutions of the ions were reagent grade, and were dried overnight at 155°, and stored over $CaCl_2$ until used.

The metal ions were applied in 1- or 2-μl samples of 0.1 M aqueous solutions of the metal nitrates. Because of the thermal gradient in the chamber, the solvent travel was limited to 60 to 65 mm.

The metal ions, except zinc, were detected by spraying the hot chromatograms with an ethanolic solution of ammonium sulfide. Zinc was detected by spraying the layers with a 1% solution of 8-quinolinol in ethanol, and viewing the result under ultraviolet light. Only in the presence of high concentrations of cyanide did the background fluorescence interfere with the detection of zinc. The thin layers, after cooling, are exceptionally durable but have a tendency to be hydroscopic on standing in air.

The concentrations of complexing anions reported are in mole per cent of the total anion concentration. These were prepared by carefully weighing the dried analytical grade reagents, and the composition was checked after a series of runs by standard analytical methods. R_f values are reproducible to ±0.04.

RESULTS

A. Nitrate Eutectic Melts

Because of the thermal gradient observed within the chromatographic chamber, one of the first variables to be considered was the effect of temperature on the R_f values. In the temperature range of 270° to 350°, there is a negligible change in the R_f values. Thallium (I), cadmium(II), and lead(II) show a slight decrease with an increase in temperature, but this is roughly within the reproducibility of the R_f values.

Two different nitrate eutectics were used. The sodium nitrate–potassium nitrate eutectic, as used in the previous communication, shows the least discrimination (see Table 1). Silver and thallium(I) both move with the solvent front; lead(II) and cadmium(II) show

TABLE 1

Metal Ion R_f Values in Molten Salt Solvents at 300°C

Metal ion	$LiNO_3$–KNO_3 eutectic[a]	$NaNO_3$–KNO_3 eutectic[a]	$NaNO_3$–KNO_3 eutectic			
			5% Cl^-	3.5% CN^-	3.5% CN^-	5% OH^-
Cu^{2+}	0.18t	0.00	0.13	0.15[b]	0.20	0.00
Zn^{2+}	0.21t	0.00	0.23	0.00	0.00	0.00
Cd^{2+}	0.88	0.37t	0.92	0.27	0.03	0.27
Pb^{2+}	0.96	0.42t	0.67	0.29	0.09	0.21
Hg_2^{2+}	0.05t	0.00	—	0.46	0.64[b]	0.00
Ag^+	1.00	1.00	1.00	1.00	1.00	1.00
Tl^+	1.00	1.00	0.94	1.00	1.00	0.95

[a] t—tail.

[b] Moves with secondary solvent front.

intermediate R_f values, but have long tails; whereas mercury(I), copper(II), and zinc ions do not move at all. Because this eutectic is less susceptible toward hydroscopic behavior than is the lithium nitrate–potassium nitrate eutectic, complexing anions were added to the former to improve the separations.

The lithium nitrate–potassium nitrate (44:56 by weight) gave much better discrimination. Although silver and thallium(I) ions still moved with the solvent front, lead and cadmium ions had larger R_f values, and their tailing had been very greatly reduced. Likewise, mercury(I), copper(II), and zinc ions showed small R_f values with some tailing. With the lithium nitrate–potassium nitrate eutectic, mixtures of silver and thallium(I) ions and of zinc and copper ions could not be separated.

B. Presence of Complexing Anions

The anions chosen, chloride, cyanide, hydroxide, and thiocyanate, are known to form either insoluble products or anionic complexes in aqueous solution with a majority of the cations studied in this work (*5*). In the case of chloride ion, chloro complexes have been identified for most of the cations in chloride melts, whereas in nitrate melts, chloro complexes have been observed for lead and cadmium (*3*). For the other anions, a lack of information on complexation in molten salts limits a discussion of the results.

An unexpected result was that cyanide and thiocyanate ions were fractionated on the silica gel layers. A secondary front that varied with anion concentration could be visually observed. That this was due to these anions was shown convincingly in the case of thiocyanate by spraying the plate with a dilute solution of iron(III) chloride. Since copper(II) ion moved with the secondary cyanide front, it was very important that the plates be immersed to exactly the same depth for each of these molten salt solvents in order to obtain reproducible values.

The addition of chloride ion to the sodium nitrate–potassium nitrate eutectic resulted in an increase in the R_f values of all ions except thallium, where a slight decrease was noted at 300° and a large decrease at 350°. Silver which had moved with the solvent front in the pure nitrate melt continued to do so in the presence of chloride ion. Mercury(I) could not be detected when chloride ion was present. Apparently, mercury(I) chloride forms and this vaporizes from the plate. In a separate experiment, a small amount of mercury(I) chloride was placed in a test tube in the melt while a plate was being run. During the time required, most of the mercury chloride had vaporized to cooler portions of the test tube, confirming the suspicions. Separations of mixtures of these ions with the presence of chloride was much better. Although lead ion still showed some tailing, the presence of copper and zinc ions in mixtures could plainly be detected.

The presence of cyanide was found to be most effective in increasing the R_f values of copper(II) and mercury(I). As mentioned previously, copper(II) moved with the secondary solvent front. Mercury(I) ion which is known to form a very stable cyano complex in aqueous solvents, showed a sizeable increase in its R_f value when cyanide ion was added to the melt.

Thiocyanate also produced an increase in the R_f values of copper (II) and mercury(I) ions, but here cadmium and lead ions showed a decrease in their R_f values to the point that they could not be effectively separated. Particularly with thiocyanate, knowledge of the stoichiometry and stability of thiocyanate complexes in molten salts will be essential before the behavior here is fully understood.

The presence of added hydroxide had virtually no effect on the R_f values.

DISCUSSION

At room temperature, the mechanism of adsorption of the ionic species on silica gel appears to be via ion exchange (*4,7,9,13–15*) where the silica gel acts as a weak cation exchanger. In the usual commerical preparation of silica gel, calcium and sodium silicate solutions are slowly acidified to precipitate the silica gel, with the consequence that the gel contains large amounts of these ions. The postulated mechanism is exchange of these ions bonded to silanol sites ($\equiv$Si—O—M) for ions in solution.

Silica gel "N-HR" is a high-purity silica gel that has been commercially freed of these ions by washing the silica gel with concentrated acid so that the cations in the gel are replaced by hydrogen ions; this form of the silica gel might be thought of as a weak cation exchanger in the hydrogen form. In one experiment to check this hypothesis, 5 g of silica gel "N-HR" in 100 ml of water agitated overnight showed a pH of 7.0, whereas a similar amount of the silica gel when agitated overnight with 100 ml of 1 *M* sodium nitrate showed a pH of 5.7, indicating that some ion exchange had taken place.

Although the ion exchange mechanism appears to be valid at room temperature, the higher temperatures used in these molten salt separations could greatly reduce the number of silanol sites by further dehydration. Indeed, even prolonged activation of the thin layers greatly increases the R_f values for many of the ionic systems. Another factor that must be considered is the solvent or mobile phase. Conventional solvents involve a limited concentration of electrolytes solvated by polar solvent molecules. Cations are present as solvated ions, solvated ion pairs, or solvated molecular species such as $HgCl_2$. On the other hand, in molten salts, it is thought that cations are solvated by occupying cation sites within the molten salt lattice, a mechanism quite different from that encountered in most other solvent systems. Because of these different circumstances, comparison of R_f values obtained with molten salts with those obtained in conventional solvents will not be valid.

That an ion exchange mechanism is still valid for the molten salt solvent system may be seen by a comparison of charge/size ratios, as calculated from a table of Goldschmidt ionic radii, with the R_f values in both the sodium nitrate-potassium nitrate and lithium nitrate-potassium nitrate eutectics (Table 2).

Ignoring any solvation problems in the melt because a foreign cation does not fit properly in the salt lattice, one would expect an ion exchange mechanism such that the R_f values increase as the charge-to-size ratio decreases. Except for mercury(I) ion, this was so observed. Mercury(I) is a diatomic ion and could have two possible points of

TABLE 2

Comparison of Ionic Charge/Size with Ion Mobility

Parameters	Cu^{2+}	Zn^{2+}	Cd^{2+}	Pb^{2+}	Hgœ	Ag^+	Tl^+
Charge/size	2.90	2.86	2.17	1.17	0.99	0.88	0.67
R_f at 270°C							
$NaNO_3$–KNO_3	0.00	0.00	0.37t[a]	0.42t[a]	0.00	1.00	1.00
$LiNO_3$–KNO_3	0.18t[a]	0.21t[a]	0.88	0.96	0.05t[a]	1.00	1.00

[a] t — tail.

attachment to the silica gel. Since the charge-to-size ratio is a crude indication of only the enthalpy, the additional entropy factor of chelation of mercury(I) could account for its low R_f value.

If one considers that the solvent cations also may be retained by the silica gel, additional evidence in favor of the ion exchange mechanism is apparent. The smaller of the cations in each of the nitrate eutectics, sodium and lithium, have charge/size ratios of 1.02 and 1.49, respectively. Again, excepting the special case of mercury, those ions with a smaller charge/size ratio than the smallest ion in the solvent move with the solvent front. Although sodium and lithium ions have charge/size ratios between lead(II) and mercury(I) ions, lithium, because of its smaller size is more effective at displacing other ions from the silica gel. Unfortunately, no analyses of the thin layer were carried out after a run to determine the lithium concentration on the silica gel.

The cation exchange mechanism also accounts for the observed effects when complexing anions are present. Where anionic complexes are formed, the charge-to-size ratio will decrease and the R_f value should increase. This is particularly noticeable when chloride ion is added. Those ions that are well known to form chloro complexes in molten nitrate melts, cadmium(II) and lead(II), both show an increase in R_f's. The observed decrease for thallium(I) ion may be due to the formation of an insoluble (in molten nitrates) chloride. Cyanide and thiocyanate complexes have not yet been studied in molten salts for any of these metal ions; however, the travel of copper(II) ion with the secondary cyanide front, and mercury(I) with the secondary thiocyanate front correlates with the known ability of those ions to form strong complexes with the corresponding anion in aqueous systems (*11*). Lead and cadmium ions which show lower R_f values again may be forming insoluble products. Hydroxide ion does not appear to complex greatly or otherwise affect these metal ions in the nitrate melts by reason of the negligible changes noted in the R_f values. It is possible that any metallates that do form have the same potential toward the silica gel as do the nitrate-solvated cations.

CONCLUSION

By an appropriate choice of molten salt mixtures and complexing anions, it was possible to separate most of the post-transition metal ions from one another by thin-layer chromatography using molten salts as a solvent. Applications now being studied include the separation and identification of ionic species not otherwise stable at room temperature and the nature and identity of metal ion complexes in molten salts.

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