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USE OF UNCHARGED NEUTRAL LIGANDS IN THE ISOTACHOPHORETIC ANALYSIS OF ALKALI AND ALKALINE EARTH METALS

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The use of uncharged complexing agent in the isotachophoretic separation of ions is described. 18-Crown-6 interacted with ammonium and some alkali and alkaline earth metal ions, improving the separation among these ions. α-Cyclodextrin assisted the separation of anions through a host-guest interaction.

Isotachophoresis is gaining importance in treating the ionic species in practical analysis as well as in physico-chemical research works.[1,2] As to the application in analysis, the research efforts have mostly been devoted to alter the effective mobility of the specific analyte ions by various chemical or physical means, since the electrophoretic separation is based on the difference in the mobility of the individual ions.

Difficulties encountered in the electrophoretic separation of the mixture containing the three heavier alkali metals and ammonium ion have been known. A solution containing sodium and magnesium or containing the mixture of alkaline earth metals other than magnesium is difficult to handle, because the mobility of the analyte ions is in the similar order of magnitude. In this communication, we show that the problem is solved by using a crown ether, an uncharged complexing agent specific to these metal ions. Similarly, the separation of anionic species of similar mobility is assisted by the presence of α-cyclodextrin, which affected the mobility of some lipophilic anions through a host-guest interaction.

The isotachophoresis of metal ions under our conditions is illustrated in Fig. 1. An aqueous solution containing 5 mM (1 M = 1 mol dm^{-3}) p-toluenesulfonic acid, 0.01 % Triton X-100, and a specified amount of a crown ether was used as a leading solution. The terminating solution was a 5 mM aqueous tetrabutylammonium bromide. A Shimazu IP-2A isotachophoretic analyzer fitted with a pre-analyzing column (1 mm i.d. x 40 mm), an analyzing column (0.5 mm i.d. x 150 mm), and a potential gradient detector was operated at 40 μA and at 25°C.

The equilibrium in the sample zone and the isotachophoretic parameters are expressed in Eqs.

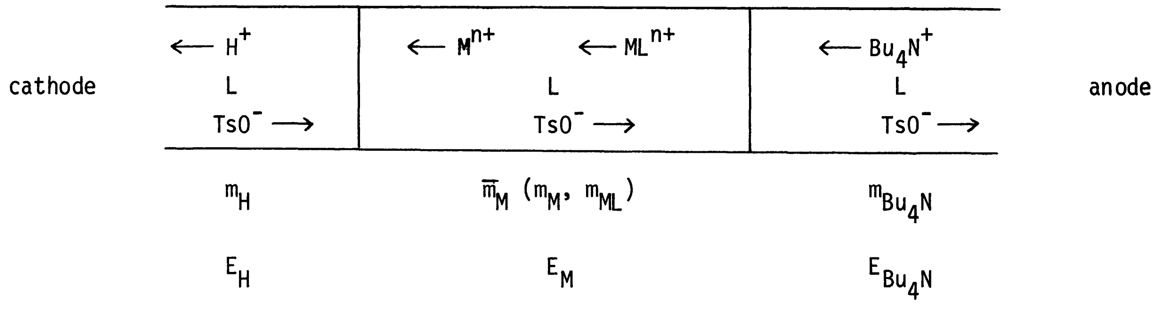

Fig. 1. Isotachophoresis of metal ion in the presence of neutral ligand

1 - 3, where m and E stand for the mobility of an ion and the electric potential gradient under which the ion migrates, respectively.

$$\bar{m}_M = (m_M + m_{ML}\cdot K_{ML}[L])/(1 + K_{ML}[L]) \qquad (1)$$

$$K_{ML} = [ML^{n+}]/[M^{n+}][L] \qquad (2)$$

$$PU = (E_M/E_H - 1)/(E_{Bu_4N}/E_H - 1) \qquad (3)$$

$$= (m_H/\bar{m}_M - 1)/(m_H/m_{Bu_4N} - 1) \qquad (4)$$

A sample solution (5 µl) containing 1 mM metal chlorides and tetraethylammonium (TEA, an internal standard) perchlorate was injected for analysis under various ligand concentrations. The results were analyzed in terms of PU value and are summarized in Fig. 2 for 18-crown-6.

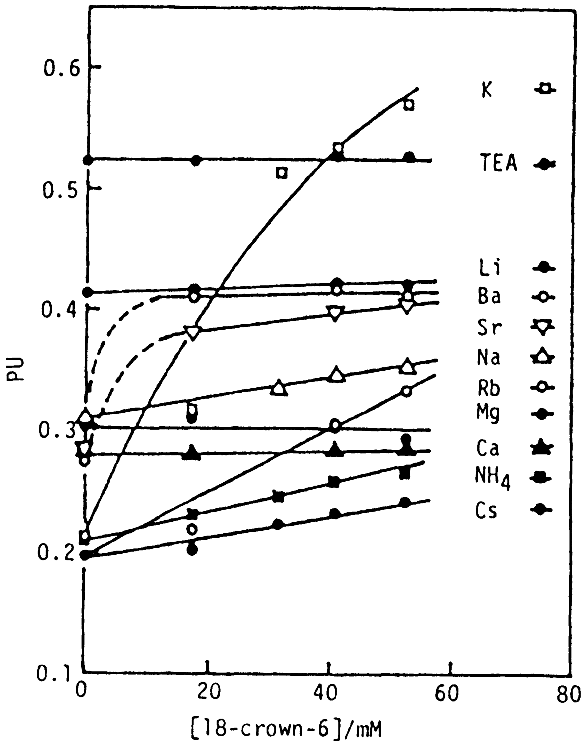

Fig. 2. Variation of PU values as a function of 18-crown-6 concentration

It is seen from Fig. 2 that (i) lithium, magnesium, calcium, and TEA do not interact with 18-crown-6 (the PU value is not affected), (ii) the PU velue for alkali metals other than lithium depends on the crown ether concentration, the magnitude of the dependence, K > Rb > Na, Cs, NH_4, being in line with the stability of the complexes. (iii) under the crown ether concentration studied, strontium and barium are present mostly in the complexed form, and the variation of PU value is slight. (iv) the addition of crown ether generally decreases the mobility of metal ions, *i. e.*, the complexes have a lower mobility or a larger molecular size than the free metal ions. Taking advantage of these observations, a mixture containing potassium, sodium, ammonium, magnesium, and calcium was successfully analyzed using 20 - 40 mM 18-crown-6. 12-Crown-4 and 15-crown-5 were practically without effect on the electrophoresis, reflecting their low tendency to associate with metals in aqueous solution.

The molecular size of anions is usually larger than that of cations, and a larger "host" molecule is needed for their complexation. Cyclodextrins are suitable for this purpose. Since the solubility of β-cyclodextrin in water is limited, α-cyclodextrin was studied in detail. The use of 2 % α-cyclodextrin allowed the otherwise impossible separation of an iodide ion in the chloride-bromide mixtures. In some practical analyses in our laboratory, a perchlorate ion in the presence of ferricyanide and ferrocyanide ions was easily determined using 1 % α-cyclodextrin. Without α-cyclodextrin, the ferricyanide caused a serious interference.

A neutral ligand complexation method is simple in principle, easy to carry out, and applicable to both cations and anions. It should be highly useful in treating ionic species in research works as well as in practical analyses.

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References

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