A IONOPHORETIC STUDY OF THE ASSOCIATION OF Pm^{3+} AND Am^{3+} IONS IN CONCENTRATED SOLUTIONS OF CALCIUM PERCHLORATE AND NITRATE

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Paper ionophoresis has been studied of promethium and americium ions in solutions of calcium perchlorate and/or calcium nitrate, the molarity of ClO_4^- or NO_3^- being 1 to 8. The results show that the predominant form of either ion in nitrate media containing more than 1 mol of NO_3^- per liter is the cation $[Me(NO_3)_2]^+$, whose mobility is lower than that of the free hydrated ion.

Cations of trivalent lanthanides and actinides in aqueous media have little tendency to form complexes or ion pairs with anions of strong mineral acids, Actinides, with 5 f electrons, undergo complexing or ion pairing more readily than lanthanides with their 4 f electrons[1]. At low concentrations of the ligands (below 1M) there are formed mainly ion pairs, with increasing concentration of a ligand they are transformed into inner-sphere complexes[2,3]. The two types of complex can coexist. Their stability constants determined by methods detecting the formation of ion pairs are often greater (as much as 100 times with $[AmNO_3]^{2+}$) than constants determined in another way, *e.g.* by spectrophotometry, indicating the formation of inner-sphere complexes[1].

The sum of concentrations of inner-sphere complexes and ion pairs can be determined by the methods of extraction, ion exchange, conductance and ionophoresis. The extraction method determines only the difference between the numbers of ligands bound in the extracted complex and in the complex prevailing in the aqueous phase. To determine the chemical composition of the complex in the organic phase it is necessary to determine the average composition of complexes of the extracted metal in the aqueous phase. This can be achieved by the use of a method detecting the formation of either type of complex, as does the method of extraction. The method of ionophoresis, developed previously to study the complexes in strongly concentrated aqueous electrolytes[4-7], has proved suitable for this purpose.

EXPERIMENTAL

Chemicals

The reagents employed, chemically pure, were recrystallized before use. The preparation of ^{147}Pm was supplied by the firm V. O. Izotop (U.S.S.R.) and the preparation of ^{241}Am by Amersham Centre A.E.R.E. (England).

Procedure

A high-voltage (1 000 V) electrophoresis apparatus, constructed in the Institute for Research, Production and Use of Radioisotopes, was employed; it had hollow plates cooled by circulating CCl_4 (0 to 4°C). A strip 456 mm × 114 mm of Whatman chromatographic paper No 1 was soaked with an electrolyte. Its excess was blotted out and a solution of the ion to be investigated was applied onto the start. All solutions of the supporting electrolyte were acidified with the corresponding acid (0·01M). The strip was placed between metal plates covered with polyethylene sheets. The time of electrophoresis was 20 min. The measured shifts of the spots were corrected according to Pučar[8]. The shift of the zero point was determined with hydrogen peroxide, in the media of $Ca(ClO_4)_2$ and $Ca(NO_3)_2$ it was about 5 mm toward the anode. The values of R_F (Figs 1 and 2) were determined as previously described[5]. The shifts of the spots (u') are given in mm/kV for a common time of 20 min and a strip length of 456 mm. Every value is the average of two independent measurements; the mean deviation from the average was 7% in the perchlorate solutions and 12% in the nitrate ones.

^{147}Pm and ^{241}Am were detected by autoradiography (RTC film ORWO). Hydrogen peroxide was detected with a 10% solution of KI.

RESULTS AND DISCUSSION

The corrected shifts of the spots u' are plotted in a semilogarithmic scale in Fig. 3. In the perchlorate media the values of log u' for either ion fit a straight line throughout the concentration range of the supporting electrolyte (1 to 8M-ClO_4^-). This demonstrates that within this concentration range the two ions exist as one chemical species with unchanging u^0-mobilities. In view of the lower ability of ClO_4^- ions to enter complexes it can be assumed that this species is either a free hydrated ion or a positively charged complex ion of the same mobility. Such an ion may be[2,9] the ion pair $[MeClO_4]^{2+}$, which cannot be distinguished electrophoretically from the ion Me^{3+}.

With the nitrate solutions (1 to 8M-NO_3^-) the ionophoretic plots are also linear and their slopes are approximately equal to those for the perchlorate medium. The direction of migration was the same. This means that the prevailing species were positively charged too, but the mobility was about 30% lower than the mobility of forms existing in the perchlorate solutions. It could not be a free hydrated ion or a complex $[MeNO_3]^{2+}$, since the mobilities of these would be close to the mobilities of the two ions in the perchlorate media. Nor could it be a trinitrato complex, since its mobility would be zero, and complexes still higher would migrate to the anode.

As has been shown[5] with some trivalent ions in concentrated solutions of chlorides, a cation with a mobility by 30% lower than that of a free hydrated ion or a cation $[MX]^{2+}$ may be the univalent cation $[MeX_2]^+$. Since the migration of ions in the paper is affected by the size of the migrating particle a change in its shift may be due to a change in its size.

The radius of the hydration sheath firmly bound to a trivalent ion[10] amounts approximately to 5·5 Å. If an inner-sphere complex $[MeNO_3]^{2+}$ is formed the radius of the hydration sheath of this divalent ion is reduced to about 4·5 Å. The crystallo-
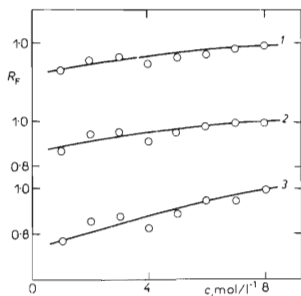

FIG. 1

R_F Values of the Investigated Ions in Relation to Concentration (Molarity) of ClO_4^-
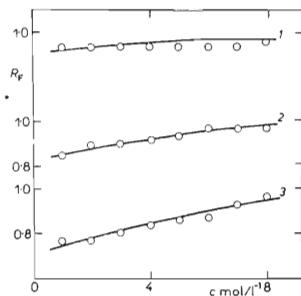1 Pm^{3+}, 2 Am^{3+}, 3 H$_2$O$_2$.

FIG. 2

R_F Values of the Investigated Ions in Relation to Concentration of NO_3^-
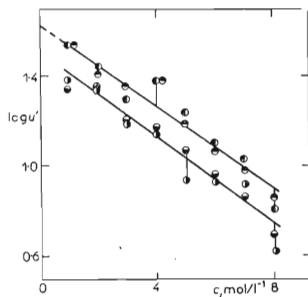1 Pm^{3+}, 2 Am^{3+}, 3 H$_2$O$_2$.

FIG. 3

Logarithms of the Corrected Shifts, u', of the Investigated Ions in Relation to Concentration of ClO_4^- or NO_3^-
◐ Pm^{3+} in media of Ca(ClO$_4$)$_2$, ◕ Am^{3+} in media of Ca(ClO$_4$)$_2$, ◑ Pm^{3+} in media of Ca(NO$_3$)$_2$, ◒ Am^{3+} in media of Ca(NO$_3$)$_2$.

graphic "hard-body" radius of the two ions being approximately 1·2 Å, there should remain a free space of some 3·3 Å up to the outer boundary of the hydration sheath. This value may not be sufficient for the formation of a spherically symmetrical hydration complex if the crystallographic radius of the nitrate ion[11] is 1·9 Å. Thus the hydrated particle is probably a moderately deformed one, with the ion Me^{3+} and the ligand NO_3^- excentrically arranged in the interior of the hydration sphere of this divalent complex. The difference in size of the migrating particle, however, may still compensate for the difference in the net charge, so that the ionophoretic mobility of such a particle on paper will practically be the same (within the experimental error) as that of a free hydrated trivalent ion.

If two nitrate ligands enter the co-ordination sphere of a trivalent ion there is formed $[Me(NO_3)_2]^+$ and the reach of the hydration forces will decrease[10] to 3·5 Å, which is not sufficient for the nitrate ligands to be embedded in the interior of the hydration sphere of the central ion. There will be formed a larger and markedly non-spherical ion and its size will not allow of compensation for the drop in charge from +2 to +1 by a further reduction of the hydration sheath. Consequently, its mobility will be markedly lower than that of a free hydrated ion.

The foregoing considerations lead to the conclusion that an ion of reduced mobility may be a univalent inner-sphere dinitrato complex $[Me(NO_3)_2]^+$. Abrahamer and Marcus[12] inferred from the absorption spectra of lanthanides the existence of stable dinitrato complexes in nitrate solution, which is in agreement with our results.

The stability constants of the dinitrato complexes could not be determined from the measured ionophoretic data, since the region of transition from lower complexes or associated forms to higher ones was not detected. It can only be stated that their values exceed 1, because even in the medium of $1M\text{-}NO_3^-$ the shifts correspond to a complete conversion of Pm^{3+} and Am^{3+} cations into dinitrato complexes.

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