

# DENSIMETRIC STUDY OF PRASEODYMIUM AQUO AND NITRATO COMPLEX FORMATION IN AQUEOUS SOLUTIONS OF ELECTROLYTES

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Received July 30th, 1976

The method of apparent molar volumes was used for a study of the formation of nitrate complexes in systems  $\text{Pr}(\text{NO}_3)_3\text{---NaNO}_3\text{---H}_2\text{O}$  (with  $c_{\text{Pr}(\text{NO}_3)_3} = 0.02$  to  $0.05 \text{ mol l}^{-1}$ ,  $c_{\text{NaNO}_3} = 0.1$  to  $8 \text{ mol l}^{-1}$ ) and in solutions of  $\text{Pr}(\text{NO}_3)_3$ , concentration  $0.02$  to  $5.23 \text{ mol l}^{-1}$ . The aquo- and mononitratopraseodymium(III) ions possess the overall coordination number 6. Praseodymium nitrate in the medium of sodium perchlorate as well as praseodymium perchlorate itself dissociates to the aquo ion  $[\text{Pr}(\text{H}_2\text{O})_6]^{3+}$  and the  $\text{NO}_3^-$  or  $\text{ClO}_4^-$  ions. In solutions with high concentrations of sodium nitrate, the coordination number alters from 6 to 4 as the second and the third  $\text{NO}_3^-$  ligands enter the coordination sphere of the central ion.

Formation of nitrate complexes of lanthanides in highly concentrated nitrate solutions is of interest, as the separation of lanthanides, whether on ion exchangers or by extraction, is performed from nitrate solutions, frequently in the presence of a salting-out agent ( $\text{NaNO}_3$ ,  $\text{LiNO}_3$  or  $\text{Mg}(\text{NO}_3)_2$ , anion concentration up to  $8 \text{ mol l}^{-1}$ ) in conditions where the lanthanide concentration is by three orders of magnitude lower than the nitrate concentration. Two phenomena are to be investigated in this respect: firstly, the formation of lanthanide complex compounds in solutions containing a high excess of the nitrate ions, and secondly, the difference in the complex ion formation, as compared with the previous case, in solutions containing only the lanthanide nitrate, with no excess of the complexing ligand. The second problem could be solved based on the values of densities and the derived apparent molar volumes according to Spedding and coworkers<sup>1,2</sup>, who report the densities of lanthanide nitrates and perchlorates in the concentration range of  $0.02$  to  $5.23 \text{ mol l}^{-1}$ . The difference in the nitrate complex formation is treated for one of them —  $\text{Pr}(\text{NO}_3)_3$ .

## EXPERIMENTAL

### Chemicals

All the substances used were commercial chemicals, reagent grade purity. The solutions of the base electrolytes were prepared in freshly boiled distilled water, in order to avoid the possible

errors in the density measurements associated with the evolution of the dissolved gases during the temperation.

### Apparatus and Analytical Determinations

The densimetric determination of the molar volumes of praseodymium nitrate was carried out at  $25 \pm 0.02^\circ\text{C}$  by employing the float technique described previously<sup>3,4</sup>. The concentrations of sodium nitrate and sodium perchlorate were determined from their densities<sup>5</sup>. The praseodymium concentration was determined by titration with Complexon III (disodium salt of (ethylene-dinitrilo)tetraacetic acid) using xylenol orange as the indicator.

### Data Evaluation

The apparent molar volumes were calculated from the experimental data as described previously<sup>3,6</sup>. The values of the apparent molar volumes obtained from the data given by Spedding and coworkers<sup>1,2</sup> were evaluated from the densities according to the relation<sup>7</sup>

$$V_i = [1 - (\Delta d/\Delta p)(100 - p)/d](M/d) \quad (1)$$

where  $M$  is the molecular weight of the electrolyte,  $p$  is its concentration in the solution (%),  $d$  is the solution density, and  $\Delta d$  and  $\Delta p$  are the differences between the closest higher and lower values of  $d$  and  $p$ , respectively, for the electrolyte under study. The concentrations of the "anhydrous states" of the electrolytes examined were applied as given in the paper<sup>7</sup>. For the "anhydrous state" of  $\text{Pr}(\text{NO}_3)_3$  and  $\text{Pr}(\text{ClO}_4)_3$  the  $c^0$  concentrations, expressed through the relation<sup>8</sup>  $c^0 = 1000/V^0$ , are 9.20 and 10.40  $\text{mol l}^{-1}$ , respectively.

The experimental or calculated dependences of molar volumes on the square root of concentration in molarity units were compared with the calculated theoretical curves of the volume balances, evaluated for the reactions considered.

TABLE I

Apparent Molar Volumes of the Complexes of the  $\text{Pr}^{3+}$  Ion (Evaluated for  $\text{Pr}(\text{NO}_3)_3$  in solutions of nitrates)

Complex, ion	$V^0$ $\text{ml mol}^{-1}$	$V^\infty$ $\text{ml mol}^{-1}$	Complex, ion	$V^0$ $\text{ml mol}^{-1}$	$V^\infty$ $\text{ml mol}^{-1}$
$[\text{Pr}(\text{H}_2\text{O})_9]^{3+}$	66.3	34.5	$[\text{Pr}(\text{H}_2\text{O})_2(\text{NO}_3)_2]^+$	100.0	92.0
$[\text{Pr}(\text{H}_2\text{O})_8(\text{NO}_3)]^{2+}$	67.7	51.0	$[\text{Pr}(\text{H}_2\text{O})(\text{NO}_3)_3]$	101.9	101.9
$[\text{Pr}(\text{H}_2\text{O})_7(\text{NO}_3)_2]^+$	68.8	61.0	$[\text{Pr}(\text{NO}_3)_4]^-$	103.7	107.0
$[\text{Pr}(\text{H}_2\text{O})_6(\text{NO}_3)_3]$	69.2	69.2	$[\text{Pr}(\text{H}_2\text{O})_8(\text{ClO})]^{2+}$	57.7	83.0
$[\text{Pr}(\text{H}_2\text{O})_6]^{3+}$	84.0	48.0	$[\text{Pr}(\text{H}_2\text{O})_7(\text{ClO}_4)_2]^+$	49.5	45.0
$[\text{Pr}(\text{H}_2\text{O})_5(\text{NO}_3)]^{2+}$	86.4	73.0	$[\text{Pr}(\text{H}_2\text{O})_6(\text{ClO}_4)_3]$	41.3	47.4
$[\text{Pr}(\text{H}_2\text{O})_4(\text{NO}_3)_2]^+$	87.5	80.0	$[\text{Pr}(\text{H}_2\text{O})_5(\text{ClO}_4)]^{2+}$	77.3	61.0
$[\text{Pr}(\text{H}_2\text{O})_3(\text{NO}_3)_3]$	89.3	89.3	$[\text{Pr}(\text{H}_2\text{O})_4(\text{ClO}_4)_2]^+$	69.6	66.5
$[\text{Pr}(\text{H}_2\text{O})_4]^{3+}$	95.8	59.5	$[\text{Pr}(\text{H}_2\text{O})_3(\text{ClO}_4)_3]$	60.8	67.4
$[\text{Pr}(\text{H}_2\text{O})_3(\text{NO}_3)]^{2+}$	98.4	78.5			

## RESULTS AND DISCUSSION

The method of apparent volumes served for the investigation of the formation of nitrate complexes of the  $\text{Pr}^{3+}$  ion in the system  $\text{Pr}(\text{NO}_3)_3\text{—NaNO}_3\text{—H}_2\text{O}$  at pH 1 (adjusted with  $\text{HNO}_3$ ) for concentrations of  $\text{Pr}(\text{NO}_3)_3$  0.02 to 0.05 mol  $\text{l}^{-1}$  and those of  $\text{NaNO}_3$  0.1 to 8 mol  $\text{l}^{-1}$  (Fig. 1, Table I). In solutions with very low concentrations of sodium nitrate and high activities of water, praseodymium nitrate dissociates completely to hexaaquopraseodymium(III) ion and  $\text{NO}_3^-$  ions. The penta-aquomononitratopraseodymium(III) ion is formed gradually on increasing the  $\text{NaNO}_3$  concentration, the entering of the nitrate ion being not accompanied by a change of the coordination number.

When high concentrations ( $\geq 4$  mol  $\text{l}^{-1}$ ) of the ligand-forming salt  $\text{NaNO}_3$  are applied, the dinitratopraseodymium(III) ion forms in the solutions. The entering of the second  $\text{NO}_3^-$  ligand is associated with a decrease of the overall coordination number from 6 to 4, which manifests itself in the molar volume values by a considerable increase of the  $V_i$  values by more than 25 ml  $\text{mol}^{-1}$  (Fig. 1, Tab. I). For the concentration of the base electrolyte higher than 6 mol  $\text{l}^{-1}$ , formation of the complex  $[\text{Pr}(\text{H}_2\text{O})(\text{NO}_3)_3]$  can be observed, which indicates that the difference additions of praseodymium nitrate do not undergo dissociation in the solutions.

Comparing the formation of complex ions in aqueous solutions of praseodymium nitrate (Fig. 1, curve 2), we find for the association up to the concentration of  $\text{Pr}(\text{NO}_3)_3$  of 3 mol  $\text{l}^{-1}$  the same results as for 0.05M- $\text{Pr}(\text{NO}_3)_3$  in 0.1 to 3.0M- $\text{NaNO}_3$ . With increasing concentration of praseodymium nitrate the  $[\text{Pr}(\text{H}_2\text{O})_6]^{3+}$  ion converts to the cation  $[\text{Pr}(\text{H}_2\text{O})_5\text{NO}_3]^{2+}$ , which is in an equilibrium with the complex aquoion. In praseodymium nitrate solutions, however, the dinitratopraseodymium(III) ion is not formed and the coordination number of the complex form does not alter either. The equilibrium is here merely shifted towards the  $[\text{Pr}(\text{H}_2\text{O})_5\text{NO}_3]^{2+}$  ion formation, and in solutions of praseodymium nitrate of the concentration of 3.2

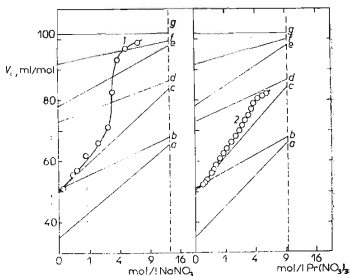


FIG. 1

Apparent Molar Volumes of  $\text{Pr}(\text{NO}_3)_3$  in Aqueous Solutions

1 in  $\text{NaNO}_3$ ; 2 in  $\text{H}_2\text{O}$ . Theoretical curves for the formation of a  $[\text{Pr}(\text{H}_2\text{O})_9]^{3+}$ ; b  $[\text{Pr}(\text{H}_2\text{O})_8\text{NO}_3]^{2+}$ ; c  $[\text{Pr}(\text{H}_2\text{O})_6]^{3+}$ ; d  $[\text{Pr}(\text{H}_2\text{O})_5\text{NO}_3]^{2+}$ ; e  $[\text{Pr}(\text{H}_2\text{O})_3\text{NO}_3]^{2+}$ ; f  $[\text{Pr}(\text{H}_2\text{O})_2(\text{NO}_3)_2]^+$ ; g  $[\text{Pr}(\text{H}_2\text{O})(\text{NO}_3)_2]$ .

$\text{mol l}^{-1}$  the ions  $[\text{Pr}(\text{H}_2\text{O})_5\text{NO}_3]^{2+}$  and  $[\text{Pr}(\text{H}_2\text{O})_6]^{3+}$  are present in an equilibrium in the ratio 1 : 1.

It was of interest to find out, how praseodymium nitrate would behave in the medium of a noncomplexing electrolyte — whether dissociation to the aquo ion and the corresponding salt anion would take place, as is the case with all the bivalent ions of the 3d group<sup>3,9</sup> and with some other ions, or whether only a partial dissociation would occur in solutions with low activity of water. We investigated this problem in the system  $\text{Pr}(\text{NO}_3)_3\text{--NaClO}_4\text{--H}_2\text{O}$  (Fig. 2, Tab. II), and observed complete dissociation of praseodymium nitrate to the  $\text{Pr}(\text{H}_2\text{O})_6^{3+}$  cation and  $\text{NO}_3^-$  anions in the whole concentration span of  $0.1\text{--}9\text{ mol l}^{-1}$  of  $\text{NaClO}_4$ . The fact that complex ions with the  $\text{ClO}_4^-$  ligand are not formed in perchlorate solutions is also confirmed by the results obtained from the densities of lanthanide perchlorates reported in<sup>2</sup>

TABLE II

Apparent Molar Volumes of the Complexes of the  $\text{Pr}^{3+}$  Ion (Evaluated for  $\text{Pr}(\text{ClO}_4)_3$  in solutions of perchlorates)

Complex, ion	$V^0$ $\text{ml mol}^{-1}$	$V^\infty$ $\text{ml mol}^{-1}$	Complex, ion	$V^0$ $\text{ml mol}^{-1}$	$V^\infty$ $\text{ml mol}^{-1}$
$[\text{Pr}(\text{H}_2\text{O})_9]^{3+}$	117.9	82.0	$[\text{Pr}(\text{H}_2\text{O})_3(\text{ClO}_4)_3]$	113.0	113.0
$[\text{Pr}(\text{H}_2\text{O})_8\text{ClO}_4]^{2+}$	110.0	89.0	$[\text{Pr}(\text{H}_2\text{O})_4]^{3+}$	147.5	105.0
$[\text{Pr}(\text{H}_2\text{O})_7(\text{ClO}_4)_2]^+$	101.8	93.0	$[\text{Pr}(\text{H}_2\text{O})_3(\text{ClO}_4)_2]^{2+}$	141.1	117.0
$[\text{Pr}(\text{H}_2\text{O})_6(\text{ClO}_4)_3]$	93.4	93.4	$[\text{Pr}(\text{H}_2\text{O})_2(\text{ClO}_4)_2]^+$	133.8	124.0
$[\text{Pr}(\text{H}_2\text{O})_6]^{3+}$	135.6	93.0	$[\text{Pr}(\text{H}_2\text{O})(\text{ClO}_4)_3]$	125.0	125.0
$[\text{Pr}(\text{H}_2\text{O})(\text{ClO}_4)_2]^{2+}$	128.5	106.0	$[\text{Pr}(\text{ClO}_4)_4]^-$	117.8	124.0
$[\text{Pr}(\text{H}_2\text{O})_4(\text{ClO}_4)_2]^+$	121.2	111.5			

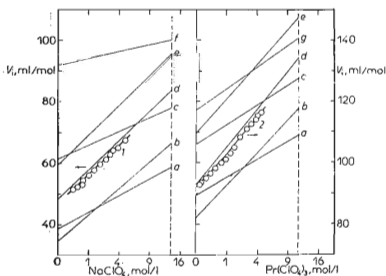


FIG. 2

Apparent Molar Volumes of  $\text{Pr}(\text{ClO}_4)_3$  and  $\text{Pr}(\text{NO}_3)_3$  in Aqueous Solutions

1  $\text{Pr}(\text{NO}_3)_3$  in  $\text{NaClO}_4$ ; 2  $\text{Pr}(\text{ClO}_4)_3$  in  $\text{H}_2\text{O}$ . Theoretical curves for the formation of a  $[\text{Pr}(\text{H}_2\text{O})_8\text{ClO}_4]^{2+}$ ; b  $[\text{Pr}(\text{H}_2\text{O})_9]^{3+}$ ; c  $[\text{Pr}(\text{H}_2\text{O})_5\text{ClO}_4]^{2+}$ ; d  $[\text{Pr}(\text{H}_2\text{O})_6]^{3+}$ ; e  $[\text{Pr}(\text{H}_2\text{O})_4]^{3+}$ ; f  $[\text{Pr}(\text{H}_2\text{O})_2(\text{NO}_3)_2]^+$ ; g  $[\text{Pr}(\text{H}_2\text{O})_3\text{ClO}_4]^{2+}$ .

by applying the above-mentioned method<sup>7</sup>. In praseodymium perchlorate solutions, similarly as in solutions of praseodymium nitrate in sodium perchlorate solutions, complete dissociation proceeds to the aquo ion and perchlorate ions,  $[\text{Pr}(\text{H}_2\text{O})_6]^{3+} + 3 \text{ClO}_4^-$ .

The above results also indicate that the lowering of the activity of water does not play the decisive part in the nitrate complex formation: the formation results primarily from the excess of the ligand ions, which was confirmed in cases where the concentration of the nitrate ions was higher than  $1 \text{ mol l}^{-1}$ .

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Translated by P. Adámek.