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Anion-Exchange Distribution Studies of Lighter Rare Earth Metal Ions in Sodium Nitrite Organic Solvent-Water Media

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Anion-exchange equilibrium distribution coefficient of some lighter rare earth metal ions has been studied in aqueous sodium nitrite and sodium nitrite-organic solvent water media using Dowex-1-X8 in nitrate form. Out of the less common metal ions studied, U(VI) gave very high distribution value followed by lighter rare earth. High K_D values were expected for metal forming stabler metal-nitrite complexes.

INTRODUCTION

The use of aqueous cations for separation met with little success.[1, 2] But when complexing media were tried, separation posibilities increased considerably. The use of citrate buffer was made by Tompkins[3] and the method was improved considerably by other workers[4–6]. The missing element from this series, now named as promethium, was first separated by Marinsky[7]. Many other complex forming elements were studied by Tompkins and Mayer[8] to make the rare earths separation easier. A number of acids, such as tartaric, lactic, oxalic, sulpo-salicylic acids were used for new complex forming organic ligands. Similarly acetylacetone, ethylacetoacetate and ethylene diamine-tetraacetic acid were also used. But the use of α-hydroxy isobutyric acid as its ammonium salt used and investigated by Choppin *et al.*[9, 10] proved much better than the above α-hydroxy carboxylic acids. It provided better separation factors a compared to other carboxylic acids.

Lanthanides have been studied for their distribution in lower aliphatic alcohols or ketones and hydrochloric acid using cation exchanger[11] and anion exchanger.[12] Similarly nitric acid and sulphuric acid solution with organic solvents of this type were used by Korkisch,[12] ammonium thiocyanate with ethanol by Pietrzyk and Kiser[13] and acetic acid with organic solvent were used for lanthanide ion distribution studies and anion exchange by Hazan and Korkisch.[14]

Non-aqueous and mixed solvents have been used in recent years; such solvents further modify selectivities on account of the fact that they bring about polarity differences in the medium, thereby changing the stabilities of different complexed species in solution.[15–17]

Bhatnagar and coworkers[18] have used sodium nitrite as a complexing agent to provide distribution data for quite a good number of metal ions in aqueons organic solvents.

This paper reports equilibrium distribution results for lighter rare earth metal ions. The studies have been carried out in aqueous methanol, ethanol and

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isopropanol solvents with varying quantities of sodium nitrite as a complexing salt for metal ions using a strongly basic anion exchanger in nitrate form.

EXPERIMENTAL

Air dried anion exchange resin, Dowex-1-X8 in nitrate form, has been used for all anion exchange distribution studies. It is a strongly base anion exchanger of analytical grade (40–60 mesh). The air dried resin (25°C) has an exchange capacity of 2.2 M_{eq}/g and a moisture content of *ca.* 20%.

0.2 N stock solution of each metal ion was prepared from their analytical grade nitrates in double distilled water. Rare earths obtained from Rare Earth Factory, Alwaye were of 99.999% purity. Sodium nitrite B.D.H., AnalaR was used to prepare the complexing media. Three organic solvents, namely methanol, ethanol and isopropanol, were used. All these solvents were Analar products of British Drug House and were used for distribution co-efficient of lighter rare earths. Pure (AR. BDH) nitric acid was used to decompose (by oxidation) nitrite ion before doing the complexometric titrations for metal ion estimations at proper pH after the distribution studies. A buffer solution of pH –5 was prepared by dissolving separately 6.25 mL of glacial acetic acid in 500 mL (0.2 N) and 16.4 g per L of sodium acetate (0.2 N). Both the solutions were then mixed in the ratio 3 : 7 to give a buffer of pH –5. Bromopyrogallol red was used for titrating all the rare earth metal ions. It was used as a 0.05 % solution in 1 : 1 ethyl alcohol-water mixture; colour change was marked from violet to red.

Estimation of Rare Earth Metal Ions

Estimation of lighter rare earths (*i.e.* lanthanum, cerium, praseodymium, samarium and neodymium) was performed after removal of nitrite ions. The solution was cooled and nurtralised by ammonia. 10 mL of pH –5 solution was used as buffer and few drops of indicator were added. The end point was marked by change in colour from blue-violet to red.

Metal-ion Titrant

Disodium EDTA (BDH, AR) was used as a complexometric titrant for all rare earth ions. EDTA (0.025 N) was standardized against a standard $MgSO_4{\cdot}7H_2O$ (0.025 N) solution using Eriochrome black-T at pH-10 as an indicator.

Experimental Procedure

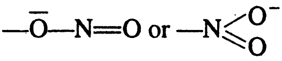
The distribution studies have been carried out by batch process. 25 mL of ion solution (in water or mixed solvent) was taken in conical Erlenmeyer flasks of capacity 100 mL. To this a requisite quantity of exactly weighed sodium nitrite was added. Then 0.25 g of anion exchanger (Dowex-1 × 8) was added. They were kept as such for 24 h, with intermittent shaking. 2 mL of aliquo were pipetted out from these sets after equilibrium had been attained and this was treated with nitric acid for destroying the nitrite ions, and then metal ion concentration was determined titrimetrically.

These distribution studies were carried out at room temperature (25°C) with varying nitrite concentrations ranging from 0.1, 0.2, 0.5, 0.7, 1.0, 1.5 N in different sets and in aqueous and mixed solvents having solvent concentrations as 10% to 50%. The anion exchange distribution co-efficient values have been calculated by the following formula:

$$K_D = \frac{M_{eq}\text{ metal ion per g of dry resin}}{M_{eq}\text{ metal ion in 1 mL of solution}}$$

RESULTS AND DISCUSSION

As a matter of fact the lanthanides are slack in forming complexes particularly due to remote chances of 5d or 6s forming hybrid orbitals with 4f orbitals. The trivalent lanthanide ions are also rather larger in size (radii 0.85–1.06 Å) as compared to similar transition metal ions such as Cr^{3+} and Fe^{3+} (radii 0.60–0.65 Å). This lowers the tendency to exert electrostatic forces of attraction for dipolar ligand molecules. Still the temptation of use of inorganic oxygen containing simple ligand



$$—\bar{O}—N{=}O \text{ or } —N\begin{smallmatrix}\nearrow O^- \\ \searrow O\end{smallmatrix}$$

could not be resisted. Hence attempts were made in this part of the work to study some five rare earth metal ions for their distribution in nitrite complexing media with and without organic solvents of low dielectric constants using an anion exchanger.

The results of such studies in aqueous methanol, ethanol and isopropanol are given in Table-1 to 6. These results are peculiar in many ways.

TABLE-1

ANION-EXCHANGE DISTRIBUTION CO-EFFICIENT DATA OF LIGHTER RARE EARTH METAL IONS IN AQUEOUS SODIUM NITRITE MEDIA

S. No.	Ions	K_D Sodium Nitrite concentration, N 0.1	0.2	0.5	0.7	1.0	1.5
1.	La(III)	1.26	3.90	9.60	11.10	13.55	14.32
2.	Ce(III)	13.54	16.00	17.64	19.41	23.09	25.00
3.	Pr(III)	1.26	2.98	2.98	3.90	6.60	9.59
4.	Nd(III)	9.59	9.59	11.10	13.54	16.00	21.21
5.	Sm(III)	2.98	3.90	5.27	6.60	8.14	11.10
6.	Th^{4+}	8.10	21.20	40.30	53.80	56.80	95.10
7.	U^{6+}	48.70	67.80	93.20	198.50	1191.30	2344.00

Table-1 gives K_D values for rare earth ions in presence of varying quantities of sodium nitrite in aqueous solutions. An increase in nitrite concentration (0.1 to 1.5 N) gave an increase in K_D value of all metal ions investigated. The values at 1.0 or 1.5 N sodium nitrite concentration can be used to provide following trivalent lighter rare earths, thorium(IV) and uranium(VI) sequence of uptake is as below:

U(VI) > Th(IV) > Ce(III) > Nd(III) > La(III) > Sm(III) > Pr (III)

TABLE-2

ANION EXCHANGE DISTRIBUTION CO-EFFICIENTS OF La(III) IN SODIUM NITRITE COMPLEXING MEDIA IN MIXED SOLVENT SYSTEM

Organic solvent %	K_D					
	Sodium nitrite concentration, N					
	0.1	0.2	0.5	0.7	1.0	1.5
Methanol						
0	1.26	3.90	9.60	11.10	13.55	14.32
10	18.85	20.67	24.64	26.62	33.17	37.76
20	5.27	6.60	8.13	11.10	16.00	23.90
30	18.85	20.67	20.67	21.69	24.64	52.88
40	13.55	13.26	17.44	18.85	17.44	20.67
50	35.48	35.48	40.45	46.92	48.53	50.86
Ethanol						
10	33.33	40.31	60.00	66.66	73.91	100.00
20	36.53	48.15	63.32	66.66	70.12	86.05
30	40.31	42.86	50.95	53.86	60.00	60.00
40	14.32	17.64	42.86	42.86	48.15	50.95
50	16.00	19.41	23.09	27.00	29.03	21.21
Isoproponol						
10	28.11	36.53	37.93	37.93	42.57	50.95
20	23.96	25.00	28.11	32.25	36.53	40.38
30	63.32	66.66	70.21	70.21	77.77	81.81
40	73.91	73.91	77.77	81.88	86.05	95.21
50	63.32	73.91	81.81	86.05	100.00	100.00

TABLE-3

ANION EXCHANGE DISTRIBUTION CO-EFFICIENT OF Ce(III) IN SODIUM NITRITE COMPLEXING MEDIA IN MIXED SOLVENT SYSTEM

Organic solvent %	K_D					
	Sodium nitrite concentration, N					
	0.1	0.2	0.5	0.7	1.0	1.5
Methanol						
0	13.54	16.00	17.64	19.41	23.09	25.00
10	13.54	14.32	19.41	25.00	27.00	27.00
20	9.59	11.11	19.41	21.21	23.09	23.09
30	1.26	3.90	5.77	6.60	6.60	ppt
40	6.80	8.14	9.59	9.59	ppt	ppt
50	9.59	13.59	ppt	ppt	ppt	ppt
Ethanol						
10	6.60	8.14	5.59	11.10	14.32	21.21
20	9.59	11.10	11.10	11.10	13.54	14.32
30	5.27	5.27	8.14	8.14	9.59	16.00
40	5.27	6.60	11.10	9.95	ppt	ppt
50	3.90	3.90	ppt	ppt	ppt	ppt
Isopropanol						
10	2.98	5.27	6.60	8.14	9.59	16.00
20	3.90	5.27	6.60	8.14	9.59	14.32
30	1.26	2.98	3.90	6.60	ppt	ppt
40	3.90	5.27	ppt	ppt	ppt	ppt
50	11.10	ppt	ppt	ppt	ppt	ppt

This sequence has nothing to do with the ionic size of the ions concerned. Only the possibilities of stabler complex formation by these ions, in the order shown above, may be the reason of observed K_D values. However, they appear to be highly dissociated and hence the values of K_D are not very high. Uranium(VI) gave highest distribution co-efficient in nitrite media, while thorium(IV) was next to it.

TABLE-4

ANION EXCHANGE DISTRIBUTION CO-EFFICENT OF Pr(III) IN SODIUM NITRITE COMPLEXING MEDIA IN MIXED SOLVENT SYSTEM

Organic solvent %	K_D					
	Sodium nitrite concentration, N					
	0.1	0.2	0.5	0.7	1.0	1.5
Methanol						
0	1.26	2.98	2.98	3.90	6.60	9.59
10	2.98	5.27	11.10	17.64	23.09	ppt
20	2.98	3.90	5.27	6.60	ppt	ppt
30	6.60	9.59	11.10	13.54	ppt	ppt
40	2.98	3.90	5.27	ppt	ppt	ppt
50	5.27	6.60	ppt	ppt	ppt	ppt
Ethanol						
10	2.98	3.90	9.59	11.10	14.32	14.32
20	3.90	6.60	9.59	14.32	17.64	ppt
30	2.98	3.90	5.27	ppt	ppt	ppt
40	3.90	6.60	ppt	ppt	ppt	ppt
50	5.27	6.60	ppt	ppt	ppt	ppt
Isopropanol						
10	2..98	5.29	6.60	6.60	9.59	11.10
20	3.90	5.27	6.60	8.14	9.59	14.32
30	2.98	5.27	6.60	8.14	11.10	ppt
40	8.14	13.54	ppt	ppt	ppt	ppt
50	11.10	14.32	ppt	ppt	ppt	ppt

With the change of solvent system from pure water to mixed solvents with low dielectric constant organic liquid in them, changes in K_D values were expected due to stabilisation of complexed species formed in such media[19, 20]. By going from 10% to 50% methanol in solvent media, the K_D for La(III) has definetely increased (Table-2). It has also shown an increase in isopropanol concentration. But with increasing ethanol concentration in the solvent the K_D values at 1.5 N sodium nitrite have shown a progressive decrease.

These observations make us to think that either this medium destabilises the complexed species formed or the ionization of salts used in the system (say at 40% or 50% ethanol) is suppressed so much that enough complexed ions are not made available to show the expected increased K_D values. First explanation is not correct as at 10% ethanol, the K_D goes up to *ca.* 100 which shows definitely that complexed species have been stabilised by decrease in the dielectric constant of the solvent media. Decrease in K_D with high ethanol percentage is therefore due to check on the ionization process of salts involved.

TABLE-5
ANION EXCHANGE DISTRIBUTION CO-EFFICIENT OF Nd(III) IN SODIUM NITRITE COMPLEXING MEDIA IN MIXED SOLVENT SYSTEM

Organic solvent %	K_D					
	Sodium nitrite concentration, N					
	0.1	0.2	0.5	0.7	1.0	1.5
Methanol						
0	9.57	9.59	11.10	13.54	16.00	21.21
10	11.10	13.54	14.32	16.00	16.00	19.41
20	11.10	11.10	13.54	13.54	16.00	19.41
30	6.60	9.59	11.10	13.54	ppt	ppt
40	6.60	8.14	9.59	9.59	ppt	ppt
50	9.59	11.10	ppt	ppt	ppt	ppt
Ethanol						
10	5.27	8.14	11.10	13.54	14.32	16.00
20	8.14	9.59	13.54	14.32	17.64	17.64
30	6.60	11.10	17.64	17.64	ppt	ppt
40	6.60	19.41	23.09	ppt	ppt	ppt
50	8.14	11.10	ppt	ppt	ppt	ppt
Isopropanol						
10	13.54	14.32	23.07	25.00	27.00	27.00
20	1.26	1.26	11.10	16.00	23.90	27.00
30	10.13	17.48	31.50	35.53	42.12	ppt
40	11.18	14.47	24.09	ppt	ppt	ppt
50	10.13	15.93	ppt	ppt	ppt	ppt

In the case of Ce(III), Pr(III), Nd(III) and Sm(III) the results (Table-3 to 6) of mixed solvents show that at higher organic solvent concentration (*i.e.* above *ca* 20%) precipitation occurs at 1.0 or 1.5 N nitrite in the solvent phase. This is a clear indication that salts used become more and more insoluble, when the dielectric constant of the solution falls considerably by increasing organic solvent concentration from 30 to 40% on volume to volume basis.

The comparison of their selectivity sequence for anion exchangers in mixed solvent media, therefore, can be made only at 10% or 20% organic solvent composition. At higher concentrations (>30%) the data is not authentic on account of partial or complete precipitations observed in solvent media. Thus the sequence appears to be as below:

In aqueous methanol (10% v/v)—La > Ce > Pr > Nd > Sm
In aqueous ethanol (10% v/v)—La > Sm > Nd ≈ Pr > Ce
In aqueous isopropanol (10% v/v)—La ≈ Sm > Nd > Ce > Pr

This type of data has been provided for the first time from the present studies in nitrite complexing media. Much usefulness of it could not be predicted on account of the limitations of solubilities in aqueous phase. The separation possibilities of rare earth ions amongst themselves cannot be suggested or predicted. The K_D values in aqueous or even in mixed solvent media are not so different that can provide a good separation factor for these ions. However, it is clear that these metal ions as a group can be very easily separated from U(IV) in nitrite media by using an anion exchanger.

TABLE-6
ANION EXCHANGE DISTRIBUTION CO-EFFICIENT OF Sm (III) IN SODIUM NITRITE COMPLEXING MEDIA IN MIXED SOLVENT SYSTEMS

Organic solvent %	K_D					
	Sodium nitrite concentration, N					
	0.1	0.2	0.5	0.7	1.0	1.5
Methanol						
0	2.98	3.90	5.27	6.60	8.14	11.10
10	3.90	5.27	6.60	9.59	11.11	13.54
20	5.27	6.60	9.59	11.10	11.10	13.54
30	2.98	2.98	3.90	5.27	8.14	ppt
40	1.26	3.90	3.90	ppt	ppt	ppt
50	1.26	2.98	ppt	ppt	ppt	ppt
Ethanol						
10	2.83	2.83	14.35	14.35	16.55	16.55
20	6.33	8.22	18.84	26.26	28.95	34.68
30	8.23	16.55	18.84	21.21	21.21	ppt
40	12.23	16.55	21.21	ppt	ppt	ppt
50	12.23	16.55	ppt	ppt	ppt	ppt
Isopropanol						
10	10.19	12.23	12.23	21.21	37.74	40.97
20	12.23	14.75	18.83	23.68	37.44	40.97
30	14.35	16.55	21.21	28.94	31.74	ppt
40	16.55	18.83	23.68	ppt	ppt	ppt
50	18.83	21.21	ppt	ppt	ppt	ppt

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