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Cation Exchange Equilibrium and Affinity Studies of Some Lanthanides(III) in Isopropanol Solvents

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Studies of cation exchange equilibrium and affinity of some lighter lanthanides *e.g.*, lanthanum, cerium, praseodymium, neodymium and samarium ions in isopropanol solvents. Equili-brium exchanges studies were carried at room temperature in this way for La^{3+}, Ce^{3+}, Pr^{3+}, Nd^{3+} and Sm^{3+} ions of three (0.1, 0.05 and 0.025 N) ionic concentration in aqueous isopropanol solvents and containing 10, 20, 30, 40 and 50 % (v/v) isopropanol and by using cation exchanges IC NAC-C-267, having 5.7 meg capacity and 40-60 mesh resin size.

Key Words: Lanthanides(III), Cation exchange, Equilibrium, Isopropanol.

INTRODUCTION

Samualson[1] has shown that the relative affinities depend on the total ionic concentration in the resin phase. This has been confirmed by several workers[2]. But affinities are also related to the ionic sizes or the radii of the ions involved in free exchange ions of larger size or radii are held more strongly than the ions of the smaller size[3].

Bonner[4] has established a quantitative selectivity scale for the common univalent ions taking lithium selectivity arbitrarily as unity. It is well known that the selectivities vary when the relative amounts of ions in the resin are altered and even reversals in selectivity may occur[5].

The uptake of lanthanides from 0.11 M perchloric acid has been studied by Suris and Chappin[6]. In present studies, the cation exchange equilibrium and affinity of lighter lanthanides(III) in isopropanol solvent are reported.

EXPERIMENTAL

Isopropanol and disodium ethylenediamine-tetracetic acid (AR, BDH) were used as received. The nitrates of La(III), Ce(III), Pr(III), Nd(III) and Sm(III), (Indian Rare Earths, India) were used to prepare the 0.2 N of stock electrolyte solutions. A cation exchanger ICNAC-C-267 (ion exchange capacity = 5-7 meq/g, moisture content = 20% and mesh resin size = 40-60) was used throughout the study.

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In each batch study, the total electrolyte volume was kept as 25 mL while resin quantity taken in each case was exactly 0.25 g. The $Ln(NO_3)_3$ solution of 0.1, 0.05, 0.033 and 0.025 N were used in different equilibria studies the organic solvents and deionized water in suitable proportions, were so fixed that they provide mixed solvent systems. Containing 10, 20, 30, 40 and 50 % v/v isopropanol. The total electrolyte solution was used 25 mL and 0.25 g of the resin in hydrogen form in all exchanger studies in 150 mL elenmeyer flask, kept at room temperature for 24 h for attaining complete equilibrium. Aliquots (2 mL) were then withdrawn from each such batch and metal ion concentrations in them were determined titrimetrically at pH 5 using disodium EDTA as the titre and bromopyarogallol red as an indicator.

Equilibrium exchange studies were carried out in this way for La^{3+}, Ce^{3+}, Pr^{3+}, Nd^{3+} and Sm^{3+} ions in aqueous isopropanol solvents. Containing 10, 20, 30, 40 and 50 % (v/v) organic component in the mixture.

Knowing the initial and final metal ion concentrations in the external solution before and after attaining complete equilibrium with the exchanger, the equilibrium constants were calculated by using the following expression:

$$K_a = \frac{X_B 3 + R}{X_A + R} = \frac{C_A + w}{C_B 3 + w}$$

where $X_B 3 + R$ is the equivalent fraction of the tripositive lanthanide metal ion in the resin phase and $X_A + R$ is the equivalent fraction of the univalent hydrogen ion in the resin phase. $C_A + w$ and $C_B 3 + w$ are the ionic concentrations of H^+ and m^{3+} lanthanide ions in the solution phase. The K_a terms may be termed as selectivity coefficients for the ion under study at different ionic loading.

RESULTS AND DISCUSSION

The studies of ion exchange equilibrium in mixed solvents have many complications. A number of authors have measured the selectivity of certain pair of ions in mixed and non-aqueous as a function of resin cross-linking composition and capacity, resin functional group, solution ionic strength and composition, temperature and some other variables. But their results are vary in consistent, though the general conclusions are more or less similar. Still whatever data has been collected so far for ion-exchange selectivities in mixed or non-aqueous solvents, is on the basis of uni-univalent exchanges[7,8]. However, the data of this type is not available for multivalent ions in non-aqueous or mixed solvents.

The various relationship used to calculate selectivity coefficient by Kressman and Kitchener[9] does not include activity co-efficients of the ions in either phase and has been used earlier for computing apparent equilibrium constant by Bhatnagar *et al.*[10], for aqueous and organic solvent media studies.

The constant (K_a) is a variable factor which varies with the equivalent fraction of the ion in the resin phase (X_{BR}).

The results in Table-1 in case of exchanges involving trivalent lanthanide ions, compare the selectivity trends of these ions only at similar initial ionic concentrations. It gives the selectivity sequence for these metal ions in aqueous solution ionic concentrations, with the concentrations range of 0.1 to 0.05N, 0.025 all ions individually. This shows increase in K_a with decreasing concentration. Thus in aqueous media too the dilute solutions give higher exchange.

TABLE-1
EQUILIBRIUM EXCHANGE AT DIFFERENT IONIC CONCENTRATIONS IN AQUEOUS MEDIA

Ion	Metal ion conc. (N)	X_{BR}	log K_a	K_a
La^{3+}	0.100	0.526	0.079	1.199
	0.050	0.460	0.149	1.408
	0.025	0.395	0.706	6.077
Ce^{3+}	0.100	0.526	0.079	1.199
	0.050	0.460	0.149	1.408
	0.025	0.395	0.706	5.077
Pr^{3+}	0.100	0.570	-0.258	-1.817
	0.050	0.460	-0.148	-1.408
	0.025	0.373	0.372	2.355
Nd^{3+}	0.100	0.504	-1.938	-0.867
	0.050	0.460	-0.148	-1.408
	0.025	0.373	0.372	2.355
Sm^{3+}	0.100	0.417	-1.449	-0.281
	0.050	0.395	1.666	0.463
	0.025	0.351	0.109	1.204

In Tables 2-4, the data for K_a with different ionic loadings *i.e.* external ionic concentrations from 01 to 0.025 N. In case of M^{3+}/M^{+} exchange in isopropanol solvent percentages in the solvent system, Ka has shown variation with X_{BR}. This variation has been quite irregular, though in most cases K_a increased with decreasing ionic concentrations.

The variation in K_a with X_{BR} has been so peculiar in these cases that plots of K_a with X_{BR} gave a sharp upward trend for K_a at higher X_{BR} values. Most of the X_{BR} values were between 0.3 to 0.55 and therefore the extrapolation of K_a values for X_{BR} = 1.0 were difficult. In case of isopropanol solvents La^{3+} ion shows the highest exchange, which is expected from its smallest hydrated ionic size as compared to all other rare earths. The other ions show reversals in their affinity sequences in solvents.

TABLE-2
La^{3+}/H^+ AND Ce^{3+}/H^+ EXCHANGE AT DIFFERENT IONIC CONCENTRATIONS IN AQUEOUS ISOPROPANOL MEDIA

Isopropanol (%, v/v)	Metal ion conc.	La^{3+}/H^+			Ce^{3+}/H^+		
		X_{BR}	K_a	1 + log K_a	X_{BR}	K_a	1 + log K_a
10	0.100	-0.491	-2.838	-1.450	-0.482	-0.620	-0.793
	0.050	-0.509	-12.480	-2.090	-0.395	-1.844	-1.266
	0.025	-0.424	-76.700	-2.000	-0.351	-5.132	-1.710
20	0.100	-0.450	-1.742	-1.240	-0.459	-0.439	-0.543
	0.050	-0.509	-12.480	-2.090	-0.373	-1.263	-1.101
	0.025	-0.412	-42.020	-2.630	-0.342	-4.047	-1.607
30	0.100	-0.465	-1.655	-1.220	-0.439	-0.319	-0.504
	0.050	-0.509	-12.480	-2.090	-0.373	-1.263	-1.101
	0.025	-0.390	-19.580	-2.790	-0.338	-3.063	-1.557
40	0.100	-0.421	-0.986	-0.994	-0.439	-0.319	-0.504
	0.050	-0.509	-12.480	-2.090	-0.373	-1.263	-1.101
	0.025	-0.380	-14.150	-2.150	-0.316	-2.050	-1.312
50	0.100	-0.397	-0.541	-0.730	-0.417	-0.231	-0.364
	0.050	-0.490	-0.340	-1.970	-0.373	-1.263	-1.101
	0.025	-0.388	-	-	-0.307	-1.648	-1.217

TABLE-3
Pr^{3+}/H^+ AND ND^{3+}/H^+ EXCHANGE AT DIFFERENT IONIC CONCENTRATION IN AQUEOUS ISOPROPANOL MEDIA

Isopropanol (%, v/v)	Metal ion conc.	Pr^{3+}			Nd^{3+}		
		X_{BR}	K_a	2 + log K_a	X_{BR}	K_a	1 + log K_a
10	0.100	0.500	1.265	2.102	0.463	0.467	0.669
	0.050	0.307	0.095	0.978	0.439	0.967	0.986
	0.025	0.395	5.066	2.705	0.430	42.630	2.627
20	0.100	0.482	0.624	1.795	0.421	0.247	0.393
	0.050	0.287	0.068	0.839	0.439	0.967	0.986
	0.025	0.395	5.066	2.705	0.425	27.010	2.432
30	0.100	0.482	0.624	1.795	0.421	0.247	0.393
	0.050	0.287	0.068	0.830	0.439	0.967	0.986
	0.025	0.395	5.066	2.705	0.425	27.010	2.432
40	0.100	0.473	0.547	1.795	0.421	0.247	0.393
	0.050	0.272	0.048	0.680	0.439	0.967	0.986
	0.025	0.386	3.612	2.556	0.425	27.010	2.432
50	0.100	0.464	0.475	1.677	0.400	0.178	0.250
	0.050	0.257	0.022	0.351	0.417	0.686	0.836
	0.025	0.386	3.612	2.558	0.425	27.010	2.432

TABLE-4
Sm^{3+}/H^{+} EXCHANGE AT DIFFERENT IONIC CONCENTRATION IN AQUEOUS ISOPROPANOL MEDIA

Isopropanol (%, v/v)	Metal ion concentration (N)	Sm^{3+}/H^{+}		
		X_{BR}	K_a	$2 + \log K_a$
10	0.100	0.548	1.652	1.218
	0.050	0.505	2.902	1.463
	0.025	0.421	10.750	2.273
20	0.100	0.526	1.192	0.759
	0.050	0.505	2.902	1.463
	0.025	0.404	7.230	1.859
30	0.100	0.526	1.192	0.759
	0.050	0.461	1.396	1.145
	0.025	0.404	7.230	1.859
40	0.100	0.526	1.192	0.759
	0.050	0.461	1.396	1.145
	0.025	0.390	4.303	1.634
50	0.100	0.504	0.862	0.935
	0.050	0.461	1.396	1.145
	0.025	0.390	4.303	1.634

The results of exchanges involving rare earth ions against H^+ have resulted in changes in affinity sequence on account of possible changes in their association tendencies in organic solvents. The affinity sequences of isopropanol solvent at 0.1, 0.050 and 0.025 N, ionic concentration show that at higher organic solvent percentages (50 %) Pr has shown least exchange but at 10 % Sm was the least exchanged ion.

Obviously such changes have no other explanation except the possible ion pairing or association processes that this solvent might be bringing about in the solvent systems. At higher concentration of 0.1 N these processes appear to be favoured. Thus, it appears that rare earth ions behave quite peculiarly in organic solvents.

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