[CONTRIBUTION FROM DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MICHIGAN]

The Distribution of Several Bivalent and Trivalent Metallic Nitrates between Water and *n*-Hexyl Alcohol at 25°[1]

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The systems of the type water–*n*-hexyl alcohol–metallic nitrate involving calcium, cobalt(II), magnesium, zinc and lanthanum nitrates have been studied up to saturation in the liquid-liquid region at 25°. Calcium nitrate is much less extractible into the alcoholic phase than are the other bivalent nitrates. The hydration tendencies of the salts when dissolved in the alcoholic phase are discussed.

The study of metallic nitrate–water–organic solvent systems in the liquid–liquid range can yield two types of useful information: (a) the order of extractibility of different nitrates by a given organic solvent and (b) the rate at which water is carried into the organic phase by the metallic nitrate. In the present paper an attempt is made to gather data which bear on these two points in the case of the extraction of several bivalent and trivalent metallic nitrates with *n*-hexyl alcohol at 25°.

Experimental

Materials.—The *n*-hexyl alcohol used was the product of two careful fractionations of the Eastman Kodak Company Practical grade, the middle fraction only being retained after each distillation.

Fisher Scientific Company Eimer and Amend C.P. lanthanum nitrate hexahydrate was used without further purification. Some of the other nitrates used had the following *maximum* limits of all impurities: Mallinckrodt Reagent grade calcium nitrate tetrahydrate, 0.24%; General Chemical Company Baker and Adamson Reagent grade cobalt (II) nitrate hexahydrate, 0.53%, and Reagent grade magnesium nitrate hexahydrate, 0.22%. General Chemical Company Baker and Adamson Reagent grade zinc nitrate hexahydrate was recrystallized four times before use (% ZnO: found, 27.25%; theoretical 27.37%).

Methods: All samples were brought to equilibrium at 25 ± 0.05°. Water was determined by the Karl Fischer method. Cobalt, lanthanum, and zinc were determined by careful ignition to their respective oxides: Co_3O_4, La_2O_3 and ZnO. Magnesium was determined by precipitation as magnesium ammonium phosphate, with subsequent ignition to magnesium pyrophosphate. Calcium was determined by precipitation as calcium oxalate, followed by ignition to CaO, or by direct ignition of the nitrate solution to the oxide.

Results and Discussion

General.—In Table I the compositions of both phases for each tie-line in the liquid–liquid region are expressed as weight percentages. The percentages of *n*-hexyl alcohol in all cases were taken by difference. For the case of lanthanum nitrate, no determination of water was made in the aqueous phase because a precipitate formed if we carried out the Karl Fischer titration in our customary manner. The lanthanum nitrate data are included only for the sake of the water content of the alcoholic phase, which data were not reported in a previous study of the distribution of rare earth nitrates.[3] For all the other cases the water contents of the aqueous phases show only that the alcoholic contents of the aqueous phases are always quite low. In all cases the liquid–liquid region ends in an invariant liquid–liquid–solid state in which the solid phase is the stable hydrate for the nitrate–water system at 25°.[4]

TABLE I

THE DISTRIBUTION OF SEVERAL METALLIC NITRATES BETWEEN WATER AND *n*-HEXYL ALCOHOL AT 25°

	Weight percentages			
	Aqueous phase		Alcoholic phase	
	$R(NO_3)_n$	H_2O	$R(NO_3)_n$	H_2O
	Weight Percentages			
Lanthanum nitrate	60.6[a]	..	7.85	4.80
	60.1[a]	..	7.95	4.78
	57.8	..	4.79	4.36
	56.3	..	3.92	4.24
	54.3	..	2.74	4.10
	51.0	..	1.64	4.08
Zinc nitrate	54.2[a]	44.8	19.1	8.50
	50.6	48.0	12.93	8.11
	49.4	48.6	10.54	7.68
	47.3	50.6	9.37	7.34
	44.4	53.7	6.37	6.54
	39.3	59.5	2.77	5.36
Calcium nitrate	57.2[a]	39.1	3.01	2.85
	55.0	44.1	1.94	2.75
	54.5	43.7	1.64	2.87
	50.4	45.8	0.945	3.04
Magnesium nitrate	42.5[a]	56.5	4.65	6.06
	42.8	58.3	4.34	6.02
	38.8	60.7	3.31	5.51
	36.3	62.2	2.09	4.77
	34.3	65.2	1.30	4.35
	28.5	69.4	0.642	4.40
Cobalt(II) nitrate	51.2[a]	48.6	12.84	8.18
	44.9	55.8	7.50	7.08
	43.8	55.3	6.55	6.56
	41.2	57.5	4.12	5.84
	36.2	61.7	2.48	5.11

[a] Saturated system.

Order of Extractibility of the Nitrates into *n*-Hexyl Alcohol.—A previous study of the aluminum nitrate–water–*n*-hexyl alcohol system[5] demonstrated the difficulty of correlating the extractibility into the alcohol phase with the concentrations of individual cations and anions in the aqueous phase. At the present state of our knowledge of such concentrated solutions there seem to be *no simple* relations between solute activity and individual ion concentrations. However, as in previous papers,[3,5] we will use the data determined for each of the nitrates separately to predict their relative extractibilities in mixtures.

In Fig. 1 the "apparent" mole-fraction of each of the bivalent metallic nitrates in the alcoholic phase

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[2] Shell Oil Company, 3737 Bellaire Blvd., Houston 5, Texas.

[3] C. C. Templeton, THIS JOURNAL, **71**, 2187 (1949).

[4] A. Seidell, "Solubilities of Inorganic and Metal Organic Compounds," Third Edition, D. Van Nostrand Co., New York, N. Y., 1940.

[5] C. C. Templeton, *J. Phys. Colloid Chem.*, **54**, 1255 (1950).

is plotted against the "apparent" mole-fraction of the metallic cation in the aqueous phase on a log-log scale.

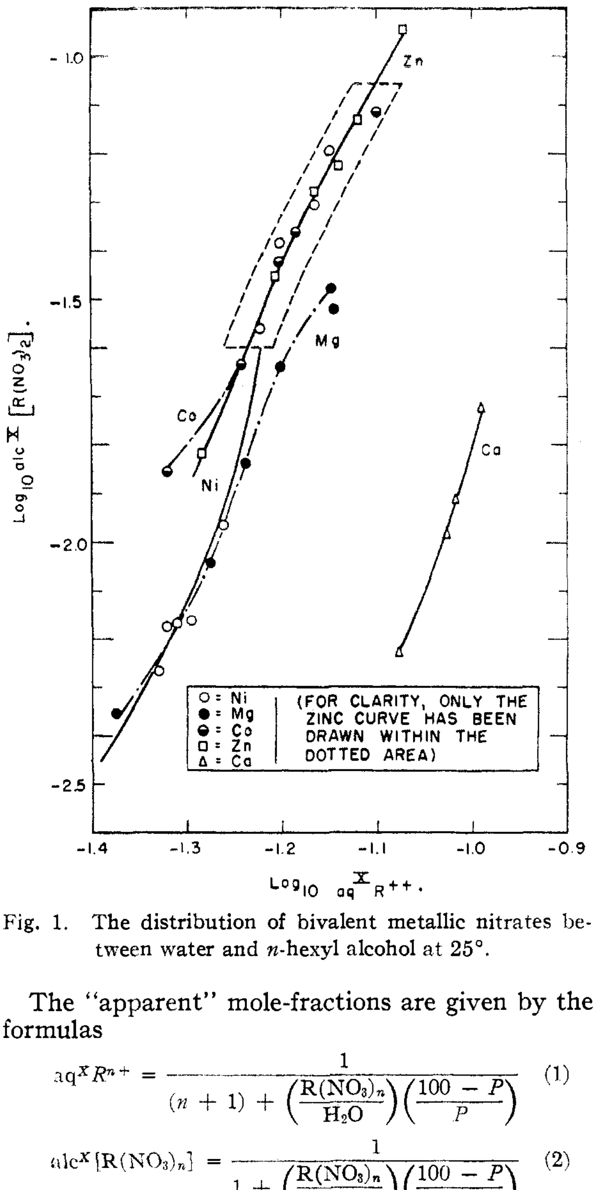

Fig. 1. The distribution of bivalent metallic nitrates between water and *n*-hexyl alcohol at 25°.

The "apparent" mole-fractions are given by the formulas

$$\text{aq}^{X}R^{n+} = \frac{1}{(n+1) + \left(\frac{\text{R(NO}_3)_n}{\text{H}_2\text{O}}\right)\left(\frac{100 - P}{P}\right)} \quad (1)$$

$$\text{alc}^{X}[\text{R(NO}_3)_n] = \frac{1}{1 + \left(\frac{\text{R(NO}_3)_n}{\text{C}_6\text{H}_{13}\text{OH}}\right)\left(\frac{100 - P}{P}\right)} \quad (2)$$

when P is the weight percentage of $R(NO_3)_n$ in the appropriate phase. As before,[3,5] these quantities were arbitrarily selected for comparing extractibilities. The data for nickel(II) nitrate are included from another report.[6] With the exception of the nickel(II) nitrate set the data are simple and regular. The curves for cobalt(II) and zinc nitrates very nearly coincide over much of their paths. They are about 50% more extractible than magnesium nitrate. Calcium nitrate is only about one-tenth as extractible as cobalt(II), zinc or magnesium nitrates. Nickel(II) nitrate behaves in a more complicated fashion. At lower concentrations it is less extractible than magnesium nitrate; it crosses over the magnesium curve at a higher concentration; and finally crosses and goes slightly above the cobalt and zinc curves at the highest concentration.

Garwin and Hixson,[7] studied the distribution of nickel and cobalt(II) chlorides between water and capryl alcohol, and found that the addition of calcium chloride increased the extractibility of cobalt 100- to 1000-fold, and that of nickel about tenfold. By some quick qualitative experiments we have determined that calcium nitrate is effective in salting out both cobalt(II) nitrate and nickel(II) nitrate into *n*-hexyl alcohol. The effect is easily observed visually, especially if one starts with a system dilute enough for the alcoholic phase to appear almost colorless.

The extreme extractibility of actinide nitrates into ethyl ether was recently cited by Glueckauf and McKay[8] as one of three types of evidence in support of their suggestion that the actinides exhibit 5 f covalency.[9] They state that the relative partition coefficients of manganese, cobalt, copper and uranyl nitrates ("measured under thermodynamically comparable conditions") are 0.1:1:2: 10,[7] and conclude that ... "Such an enormous difference in degree suggests a different kind of mechanism." The situation may be further explored if the data of the present paper are compared with those for the distribution of: (a) uranyl nitrate between water and isobutyl alcohol and ethyl ether[10]; (b) thorium nitrate between water and various alcohols and ketones[11]; and (c) aluminum[5] and several rare earth[3] nitrates between water and *n*-hexyl alcohol. It should then be apparent that all the nitrates behave very similarly in the concentrated range; *i.e.*, the salt concentration in the organic phase is nearly proportional to a high power of the aqueous salt concentration. We feel that the more inclusive range of data now available weakens the extraction argument as a support for the actinide 5 f covalency hypothesis.

Transfer of Water into the Alcoholic Phase.—Katzin and Sullivan[10] introduced the method of plotting the molality of water in an organic phase *versus* the molality of a salt in the same phase as a means of determining the hydration of the salt. The slope of this plot at any point is obviously the *rate* at which water is being carried into the organic phase by the salt at that particular concentration. If the "extra" water taken into the organic phase were actually the only water in the salt complex, and the above plot were truly linear, the slope would then be the precise hydration of the salt in the organic phase. Subject to these assumptions, Katzin and Sullivan[10] applied the idea to uranyl nitrate–water–organic solvent systems, while the authors have used it in discussing the aluminum nitrate–water–*n*-hexyl alcohol[5] and nickel(II) nitrate–water–*n*-hexyl alcohol[6] systems. Since, however, Glueckauf and McKay[8] cite the data of Katzin and Sullivan as support for writing definite formulas such as $[UO_2(NO_3)_2(H_2O)_4]$ for the extracted species

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(6) C. C. Templeton and L. K. Daly, *J. Phys. Colloid Chem.*, in press.

(7) L. Garwin and A. N. Hixson, *Ind. Eng. Chem.*, **41**, 2298, 2303 (1949).

(8) E. Glueckauf and H. A. C. McKay, *Nature*, **165**, 594 (1950).

(9) The 5 f covalency hypothesis has been criticized on other grounds by L. I. Katzin, *ibid.*, **166**, 605 (1950).

(10) L. I. Katzin and J. C. Sullivan, *J. Phys. Colloid Chem.*, **55**, 346 (1951).

(11) B. F. Rothschild, C. C. Templeton and N. F. Hall, *ibid.*, **52**, 1006 (1948).

in ethyl ether, it seems in point to re-emphasize the assumptions underlying the scheme.

Figure 2 presents such plots for all five nitrates presently studied, together with the previous data on nickel(II) nitrate. All such curves show an initial minimum (similar to that of nickel) if measurements are made on dilute enough solutions, due to the decrease in water activity of the aqueous phase before any appreciable amounts of salt enter the organic phase. The calcium curve hardly recovers from this minimum before saturation and hence gives us little information about its hydration. For the other salts smooth curves have been drawn through the points, and dotted straight lines (with their slopes) have been inserted in arbitrary regions. Some slopes have been taken as tangents to the smooth curve; others have been drawn as nearly as possible through all the points in a given region. Just beyond the minimum cobalt(II), nickel(II), magnesium and zinc nitrates gives slopes between 4.0 and 5.3, this being close to the value of 4 which Katzin and Sullivan ascribe to uranyl nitrate in several different solvents. This would suggest a fairly uniform dependence of hydration upon cationic charge, if aluminum (slope of 9.0)[5] did not show three times the hydration tendency of lanthanum (slope of 3.4).

None of these plots are truly linear, as is especially shown by the Ni, Co and Zn curves. All of our curves have a maximum slope just after the minimum and then have smaller slopes at higher concentrations. Katzin and Sullivan ascribe such a decrease in slope in the uranyl nitrate–water–diethyl cellosolve system to a transition between hexahydrated and tetrahydrated forms. If one now looks at the zinc curve in Fig. 2, where slopes of 4.1 and 1.6 have been indicated in two different regions, it is apparent that intermediate slopes of any arbitrary value (between the extreme values) could have been indicated at various points. Thus, one could assume the existence of any arbitrary complex between these extremes, such as a trihydrate, a dihydrate or even a fractional hydrate. It is just this which causes us not to favor the notion of writing definite molecular formulas *solely* on the basis of this kind of evidence. Rather, the value of these plots rests in the fact that they furnish a *relative measure of the hydration of cations.*

In a recent spectrophotometric study of solutions of cobalt(II) nitrate in *t*-butyl alcohol (containing up to 6% water), Katzin and Gebert[12] postulated a hexasolvated (not necessarily completely ionized) species $CoX_6(NO_3)_2$, where X is either water or alcohol. They deduce that on the average 3.3 of the six solvate groups are water molecules. These results are generally compatible with the range of slopes (5.3 to 2.8) exhibited by cobalt in Fig. 2.

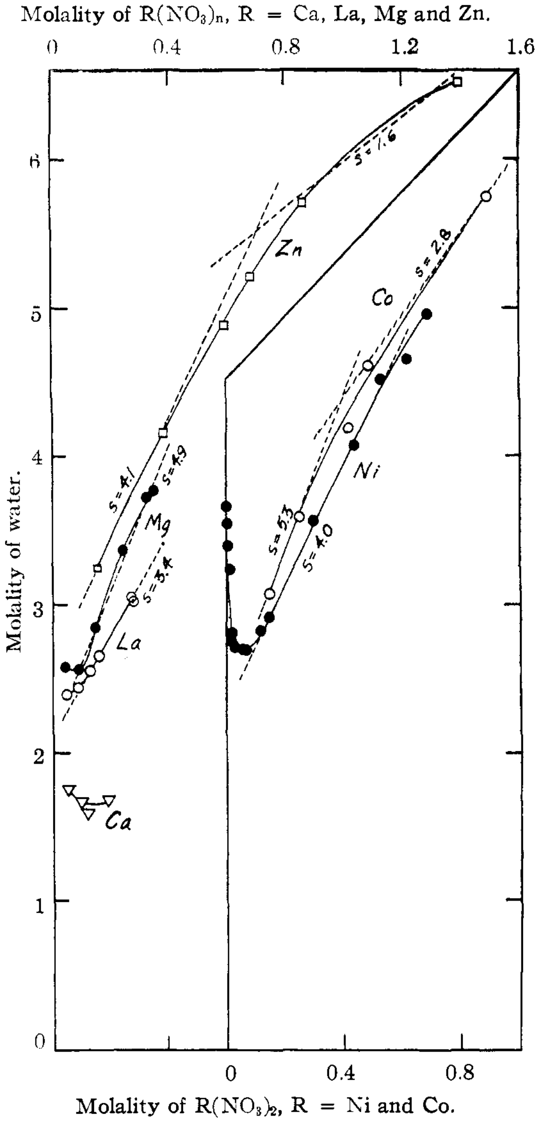

Fig. 2.—Water content as function of salt content for alcoholic phase: (○ La, Co; ● Mg, Ni; □ Zn; ▽ Ca).

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(12) L. I. Katzin and E. Gebert, THIS JOURNAL, **72**, 5455 (1950).