by interaction covalency. It is particularly gratifying to note that this effect is reflected in a peculiar change, with concentration, of the relaxation times for iron–alumina. Instead of relaxation times appearing linear with concentration as for manganese–titania there is a marked increase of catalytic effect at low concentrations. This parallels the increase of magnetic moment which occurs in this region owing to diminished numbers of iron ions being adjacent to each other in positions to exhibit a diminution of normal moment.

These results all show a definite parallelism between susceptibility and relaxation time. This is not surprising in a supported system when it is recalled that increased dispersion is generally attended by increased susceptibility, and not infrequently also by increased catalytic activity.

The sharp difference, however, between the kinds of information from susceptibility measurements and nuclear induction measurements is shown by the data on the iron–alumina solid solution.

The iron in the supported system has a very high susceptibility owing to the highly dispersed nature of a sample containing only 0.4% iron. As the sample is ignited to form a three-dimensional solid solution the degree of dispersion tends to became even greater, finally reaching infinite magnetic dilution. Hence the susceptibility also increases somewhat, tending toward a maximum. But the relaxation time behaves quite differently. In the supported system a large fraction of the iron ions are in a position to exert catalytic activity. Hence the diminution of relaxation time is very great. But as the sample is ignited, the iron atoms leave the surface to go into solid solution where they are no longer available for catalytic action. The relaxation time correspondingly increases.

It may be argued that all this could be surmised from a combination of susceptibility and surface area measurements. (The area of the sample decreases greatly during the ignition process.) This is, of course, true, but it also illustrates what promises to be a most useful application of the nuclear induction experiment, namely, that the measurements may be made on a catalyst *in situ*, that they may be completed in a few moments, and that almost any compound containing hydrogen may be used as the proton carrier.

It is a pleasure to acknowledge the invaluable assistance of Professor Arnold J. F. Siegert in connection with this work. The authors are also indebted to Marylinn Ellis and to Lorraine Lyon for assistance with the preparations and analyses.

Summary

Relaxation times as found by the nuclear induction experiment are used to extend information on solid catalyst structures.

EVANSTON, ILLINOIS RECEIVED JANUARY 22, 1949

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MICHIGAN]

The Distribution of Rare Earth Nitrates between Water and n-Hexyl Alcohol at 25°

BY CHARLES C. TEMPLETON

The possibility of the use of organic solvents for the fractionation of mixtures of rare earth salts was proposed by Fischer, Dietz and Jübermann.[1] They claimed the existence of 50% differences between neighboring rare earths in the distribution of their chlorides between an aqueous phase and an organic solvent (ether, alcohol or ketone). Although Fischer and later co-workers have given detailed reports concerning the use of solvent methods for the purification of scandium[2] and the separation of hafnium from zirconium,[3] none of the actual data for the rare earths was ever published. Appleton and Selwood[4] reported a separation factor of 1.06 in favor of neodymium for extracting an aqueous solution of neodymium and lanthanum thiocyanates with n-butyl alcohol. Recently Templeton and Peterson[5] substituted n-hexyl alcohol and nitrates in this process and obtained a separation factor of 1.5. The complete data for these distributions must be available before one may judge whether solvent extraction will either compete with or supplement other methods of separating the rare earths. Certainly it is not inconceivable that there may develop some special application for which liquid–liquid extraction will surpass even ion-exchange methods.

The study, for its own theoretical interest, of the distribution of salts between immiscible liquids has been much neglected. S. A. Voznesenskii (Wosnessensky)[6] did some work of this sort in connection with the investigation of electrolytic cells involving non-aqueous solvents. The only recent reports appear to be those of Nachtrieb, Conway and Fryxell[7] on the distribution of ferric chloride between isopropyl ether and aqueous hydrochloric acid solutions,

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[1] Fischer, Dietz and Jübermann, *Naturwissenschaften*, **25**, 348 (1937).

[2] Fischer and Bock, *Z. anorg. allgem. Chem.*, **249**, 146 (1942).

[3] Fischer and Chalybaeus, *Z. anorg. Chem.*, **255**, 79 (1947), and Fischer, Chalybaeus and Zumbusch, *ibid.*, **255**, 277 (1948).

[4] Appleton and Selwood, THIS JOURNAL, **63**, 2029 (1941).

[5] Templeton and Peterson, *ibid.*, **70**, 3967 (1948).

[6] Wosnessensky, *Z. physik. Chem.*, **104**, 46 (1923), and **115**, 405 (1925); Voznesenskii and Chmutov, *J. Russ. Phys.-Chem. Soc.*, Chem. Part, **57**, 343 (1925).

[7] Nachtrieb and Conway, THIS JOURNAL, **70**, 3547 (1948), and Nachtrieb and Fryxell, *ibid.*, **70**, 3552 (1948).

and that of Rothschild, Templeton and Hall[8] concerning thorium nitrate, water and various alcohols and ketones.

In this paper a study has been made of the distribution of lanthanum, cerous, praseodymium, neodymium and samarium nitrates between water and *n*-hexyl alcohol.

Experimental

Materials.—*n*-Hexyl alcohol (Eastman Kodak Co. Practical grade) was distilled twice through a column of about four theoretical plates, the middle fraction only being retained after each distillation. The product had a boiling range of 0.2°.

Lanthanum, cerous and neodymium nitrates were purchased from A. D. MacKay as the C. P. hexahydrates. Praseodymium nitrate was purchased from the Fairmount Chemical Co. as the C. P. hexahydrate.

Fairmount Chemical Co. "Pure" samarium oxide was used to prepare the nitrate hexahydrate. This was the most important single salt in establishing the trend of extractability with increasing atomic number; it is considered that the purity was sufficient at least for this purpose.

Probably all the nitrates contained a slight amount of excess nitric acid. For purposes of comparing extractibilities, a slight impurity of the alcohol would not be critical, since the same batch was used for all measurements.

Procedure.—All the systems were agitated in a water-bath at 25 ± 0.05°. In all cases at least twenty-four hours was allowed for the attainment of equilibrium. The only quantity measured was the weight percentage of oxide in each phase; this was done by direct ignition of a solution sample. Within a series of measurements, each system after the first was prepared by diluting the previous system with water. In the other cases, as indicated in Table I, the equilibrium was approached from lower solution concentrations. The size of all analytical solution samples was about one gram.

The mole fractions recorded in Table I were calculated on the assumption that the solvents were completely immiscible, that the salt was completely ionized in the aqueous phase, and that it was a single un-ionized molecule in the alcohol phase. From this it follows that

$$X'_{\mathrm{R}^{3+}} = \frac{P'}{4P' + \left(\frac{\mathrm{R_2O_3}}{2M'}\right)\left[100 - 2\left(\frac{\mathrm{R(NO_3)_3}}{\mathrm{R_2O_3}}\right)P'\right]} \qquad (1)$$

and

$$X''_{[\mathrm{R(NO_3)_3}]} = \frac{P''}{P'' + \left(\frac{\mathrm{R_2O_3}}{2M''}\right)\left[100 - 2\left(\frac{\mathrm{R(NO_3)_3}}{\mathrm{R_2O_3}}\right)P''\right]} \qquad (2)$$

where P is the weight percentage of R_2O_3 in a phase; X is the mole fraction of the subscript species; M is the molecular weight of the solvent; the singly primed quantities are for aqueous and the doubly primed ones for alcoholic phases; and the other symbols are chemical factors. In Fig. 1, $X''_{[\mathrm{R(NO_3)_3}]}$ has been plotted against $X'_{\mathrm{R}^{3+}}$ on a log–log scale.

TABLE I

DISTRIBUTION OF RARE EARTH NITRATES BETWEEN WATER AND *n*-HEXYL ALCOHOL AT 25 ± 0.05°

Weight % oxide Aqueous phase	Weight % oxide Alcohol phase	$X'_{\mathrm{R}^{3+}}$	$X''_{[\mathrm{R(NO_3)_3}]}$
LANTHANUM NITRATE, C. P.			
28.6[a]	2.36	0.0570	0.0153
27.4	1.575	.0529	.0101
26.15	1.05	.0486	.0067
24.85	0.73	.0449	.0046
23.5	.52	.0410	.0033
22.1	.35	.0373	.0022
21.2	.29	.0350	.0018
CEROUS NITRATE, C. P.			
30.3[a]	2.87	0.0624	0.0186
29.57	2.34	.0595	.0150
28.5	1.70	.0559	.0108
27.57	1.28	.0526	.0081
26.2	0.85	.0483	.0054
24.47	.57	.0440	.0036
22.83	.34	.0387	.0021
21.5	.26	.0352	.0016
PRASEODYMIUM NITRATE, C. P.			
28.75[a]	2.71	0.0565	0.0174
28.7[a]	2.68	.0565	.0172
28.4[a]	2.36	.0554	.0151
26.05	1.43	.0480	.0090
25.4	1.09	.0456	.0068
25.35[a]	0.99	.0455	.0062
23.9	.74	.0415	.0046
22.6	.51	.0380	.0032
21.3	.35	.0348	.0022
20.25	.25	.0324	.0016
NEODYMIUM NITRATE, C. P.			
30.45[a]	5.59	0.0611	0.0366
29.80	5.10	.0587	.0332
29.23	4.32	.0570	.0278
28.80	3.78	.0551	.0241
27.7	2.64	.0515	.0166
25.2	1.16	.0440	.0071
23.0	0.60	.0380	.0037
22.3	.52	.0363	.0032
21.25	.35	.0338	.0021
19.8	.25	.0303	.0015
18.2	.15	.0270	.0009
SAMARIUM NITRATE, PURE			
30.2[a]	5.88	0.0575	0.0371
28.0	3.33	.0502	.0204
25.1	1.37	.0418	.0082
22.7	0.64	.0357	.0038
20.6	.38	.0310	.0022
18.6	.20	.0264	.0012

[a] Equilibrium approached from lower solution concentrations; all others approached from above.

Discussion

There is seen to be a regular increase in the extractability of a rare earth nitrate into *n*-hexyl alcohol with increasing atomic number, beginning with cerium and extending at least to samarium. This has not, however, been demonstrated for the higher members of the series. The relation of cerous, praseodymium and neodymium nitrates rules out any even–odd variation. The surprising feature is that cerous nitrate is apparently

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[8] Rothschild, Templeton and Hall, *J. Phys. Colloid Chem.*, **52**, 1006 (1948).

less extractable than lanthanum nitrate. This is an argument against attributing these variations simply to the lanthanide contraction.

Quill and Robey[9] measured the solubility of these same nitrate hexahydrates in water. Finding a sharp increase in solubility in going to cerium from lanthanum as compared to the more gradual decrease after cerium, they concluded that the solubility in water was "not simply related to the atomic number." Other factors being constant, cerous nitrate, being the most soluble in water, would tend to be least extracted into the alcohol. It is possible that the ionic size is an important factor in all cases, and that the jump between lanthanum and cerium is primarily due to some other cause.

Straight lines have been drawn in Fig. 1, although a slight upward curvature might be justified in the cases of lanthanum and cerium. A linear plot indicates the existence of an empirical expression *for pure salt solutions* of the form.

$$X''_{[R(NO_3)_3]} = (\text{constant})\cdot(X'_{R^{3+}})^{A_R} \qquad (3)$$

This behavior is analogous to that found for the distribution of thorium nitrate between water and organic solvents.[8] Equations (1) and (2) are based upon the mechanism

$$\underset{\text{(aqueous phase)}}{R^{3+} + 3NO_3^-} \rightleftarrows \underset{\text{(alcoholic phase)}}{[R(NO_3)_3]}$$

The applicable equilibrium expression is

$$\frac{X''_{[R(NO_3)_3]}}{X'_{R^{3+}}(X'_{NO_3^-})^3} \times \frac{f''_{[R(NO_3)_3]}}{f'_{R^{3+}}(f'_{NO_3^-})^3} = K_R \qquad (4)$$

where the f's are activity coefficients. Equations (3) and (4) are quite similar in form since in these solutions the nitrate concentration is exactly proportional to the cation concentration. Unfortunately, there are no available activity data for either aqueous or alcohol solutions of these nitrates with which to test equation (4).

It must be emphasized that no concrete proof of the validity of the above mechanism is presented herein. It has been borrowed by analogy from the case of thorium nitrate[8,10] (where a justification for it was attempted) because of the need of a method for comparing the extractibilities on a mole basis. The fact that all the slopes A_R in Fig. 1 are between 4.3 and 4.8, near to the number of ions which the salt yields in aqueous solution, may indicate that the mechanism is at least reasonable.

Butler, Thomson and Maclennan[11] give the solubility of n-hexyl alcohol in water as 0.624 wt. % at 25°, but state that no suitable method for analyzing the alcohol-rich layer existed at that time. Ginnings and Weber[12] conspicuously omitted n-hexyl alcohol in their work on ten other hexanols. The Karl Fischer method[13] has been used by the author to determine the solubility of water in n-hexyl alcohol as 7.4 wt. % at 25°. Thus the layers are not immiscible as assumed for plotting the data. However, the author has used n-hexyl alcohol in making continuous practical extractions of both thorium[14] and rare earth nitrates[5] without visible loss of alcohol. This is true because the alcohol is so much less soluble in the aqueous phase than *vice versa* and the alcohol in continuous use stays saturated with water.

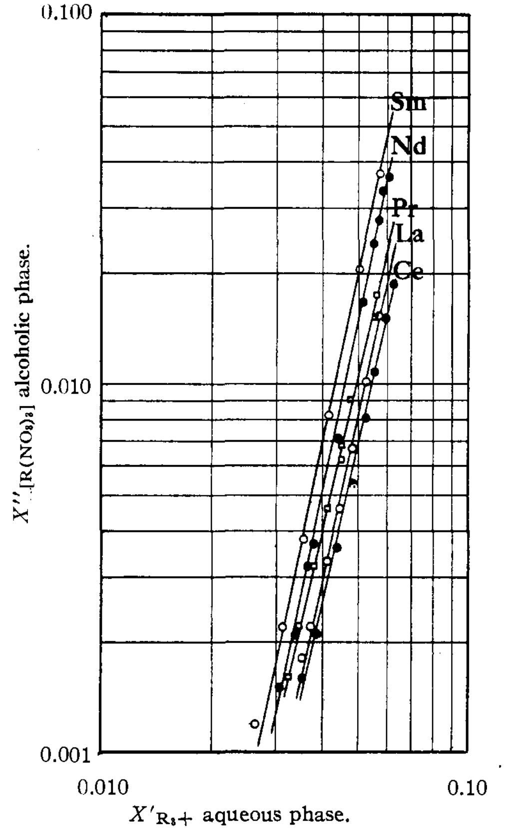

Fig. 1.—Isotherms for distribution of rare earth nitrates between water and n-hexyl alcohol at 25°: ○, La, Sm; ●, Ce, Nd; □, Pr.

If one admits the suggested three-power dependence of $X''_{[R(NO_3)_3]}$ on the aqueous nitrate concentration, the greatest source of error in this study would seem to be the possibility of excess nitric acid in the nitrate crystals. The precision of the results for the most dilute alcohol solutions is quite low, since all solution samples were about one gram. Thus this study seems to exhaust the possibilities of the present gravimetric method. Radioactive tracers might facilitate the study of these distributions at much lower concentrations.

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[9] Quill and Robey, THIS JOURNAL, **59**, 2591 (1937).

[10] Templeton, Rothschild and Hall, "Thorium Nitrate III," *J. Phys. Colloid Chem.*, in press (1949).

[11] Butler, Thomson and Maclennan, *J. Chem. Soc.*, 674 (1933).

[12] Ginnings and Weber, THIS JOURNAL, **60**, 1388 (1938).

[13] Mitchell and Smith, "Aquametry," Interscience Publishers, New York, N. Y., 1948.

[14] C. C. Templeton, Ph.D. Thesis, University of Wisconsin, 1948.

It would seem in point to study the distribution as a function of cation concentration at constant nitrate concentration and *vice versa*, especially if appropriate activity data become available. However, for a practical extraction the total nitrate concentration is hardly a process variable since it must necessarily be high for a practical extent of extraction into the alcohol.[15] A more pertinent consideration is the variation of the separation factor, α, of two cations with the ratio of their concentrations at constant nitrate concentration.

From the definition of the separation factor, it follows that the ratio of corresponding ordinates in Fig. 1 should be the theoretically attainable separation factor for an aqueous cationic ratio of unity and some particular total solute concentration. For the neodymium/lanthanum case, the ratio values are 1.70 and 1.88, respectively, for values of 0.035 and 0.060 on the abscissa. Thus for a constant neodymium/lanthanum ratio, there seems to be no great change of efficiency with total solute concentration. Templeton and Peterson[5] experimentally obtained $\alpha = 1.5$ under the conditions

$$X'_{\mathrm{Nd^{3+}}} \cong X'_{\mathrm{La^{3+}}} \cong 0.03 \text{ and } X'_{\mathrm{NO_3^-}} \cong 0.18.$$

To test the efficiency at a low neodymium/lanthanum ratio, a new measurement was made

Nd_2O_3, aqueous, % of total oxides	5.50
Nd_2O_3, alcohol, % of total oxides	7.34

$$X'_{\mathrm{Nd^{3+}}} = 0.0028 \qquad X'_{\mathrm{La^{3+}}} = 0.049$$

$$X'_{\mathrm{NO^{3+}}} = 0.156 \qquad \alpha = 1.36$$

Thus α changes only slightly over the range of practical working conditions.

The present data would seem to be sufficient for the planning of a flow separation process. The smallest flow system, if designed for complete separation, would be at least on a semi-pilot-plant scale and would involve considerable effort and amounts of material. However, because of the high concentrations inherently involved, the chief promise of this technique is in the working of large quantities with relative simplicity.

Summary

1. Data have been determined for the distribution of lanthanum, cerous, praseodymium, neodymium and samarium nitrates between water and *n*-hexyl alcohol at 25°.

2. Cerous nitrate is less extractable from water by *n*-hexyl alcohol than is lanthanum nitrate but for the other rare earths investigated there is an increased extractability into the alcohol with increasing atomic number.

3. There appear to be large enough differences in extractability for the development of a practical separation process. The separation factors change only slightly over the range of practical concentrations. Such a process would necessitate the handling of relatively large amounts of material.

ANN ARBOR, MICHIGAN RECEIVED JANUARY 5, 1949

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[15] The yield is easily recovered since even a concentrated alcohol solution will surrender all its nitrate to an equal volume of water.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Reducing Powers of Sugars under Equivalent Conditions in a Carbonate Buffered Cupric Tartrate Micro Reagent of Low *p*H

BY LAWRENCE J. HEIDT, F. WILLIAM SOUTHAM, JEAN D. BENEDICT AND MAYNARD E. SMITH[1]

The method devised by P. A. Shaffer, A. F. Hartmann and M. Somogyi[2] for estimating reducing sugars is one of the most sensitive and reliable ways to follow the rates of hydrolysis of sugars and glycosides.[3] Shaffer and Somogyi have studied the method in great detail and have given many precautions and the reasons for them in order to insure the proper use of the method. But they recommend a copper reagent, SS 50, that is at a *p*H, about 9.3, where the yield of cuprous oxide is sensitive to slight changes in the *p*H of the reagent. This necessitates frequent recalibration of each batch of the reagent and great care in reproducing the experimental conditions in order to obtain reliable results. We have restudied the method and have made certain changes which have improved the yields of cuprous oxide and the reliability of the method especially in inexperienced hands. We have determined the reducing powers of sixteen sugars under equivalent conditions and have found that the moles of cuprous oxide produced per mole of sugar differ in a systematic way with differences in the configuration and structure of the sugars.

Materials.—The sugars were all snow-white crystalline specimens over 99% pure. Most of them were anhydrous crystals, but the L-rhamnose and lactose were monohydrates, the melibiose was a dihydrate, and the D-glucosamine was crystallized as the hydrochloride. Many

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[1] Mr. Southam did most of the experimental work presented in this article. Mrs. Benedict and Mr. Smith did some of the preliminary work. Mrs. Benedict's work is given in her Master's Thesis, September, 1947, Department of Chemistry, M. I. T., Cambridge, Mass.

[2] (a) P. A. Shaffer and A. F. Hartmann, *J. Biol. Chem.*, **45**, 377 (1920-21); (b) P. A. Shaffer and M. Somogyi, *ibid.*, **100**, 695 (1933); (c) M. Somogyi, *ibid.*, **70**, 599 (1926), **117**, 771 (1927), and **160**, 61 (1945).

[3] See for example the papers by (a) C. B. Purves and C. S. Hudson, THIS JOURNAL, **59**, 49 and 1170 (1937), and (b) L. J. Heidt and C. B. Purves, **66**, 1385 (1944).