

COMPLEX FORMATION IN THE NEODYMIUM NITRATE-TRIBUTYL PHOSPHATE-WATER SYSTEM*

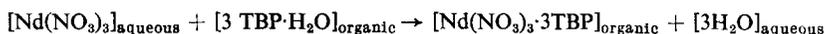
H. BOSTIAN† and M. SMUTZ

Institute for Atomic Research and Department of Chemical Engineering
Iowa State University, Ames, Iowa

(Received 26 September 1963)

Abstract—The solvent extraction system, neodymium nitrate-tributyl phosphate-water, was studied to obtain information on the nature of solvent-solute complex formation. Infra-red spectra of the organic phase and composition and weight measurements made with equilibrium experiments led to three primary conclusions:

- (1) Complexing takes place at the P=O bond on the solvent molecule.
- (2) Dependence of extraction on solvent structure variation suggests that the complex is formed by weak inter-molecular attractions depending on dipole effects.
- (3) The reaction for complex formation can be represented approximately by:



over the entire concentration range, from dilute to saturated.

The latter information may be useful in devising equilibrium data prediction methods needed for extraction process design for fractionating the lanthanides on a macroscopic scale.

Additional data were obtained on tributyl phosphate synthesis with different butyl alcohols; water solubilities, refractive indices and infra-red spectra of the synthesized tri-n-, tri-iso, and tri-sec-butyl phosphates were obtained. The tri-tert-butyl phosphate could not be synthesized, probably due to steric effects.

THE lanthanides or rare earths have been separated from each other by fractional crystallization, fractional precipitation, and recently by ion exchange.⁽¹⁾ The decreasing cost of performing these separations is beginning to make this series of elements attractive as a source of individual metals rather than as mixtures of rare-earth compounds as they have been used in the past. The pure elements have unique nuclear and structural properties.

The research discussed in this article was conducted to gain fundamental knowledge on a system proposed for separating adjacent lanthanides by solvent extraction. Such advantages as continuous processing and the ability to recover the solvent have spurred research in this area. The present work is concerned with the nature of complex formation between a rare-earth nitrate, neodymium nitrate, and a solvent that demonstrates good selective extraction for rare-earth nitrates, tributyl phosphate.

* Contribution No. 1393. Work was performed in the Ames Laboratory of the U.S. Atomic Energy Commission.

† Presently with the Applied Mathematics Division, Esso Research and Engineering Company, Madison, New Jersey.

⁽¹⁾ J. E. POWELL and F. H. SPEDDING, *Chem. Engng. Progr. Symposium Series 24*, **55**, 101 (1959).

Effective utilization of solvent extraction procedures demands accurate design procedures; a better understanding of the nature of the solvent-solute interaction sought in this research may provide keys to developing and simplifying design procedures.

A simplified system, neodymium-tributyl phosphate-water, was used. An actual process may require other secondary compounds to enhance the separation but would confuse a study of the solvent-solute effect. Three different but interrelated studies were performed:

- (1) In one area of experimental work, infra-red spectra were obtained on the organic phase of the system using tri-n-butyl phosphate.
- (2) Secondly, equilibrium data were obtained using tri-normal-, tri-iso-, and tri-secondary-butyl phosphate.
- (3) At the same time the equilibrium data were obtained, a third study was carried out: accurate measurements were made of all materials added to and removed from each equilibrium system.

Additional work was required for synthesis, analysis, and some supporting experiments and measurements.

At first, these studies may seem unrelated but each study, while giving independent information, also supported the others. For example, the infra-red data gave evidence of the location of the solute interaction on the solvent molecule and also indicated that no water was present at saturation of the organic phase. This latter point aided postulating a reaction at saturation, made possible some of the treatment of the weight measurement data, and also aided explanation of the apparent extrapolation of the equilibrium data curves to one point at saturation.

Two over-all themes emerge from the above and other inter-relations.

- (1) First, the different studies taken together provide information about the character and location of the solvent-solute interaction.
- (2) Secondly, the studies give evidence for a specific chemical reaction occurring over a wide concentration range when the organic phase complex is formed.

This latter information may be useful in predicting equilibrium data for design application.

BACKGROUND

In neutral solution, the selectivity that tributyl phosphate exhibits for extracting certain nitrates was interpreted by many authors as a good indication that the formation of a complex is involved when extraction occurs. KNAPP⁽²⁾ also pointed out that only elements with two or less electrons in the d shell immediately under the primary valence shell were extracted as nitrates with tributyl phosphate in neutral solutions. These elements include the lanthanides, hafnium, actinium, thorium, zirconium, scandium, titanium and yttrium.

When extraction of the rare-earth nitrate occurs, it seems probable that the tributyl phosphates and the nitrate groups will be co-ordinated around the rare earth rather than the tributyl phosphate bonding to the nitrate group. This is supported by the fact that the elements neighbouring scandium and yttrium are not extracted

⁽²⁾ L. L. KNAPP, Unpublished M.S. Thesis. Ames, Iowa, Iowa State University of Science and Technology Library (1956).

as nitrates by tributyl phosphate. It does not seem possible that these neighbouring elements could effect tributyl phosphate bonded through the nitrate group in such a different manner as to cause them not to be extracted, while their neighbours are. Therefore, the rare earth and the tributyl phosphate must form a close association in order that the subtle differences of ionic radii and one orbital electron may determine possibility of extraction.

Although scandium, yttrium and the rare-earth nitrates are extracted into tributyl phosphate, there are differences in extractability. Here again, direct co-ordination of tributyl phosphate groups to the metal is indicated to allow the subtle variations in ionic radii to cause differences in the association between the tributyl phosphate and the metal nitrate.

FERNELIUS⁽³⁾ listed scandium, yttrium, and the rare earths as possessing a co-ordination number of six. Consequently the rare-earth nitrate ion with six groups co-ordinated to it could be one entity. MCKAY *et al.*⁽⁴⁾ substantiated the existence of a grouping: a rare earth, three nitrate groups and three tributyl phosphate molecules. Their work was concerned with the dilute concentration range where ideality can be assumed and thermodynamic methods can be easily applied.

Tributyl phosphate has a phosphorus double bond oxygen with electrons available for covalent bonding. Ion-dipole interactions are also possible, for the molecule has a strong dipole moment. The latter was reported by ESTOK and WENDLANDT⁽⁵⁾ as 3.07 Debye units and by RAKOV and ARBUZOV⁽⁶⁾ as 3.05 Debye units. This is approximately two times the dipole moment of water, 1.84 Debye units.

As far as the rare-earths are concerned, the only difference in their electronic configurations is the filling of the $4f$ shell as one progresses to elements of higher atomic number. If one would hope to find bonds involving discrete electrons, this $4f$ shell should be involved in order to give a basis for explaining the slight differences in extractability. However, there are two considerations that make this seem improbable. First, the $4f$ shell is shielded by the outer shells and make these $4f$ electrons unavailable. Secondly, the farther out the shells are, the closer they are together. Since the rare earths have many shells, their outer shells are close together and each additional electron should not have as much "individualism" as an outer electron in an atom of lower atomic number. In other words, it would be difficult to assign specific electrons to a bond model as is done in hybridization in the cobalt and nickel complexes.

In addition to postulating complexes formed in neutral extraction, it is necessary to consider separate mechanisms in some cases of extraction because several elements, zirconium, tantalum, niobium and chromium, can only be extracted into tributyl phosphate in acid solutions. KNAPP⁽²⁾ proposed that these elements are extracted as acids through hydrogen bonding. Hydrogen bonding has also been used to explain the solution of water in tributyl phosphate and also the extraction of nitric acid by tributyl phosphate.

⁽³⁾ G. K. ESTOK and W. W. WENDLANDT, *J. Amer. Chem. Soc.* **77**, 4767-9 (1955).

⁽⁴⁾ H. A. C. MCKAY, K. ALCOCK and D. SCARGILL, Report AERE C/R-1514 (1954).

⁽⁵⁾ W. C. FERNELIUS, *Frontiers in Chemistry* **5**, 53-100 (1948).

⁽⁶⁾ P. I. RAKOV and A. E. ARBUZOV, Bulletin of the Academy of Sciences of the Union of Soviet Socialist Republics, Division of Chemical Sciences, 1950; 237-246, (1950). (Original not available for examination; *Chem. Abstr.* **44**, 8713h, (1950).

ANALYTICAL AND SUPPORTING WORK

Sample preparation and analysis. The materials used in the experiments included 99+ per cent neodymium oxide supplied by the Chemistry Division of Ames Laboratory, commercial grade tributyl phosphate (tri-n-), and carefully purified tri-n-, tri-iso-, and tri-sec-butyl phosphates. Reagent grade chemicals were used for analysis and synthesis.

The equilibrium phases were obtained by contacting aqueous nitrate solutions and tributyl phosphate. Aqueous neodymium nitrate solutions were prepared by dissolving the oxide in nitric acid and repeatedly boiling and then reconstituting with water until essentially neutral. The tributyl phosphates were pre-equilibrated with water before using them. This required prolonged shaking, but when done before contacting with neodymium nitrate solution, it allowed equilibrium in the latter step to be reached more easily. The neodymium nitrate equilibrium phases were then prepared by shaking solvent with nitrate solution. Fifty ml separatory funnels were used when accurate weighings were made. Saturated aqueous phases were prepared by evaporating nitrate solution beyond crystallization. Nearly saturated equilibrium phases were obtained by contacting saturated nitrate solution and solvent for several days with nitrate crystals present. The high viscosity of the phases presented difficulty during this latter contacting; equilibrium was approached closely but the final aqueous phase was not quite saturated.

Oxalate precipitation from aqueous solution was used to analyse the phases for neodymium. Before precipitation, the organic phases were stripped with water and dilute nitric acid. The aqueous solutions were then precipitated, filtered and the residue was fired and weighed.

Tributyl phosphate synthesis. Tributyl phosphates were synthesized from the different butyl alcohols using the reaction: $3C_4H_9OH + POCl_3 + 3 \text{ Pyridine} \rightarrow (C_4H_9O)_3PO + 3 \text{ Pyridine} \cdot HCl$. Several methods have been suggested,⁽⁶⁻¹²⁾ and the above was chosen for its convenience and its high yield of tertiary phosphate. The reaction product was subjected to an extensive purification procedure based on recommendations of LANE⁽¹³⁾ and KENNEDY and GRIMLEY.⁽¹⁴⁾ This procedure is discussed fully in the dissertation upon which this paper is based.⁽¹⁵⁾

Drawings of molecular models of the four tributyl phosphates are shown in Fig. 1. The compactness of the tri-tertiary-butyl phosphate model suggests that this synthesis would be difficult, and repeated trials to make tri-tertiary butyl phosphate were unsuccessful. Successful synthesis was achieved for the other tributyl phosphates.

Some properties of the tributyl phosphates. Several measurements were made on the pure dry tributyl phosphates that were synthesized. Karl Fisher titrations performed by the Chemistry Division of Ames Laboratory indicated that all the tributyl phosphates exhibited a water solubility giving very nearly a mole/mole ratio of water to tributyl phosphate. The mole ratios obtained were: tri-n-butyl phosphate, 0.906; tri-iso-butyl phosphate, 0.876; and tri-sec-butyl phosphate, 1.175. The commercial grade tri-n-butyl phosphate gave a mole ratio of 0.922.

Refractive index measurements were also made on the synthesized dry solvents. At 18°C, n_D values were: tri-n-, 1.4248, tri-iso-, 1.4201; tri-sec-, 1.4199. At 20°C, n_D values were: tri-n-, 1.4240; tri-iso-, 1.4194; tri-sec-, 1.4191. A Bausch and Lomb modified Abbé type refractometer, model 33-45-02 was used.

Although not interpreted in this present work, infra-red spectra were procured for the synthesized dry solvents and are presented in Fig. 2. For these spectra and those presented later, a Perkin-Elmer Infra-red Recording Spectrophotometer, Model 13, with Servofrax arsenic trisulphide cell windows,

⁽⁷⁾ L. L. BURGER, USAEC Report HW-40910 (1955).

⁽⁸⁾ P. KARRER, *Organic Chemistry* (2nd English) Ed. Elsevier, New York (1946).

⁽⁹⁾ G. M. KOSOLAPOFF, *Organophosphorus compounds*. J. Wiley, New York (1950).

⁽¹⁰⁾ T. MILOBENDSKI and A. SACHNOWSKI, *Chem. Polski* **15**, 34-7 (1917); *Chem Abstr.* **13**, 28652 (1919).

⁽¹¹⁾ K. MURAKAMI, *Chemistry of High Polymers* (Japan) **7**, 188-93 (1950); *Chem. Abstr.* **46**, 419i (1952).

⁽¹²⁾ C. R. NOLLER and G. R. DUTTON, *J. Amer. Chem. Soc.* **55**, 424 (1933).

⁽¹³⁾ E. S. LANE, Report AERE C/M-140 (1957).

⁽¹⁴⁾ J. KENNEDY and S. S. GRIMLEY, Report AERE CE/R968 (1956).

⁽¹⁵⁾ H. BOSTIAN, Ph. D. Thesis, Ames, Iowa, Iowa State University of Science and Technology Library (1959)

was used. The dotted line at 3700 cm^{-1} indicates the vapour phase OH vibrational frequency. Since little intermolecular interaction takes place in the vapour phase, this represents a nearly pure OH vibrational frequency.

INFRA-RED STUDIES

Infra-red spectra were procured to obtain evidence of interaction at specific bonds of the tributyl phosphate molecule. Commercial grade solvent and the technique mentioned in the previous section were used.

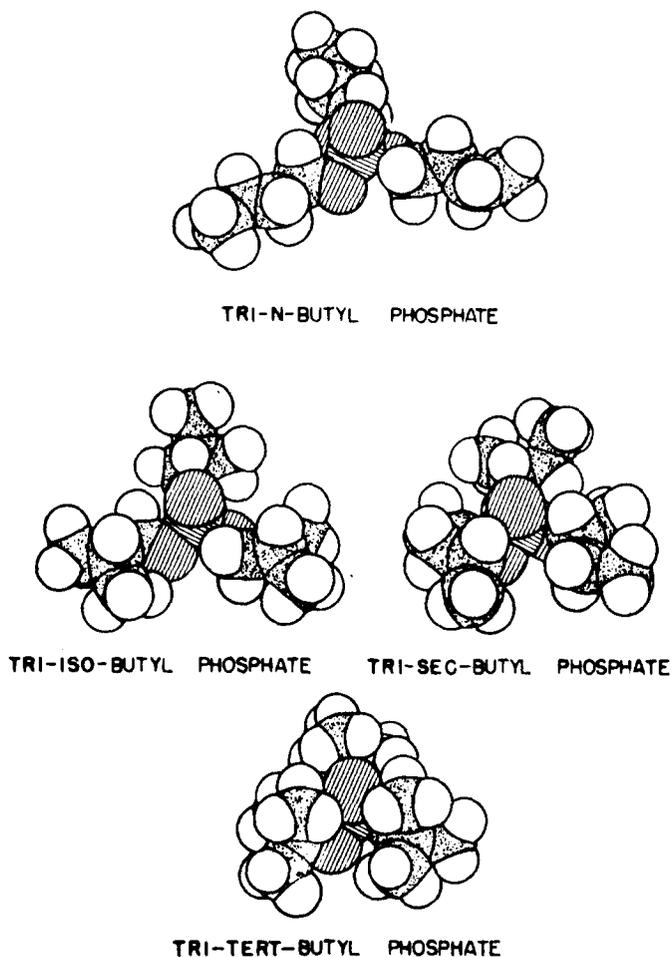


FIG. 1.—Molecular models of tributyl phosphate.

Vibrational frequencies of bonds behave analogously to simple mass and spring systems. The mass and spring system's normal frequency is $\nu = (1/2\pi\sqrt{k/m})$, where k is the spring constant, and m is the mass. An increase in the mass will cause a decrease in the frequency. Similarly, an interaction at a bond causes a decrease in the vibrational frequency of the bond (or an increase in wavelength).

The spectra shown in Fig. 3 exhibit shifted frequencies for both the OH and

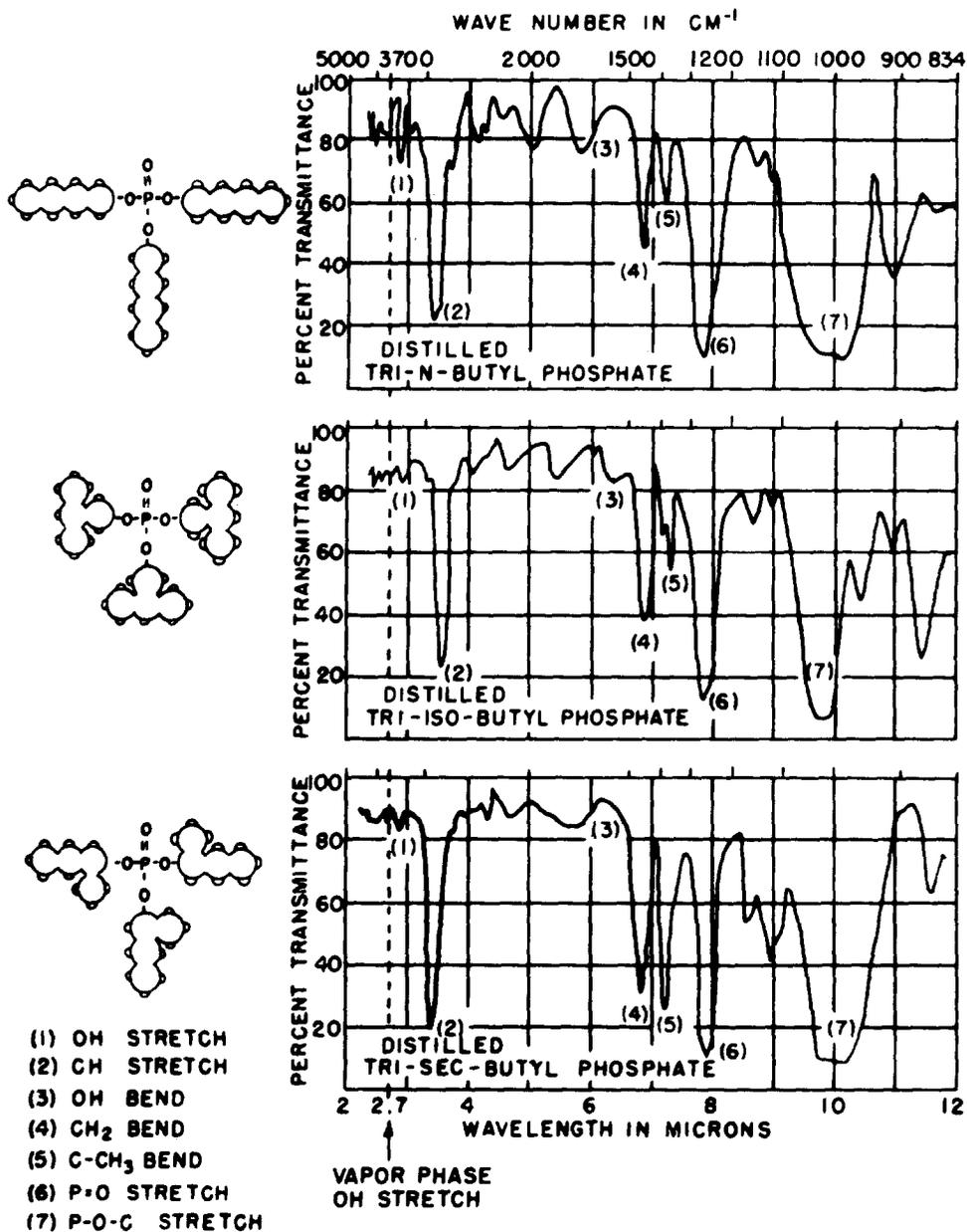


FIG. 2.—Infra-red spectra of synthesized tributyl phosphates.

sample is very near saturation. Here, m refers to molality as moles Nd per 1000 g of tributyl phosphate and water in the organic phase.

The shifted $\text{P}=\text{O}$ frequency can be interpreted as evidence of an interaction between the neodymium nitrate and the tributyl phosphate at the $\text{P}=\text{O}$ bond because the shifted frequency increases in intensity as the nitrate concentration is increased. The valley on the left does not disappear because this is due to both the uncomplexed $\text{P}=\text{O}$ stretch and to the symmetrical NO_2 stretching frequency which is growing in.

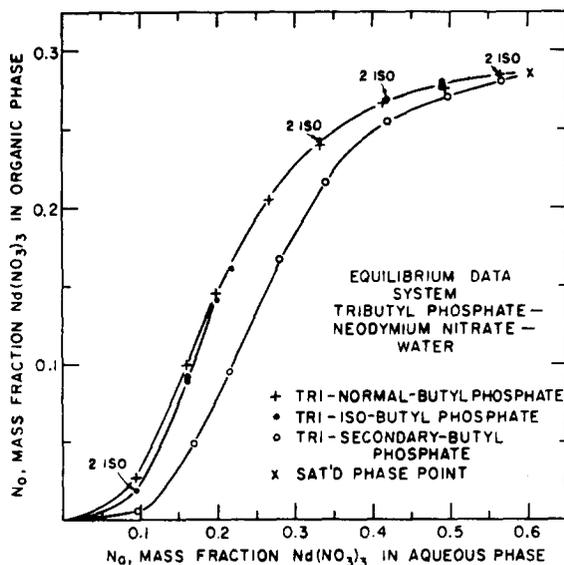


FIG. 4.—Equilibrium data for $\text{Nd}(\text{NO}_3)_3$.

EQUILIBRIUM DATA

The three solvents that were synthesized were used to obtain equilibrium data for the tributyl phosphate–neodymium nitrate–water system.

If the structural differences and the resulting different dipole moments of the tri-normal-, tri-iso- and tri-secondary-butyl phosphates are important in the solvent solute interaction, this should affect the equilibrium data. The least compact molecule, shown in Fig. 1, tri-n-butyl phosphate, should have the greatest dipole and should form the strongest complex and tri-secondary-butyl phosphate, the most compact molecule, should form the weakest complex. If dipole effects are important, the highest organic phase concentration should be exhibited for the tri-n-solvent for a given aqueous composition and the tri-secondary-solvent should give the most dilute organic phase.

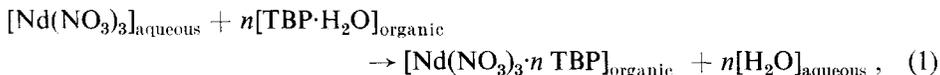
The equilibrium data, plotted in Fig. 4, show this order of decreasing organic phase concentrations from tri-normal- to tri-iso- to tri-secondary-butyl phosphate. Thus, weak intermolecular attractions due to dipole effects seem important, although the difference between the tri-normal- and the tri-iso-curve is not as pronounced as the structural difference would predict.

Another interesting characteristic of the equilibrium data is that they extrapolate to a common point in the high concentration range, a point labelled "saturated phase point." This point represents data obtained by exhaustive contacting of water-equilibrated commercial grade tributyl phosphate with a saturated aqueous solution of neodymium nitrate containing crystals. The organic phase concentration associated with this point differs by less than 5 per cent from the concentration of a solution with a 3/1 mole ratio of tributyl phosphate to neodymium nitrate. The infra-red data showed that there was little water present near saturation so that this experimental saturated organic phase must have contained essentially only tributyl phosphate and neodymium nitrate in very nearly a 3/1 mole ratio. MCKAY *et al.*⁽⁴⁾ also found this ratio in dilute solutions for the composition of the complex between the solvent and solute. The occurrence of this ratio at two extremes of the concentration range leads one to wonder if this ratio and the composition of the complex is not constant over the entire concentration range. The next section supports this conjecture.

MATERIAL BALANCES

A careful accounting of mass was made during procurement of the equilibrium data. These material balance data were used to obtain information concerning the composition of the neodymium complex in organic phases of the mid-concentration range.

Previous data showed several things: the water equilibrated tributyl phosphate can be represented closely by $\text{TBP}\cdot\text{H}_2\text{O}$, where TBP refers to tributyl phosphate; the organic phase contains no water at saturation; and the mole ratio of TBP to $\text{Nd}(\text{NO}_3)_3$ in the organic phase at saturation is approximately equal to three. Therefore, the complex formation reaction *at saturation* can be represented closely by the following equation:



where $n = 3$. This is identical to MCKAY *et al.*⁽⁴⁾ equation obtained for dilute solutions for various trivalent lanthanides. Since the approximate number, three, occurs at both ends of the concentration range, it seemed that perhaps this value might prevail over the entire range.

The prevalence of a constant n was checked in the following manner. Careful weighings were made before each addition to and after each withdrawal from the separatory funnel used to obtain equilibrium phases. Also, all phases were analysed for neodymium, including the residue of mixed phases adhering to the inside of the funnel after draining. These weights and compositions gave enough information to allow two independent determinations of the amount of water transferred between phases.

If the stoichiometry of the above saturation reaction with n unknown is also counted as available information, a third way of determining the water transfer can be devised. It should be noted, however, that up to now, only enough evidence has been presented in this paper to justify using this approximate reaction at saturation and then with $n = 3$. Actually, this third method was devised to see if the saturation reaction would predict the same n for other concentrations as the methods depending only on experimental data.

TABLE 1.—CALCULATED VALUES OF n , MOLES OF WATER DISPLACED FROM ORGANIC PHASE PER MOLE OF $\text{Nd}(\text{NO}_3)_3$ EXTRACTED BY THE ORGANIC PHASE (n_1 CALCULATED USING WEIGHTS AND COMPOSITIONS OF PHASES; n_2 CALCULATED USING WEIGHTS AND COMPOSITIONS OF ADHERING MATERIAL; n_3 CALCULATED USING ASSUMED REACTION). MOLALITY REFERS TO MOLES Nd PER 1000 g WATER AND TRIBUTYL PHOSPHATE

Organic molality	Aqueous molality	n_1	n_2	n_3
From SCHOENHERR's data with commercial tributyl phosphate ⁽¹⁷⁾				
0.231	0.502	3.69	Adhering	5.6226
0.658	0.947	2.997	weight	6.3350
0.723	1.026	2.889	fractions	3.4022
0.916	1.401	2.835	not	3.0242
0.990	1.663	2.886	measured	2.8348
1.047	1.885	2.707		2.9653
From data with tri-n-butyl phosphate				
0.5280	0.7760	5.3624	Adhering	5.300
0.7530	1.075	6.5987	weight	6.343
0.9449	1.5097	4.9743	fractions	4.919
1.1398	2.5857	3.3736	not	3.329
1.2184	3.6110	3.1372	measured	3.111
From data with tri-iso-butyl phosphate				
0.5119	0.7822	6.2463	Adhering	6.284
0.7471	1.0741	7.5476	weight	7.805
0.9525	1.5133	5.9417	fractions	5.690
1.1307	2.5674	5.2469	not	5.209
1.2133	3.6131	4.2812	measured	3.199
From data with tri-sec-butyl phosphate				
0.3272	0.8459	5.2190	Adhering	5.080
0.5640	1.1378	4.8991	weight	4.973
0.8138	1.5550	6.4650	fractions	6.397
1.0872	2.6018	4.3059	not	4.343
1.1800	3.6611	3.0449	measured	3.097
From data with tri-n-butyl phosphate				
0.0831	0.3095	-11.6674	-2.8692	-14.1427
0.3306	0.5719	-3.4117	0.7964	-3.6556
0.5149	0.7463	-0.1789	1.7761	-0.1570
0.7818	1.1029	1.3260	1.3253	1.1134
0.9571	1.5169	2.0533	2.4677	2.1018
1.0968	2.1491	2.5153	2.2157	2.4461
1.1604	2.9461	2.8802	1.4670	2.9199
1.2071	3.9665	2.8453	2.2458	2.8191

⁽¹⁷⁾ R. SCHOENHERR, Private communication. (1959).

Table 1 Contd.

Organic molality	Aqueous molality	n_1	n_2	n_3
From data with tri-iso-butyl phosphate				
0.0580	0.3119	20.0956	-1.5251	18.4812
0.3065	0.5755	3.8442	-4.0639	3.3581
0.5104	0.7505	0.6588	-0.0276	0.6511
0.5859	0.8320	3.2863	1.0174	3.6852
0.9718	1.4973	3.8551	2.0615	3.8544
1.1111	2.1735	2.7016	1.6538	2.6988
1.1584	2.0989	3.2611	2.0601	3.2487
1.2076	3.0766	2.5586	2.0771	6.2502
0.0593	0.3181	9.5906	5.8458	11.9746
0.2992	0.575	3.1911	4.1632	3.1114
0.5014	0.7530	3.2517	3.5273	3.1127
0.7835	1.0984	3.9548	2.9737	3.7917
0.9663	1.4966	3.2615	2.6864	3.3460
1.1132	2.1627	3.3348	2.8179	3.2976
1.1774	2.9187	3.1191	2.6870	3.0959
1.2179	3.9558	3.1496	2.6570	3.1170
From data with tri-sec-butyl phosphate				
0.0178	0.3253	25.0660	25.8625	24.608
0.1515	0.6224	5.3560	7.1933	4.7265
0.3141	0.8228	4.0197	3.9463	3.9242
0.6068	1.1794	3.5668	3.4188	3.4172
0.8278	1.5594	3.6936	3.4313	3.7980
1.0335	2.2059	7.3445	3.5803	3.0538
1.1223	2.0683	2.2644	3.3580	3.5042
1.1842	3.9696	3.1696	3.4703	5.1380

When the three methods were applied, comparable values of n were calculated and this means that the saturation reaction holds at all concentrations. These data are presented in Table 1, and a detailed description of the application of the above methods is given in BOSTIAN'S thesis.⁽¹⁵⁾

Experimental precision of these data was not expected to be good because the amount of water transferred is small compared to the total system weight. Also, incomplete precipitation in the analytical methods would become very significant at lower concentrations and would give very high values of n . This is generally true in the data.

On examining the data with these things in mind, values of $n = 3$ seem highly probable at mid and high concentrations. This value is also probable at low concentrations because the experimental values are generally higher.

Combining these results with the more accurate low concentration data of MCKAY *et al.*,⁽⁴⁾ it appears that the following reaction is approximately adhered to over the entire concentration range:



CONCLUSIONS

The information in this study of the neodymium nitrate-tributyl phosphate-water extraction system leads to these primary conclusions:

- (1) Complexing takes place at the P=O bond on the solvent molecule.
- (2) Dependence of extraction on solvent structure variation suggests that the complex is formed by weak intermolecular attractions depending on dipole effects.
- (3) The reaction for complex formation can be represented approximately by Equation (2) over the entire concentration range.

This latter information may be useful in devising equilibrium data prediction methods needed for extraction process design.