626. *Solvent Extraction Studies. Part I. Nitric Acid Species in "Dibutylcarbitol" (Diethylene Glycol Dibutyl Ether).*

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The extraction coefficient for the partition of nitric acid between water and dibutylcarbitol has been measured up to an equilibrium aqueous-phase concentration of 7M. From the changes in volume of the organic phase, it has been found that the species extracted is HNO_3,H_2O. A consideration of the thermodynamic partition coefficient, together with direct chemical evidence and infrared absorption spectra, shows that a hydrogen-bonded complex is formed between the nitric acid monohydrate and the solvent. At high nitric acid concentrations in the organic phase (above ~3M), addition of nitric acid takes place at a second ethereal oxygen atom of dibutylcarbitol.

DURING work [1] on the ion-exchange behaviour of solutions of quadrivalent plutonium in dibutylcarbitol (diethylene glycol dibutyl ether), it became necessary to obtain information on the behaviour of nitric acid in this solvent. The results have shown that the extraction of this acid is not a simple case of distribution between two immiscible solvents, but that the complex-forming property of the solvent is an important factor.

EXPERIMENTAL

Reagents.—Suitable quantities of nitric acid of analytical grade were diluted some time before use and allowed to cool to room temperature (~21°), at which all experiments were

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[1] Tuck and Welch, unpublished work.

performed. Acid concentrations were determined by titration against standard sodium hydroxide solution.

Dibutylcarbitol was passed slowly down a 12″ column of chromatographic alumina to remove peroxides.[2] The eluate was shaken with sodium carbonate to remove any remaining acidic impurities and then washed twice with water. The final product was stored over anhydrous calcium chloride in a dark bottle.

Measurement of Acidity and Volume Changes.—The changes in both acidity and volume associated with the extraction of nitric acid, were measured in a series of equilibrium experiments. Five ml. of nitric acid of known strength were pipetted into a 10 ml. graduated measuring cylinder; 5 ml. of dibutylcarbitol were then carefully pipetted on to the aqueous phase without disturbing the surface of the latter. The menisci at the liquid–liquid interface and air–dibutylcarbitol surface were immediately noted. The stoppered cylinder was shaken vigorously for 5 min. and left to reach equilibrium; the solutions were stored in the dark during this period in order to minimise peroxide formation. The menisci at equilibrium were read before removal of aliquot parts of each phase for titration against standard alkali. For samples of the organic phase, the aliquot parts (1 ml.) were dissolved in about 25 ml. of neutralised aqueous acetone before titration. Phenolphthalein appears to be the best indicator for use with such mixtures. In all these experiments small corrections were made for slight reductions in total volume due to hold-up of liquid in the stoppered neck of the measuring cylinder. A 100% acidity balance was achieved in practically every experiment.

Density Measurements.—In order to be able to express concentrations of nitric acid in the solvent in molal units, density determinations were made on such solutions. The method was simply to weigh, by difference, the amount of solution held in a calibrated micropipette (capacity 490·2 μl.).

Preparation of Dibutylcarbitol–Nitric Acid Complex.—The existence of a complex of dibutylcarbitol and nitric acid has been investigated, a solution of aqueous nitric acid corresponding to the formula HNO_3,H_2O being used (see Discussion). This solution was added cautiously to pure dry dibutylcarbitol, to the point of exact maximum solubility as found by preliminary experiments, giving a homogeneous solution. Analysis for nitric acid also gave the water content, and hence the amount of dibutylcarbitol by difference (Found: HNO_3, 22; H_2O, 6·3; dibutylcarbitol, 71·7%; a 1 : 1 : 1 *complex* requires HNO_3, 21·2; H_2O, 6·0; dibutylcarbitol, 72·9%). The homogeneous solution was stable for several weeks; solutions in contact with a slight excess of 18·2M-aqueous nitric acid were extremely unstable, decomposing spontaneously after 2—3 hr., with violent evolution of nitrous fumes. The complex remains liquid at −78°, but freezes to a clear solid when placed in liquid nitrogen, melting quickly on warming.

Infrared Spectra.—Changes in the infrared spectrum of dibutylcarbitol as a result of extraction of nitric acid and of complex formation were measured with a Perkin–Elmer single-beam spectrometer.

RESULTS AND DISCUSSION

Extraction Coefficients: Volume Changes.—The main results of the equilibrium experiments are given in Table 1. The values of the extraction coefficient are calculated as:

$$E_{HNO_3} = \frac{\text{molar concentration of } HNO_3 \text{ in organic phase}}{\text{,, \quad ,, \quad ,, \quad aqueous ,,}}$$

The value of E becomes constant above an equilibrium aqueous phase concentration of about 4·2M.

The dependence of the volume change of the organic phase upon the total amount of acid extracted in shown in Fig. 1. A linear relation holds over the whole acidity range studied, and the slope of the graph shows that the solution passing into the organic phase contains 18·1 mmoles of HNO_3 per ml., corresponding to 1·14 g. of HNO_3 per ml. (78·8% nitric acid [3]). This identifies the species extracted as HNO_3,H_2O; a solution of this composition contains 77·8% nitric acid, in good agreement with the value found.

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[2] Dasler and Bauer, *Ind. Eng. Chem.*, 1946, **18**, 52.

[3] "Handbook of Chemistry and Physics," Chemical Rubber Publ. Co., Cleveland, Ohio, 1949, p. 1616.

Sutton[4] found a similar result for the extraction of nitric acid into diethyl ether, by an argument which is complicated by the high solubility of the ether in aqueous nitric acid. It is clear from Fig. 1 that this is not a significant factor in the present work and in fact the volume change for mutual saturation (*i.e.*, nitric acid concentration = 0) fits well with the other results. These conclusions are in agreement with the postulate of the monohydrate as the only stable undissociated species in concentrated aqueous solution of nitric acid,[5] and suggests that it may also exist in dilute solutions.

TABLE 1. *Extraction of nitric acid into dibutylcarbitol.*

Initial aqueous HNO_3 concn. (M)	Final aqueous HNO_3 concn. (M)	Final organic HNO_3 concn. (M)	E_{HNO_3}	Initial aqueous HNO_3 concn. (M)	Final aqueous HNO_3 concn. (M)	Final organic HNO_3 concn. (M)	E_{HNO_3}
0	0	0	—	4·87	3·40	1·71	0·503
0·50	0·48	0·014	0·029	6·18	4·24	2·26	0·546
1·00	0·87	0·096	0·110	7·01	4·83	2·62	0·543
1·61	1·32	0·265	0·200	7·89	5·48	3·01	0·548
1·99	1·58	0·417	0·264	8·95	6·26	3·40	0·544
3·08	2·24	0·85	0·381	10·25	7·27	3·92	0·539
4·01	2·84	1·30	0·457				

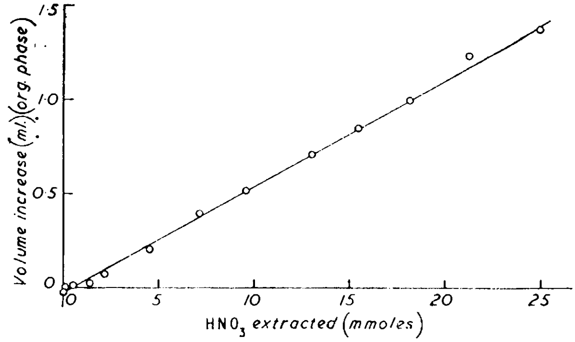

FIG. 1. *Volume changes in dibutylcarbitol due to extraction of nitric acid.*

Density of Dibutylcarbitol Solutions of Nitric Acid.—The experimentally determined densities are given in Table 2. Over the whole acidity range studied, the results are in good agreement with the linear relation, $d = 0{\cdot}885 + 0{\cdot}0388c$, where d is the density of the solution and c the molar concentration of nitric acid. The significance of this linearity is discussed below. Molal concentrations of nitric acid in dibutylcarbitol were calculated from these results.

TABLE 2. *The density of dibutylcarbitol solutions of nitric acid.*

HNO_3 concn. (M)	0	0·27	0·51	1·44	2·40	3·17	4·00
Density (g./c.c.)	0·886	0·892	0·901	0·928	0·970	0·994	1·021

Nitric Acid–Dibutylcarbitol Complex.—The solubility of nitric acid in diethyl ether has been attributed[6] to the formation of a hydrogen-bonded complex $\begin{matrix}\mathrm{Et}\\ \mathrm{Et}\end{matrix}\!>\!\mathrm{O}\cdots\mathrm{H{-}O{-}NO_2}$, although this formula must be regarded as somewhat inadequate since no allowance is made for the hydrate of nitric acid. For the extraction of nitric acid into tri-*n*-butyl phosphate (TBP), it has been shown that the compound TBP,HNO_3 is the prevalent species,[7] although

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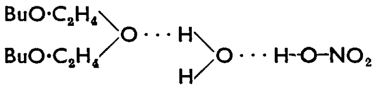
[4] Sutton, U.K.A.E.A. report A.E.R.E. C/R 516.

[5] Gillespie and Millen, *Quart. Rev.*, 1948, **2**, 277; see also Redlich, *Chem. Rev.*, 1946, **39**, 333.

[6] Desmaroux, Dalmon, and Vandoni, *Compt. rend.*, 1942, **214**, 352.

[7] Alcock, Grimley, Healy, Kennedy, and McKay, *Trans. Faraday Soc.*, 1956, **52**, 39.

there is also evidence for TBP,H_2O and TBP,HNO_3,H_2O. Since the nitric acid monohydrate is written[5] as $\genfrac{}{}{0pt}{}{H}{H}\!>\!O \cdots H{-}O{-}NO_2$, it appears that the complex of dibutylcarbitol and nitric acid monohydrate is to be written as doubly hydrogen-bonded:



Infrared absorption spectra show that the absorption peak at 1124 cm.$^{-1}$ due to the ethereal oxygen linkage in dibutylcarbitol is shifted to a wavelength lower by about 20 cm.$^{-1}$ in the complex. Solutions of dibutylcarbitol prepared by solvent-extraction, show a smaller shift in frequency, corresponding to solutions of the complex in pure solvent. The absorption due to the hydroxyl group in nitric acid is absent in such solutions, and in the complex, in agreement with the presence of the hydrate.

Extraction Coefficient: Further Considerations.—As well as the extraction coefficient discussed above, one can equally define a thermodynamic partition coefficient as

$$K_e = m_0\gamma_0/m_u\gamma_u \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

where $m_0\gamma_0$ is the activity of nitric acid in the organic phase and $m_u\gamma_u$ the activity of undissociated nitric acid in aqueous solution. There now seems to be reasonable agreement[5, 8, 9] that the ionisation constant for nitric acid is approximately 21, so that

$$m_u\gamma_u = m_\pm^{\,2}\gamma_\pm^{\,2}/21 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

whence, by substitution into (1), we obtain

$$\gamma_0 = K_e m_\pm^{\,2}\gamma_\pm^{\,2}/21m_0 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (3)$$

This gives a method of measuring the activity coefficient of undissociated nitric acid in dibutylcarbitol. Values calculated on this basis are given in Table 3. (Values of $m_\pm\gamma_\pm$ for aqueous nitric acid are from Landolt–Börnstein[10]; see also McKay.[8]) From these results, one notes that the thermodynamic partition coefficient for high nitric acid concentrations is not constant. It is difficult to believe that the calculated values for γ_0 are in fact correct since they imply a strong dissociation over the whole concentration range. It can be shown that the validity of this argument is not dependent upon the value chosen for the dissociation constant of nitric acid in aqueous solution.

TABLE 3. *Apparent activity of nitric acid in dibutylcarbitol.*

K_e	0·029	0·108	0·193	0·255	0·365	0·436	0·477	0·501	0·505	0·506	0·484	0·475
$m_\pm^{\,2}\gamma_\pm^{\,2}$...	0·122	0·412	1·036	1·584	3·87	7·61	13·26	27·19	41·66	64·4	105·0	185·7
γ_0	0·012	0·022	0·036	0·045	0·0765	0·116	0·166	0·266	0·352	0·464	0·635	0·936

McKay and his collaborators[7] have shown that the extraction of nitric acid into tributyl phosphate is governed by formation of a TBP–nitric acid complex. The experimental evidence discussed above suggests that this treatment should also be applicable to the present system, so that one can write:

$$[\text{Complex}]/[HNO_3,H_2O][\text{Dibutylcarbitol}] = \text{Constant} \quad . \; . \; . \quad (4)$$

In this relation, [complex] is the concentration of the HNO_3,H_2O,DBC species and [dibutylcarbitol] the concentration of uncomplexed solvent. The values given in Table 4 are the total number of mmoles of each species, with [Complex] = $[HNO_3]_{org.}$. The mole ratios calculated in this way have been plotted against the $m_\pm^{\,2}\gamma_\pm^{\,2}$ values given in Table 3

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[8] McKay, *ibid.*, p. 1568.
[9] Hood, Redlich, and Reilly, *J. Chem. Phys.*, 1954, **22**, 2067.
[10] Landolt–Börnstein, " Tabellen," Ergänzungsband II, p. 2145.

(Fig. 2). The resulting straight line (slope = 1 on the log–log plot) shows that equation (4) holds over the greater part of the concentration range studied. Above nitric acid concentrations of about 3M in the organic phase, deviations become appreciable and indeed, above this, negative amounts of free dibutylcarbitol are calculated (see Table 4). There are two possible explanations : either a complex is being formed between dibutylcarbitol and unhydrated HNO_3, or else addition of HNO_3,H_2O is taking place at a second oxygen of an already complexed dibutylcarbitol molecule. For complete formation of the HNO_3,H_2O,DBC complex, the concentration of uncomplexed dibutylcarbitol is obviously zero, so that the negative values found in Table 4 are in fact to be expected if the latter explanation is correct. Further, since there appear to be no deviations from linearity either in the volume increases (Fig. 1) or in the density increases (Table 2) for high nitric acid concentrations, it seems that processes involving nitric acid species other than HNO_3,H_2O can be eliminated. These results in Table 4 which show the type of deviation in question are insufficient to establish any relation similar to equation (4) for the formation of molecules such as DBC,$(HNO_3,H_2O)_2$.

TABLE 4. *Data for complex formation between nitric acid and dibutylcarbitol.*

Total complex (mmoles)	Total uncomplexed dibutylcarbitol (mmoles)	Complex / Uncomplexed solvent	Total complex (mmoles)	Total uncomplexed dibutylcarbitol (mmoles)	Complex / Uncomplexed solvent
0·07	20·25	$3·46 \times 10^{-3}$	9·42	11·10	0·848
0·48	19·84	$2·42 \times 10^{-2}$	12·9	7·4	1·74
1·33	18·99	$7·02 \times 10^{-2}$	15·3	5·0	3·06
2·11	18·21	0·116	18·0	2·3	7·84
4·42	15·90	0·278	21·1	—0·78	—
7·01	13·31	0·527	24·9	—3·6	—

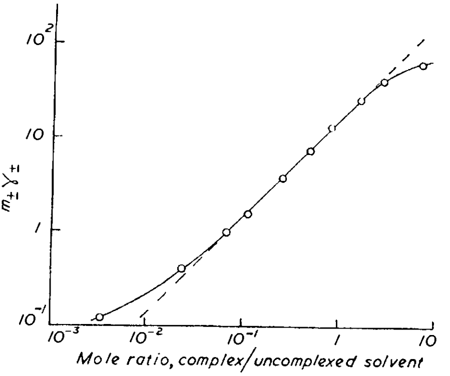

FIG. 2. *Complex formation between dibutylcarbitol and nitric acid.*

Deviations from equation (4) in regions of low nitric acid concentration do not become significant until the organic phase acidity falls below 0·1M. Such deviations can be ascribed to dissociation of the complex, but it is not possible to distinguish between the formation of free dibutycarbitol and nitric acid, and the formation of a nitrate ion and a solvated H_3O^+ ion. From the deviations of the two lowest results, dissociation constants of about 5×10^{-2} and 10^{-4} (respectively) are found, but in this region the experimental results are rather inaccurate. In general, it appears that dissociation is unimportant over the range of nitric acid concentrations studied.

Infrared measurements were carried out by E. Hughes. This paper is published by permission of the Managing Director, Industrial Group, United Kingdom Atomic Energy Authortiy.

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