18. *The Extraction of Nitric Acid from Aqueous Solution by Organic Solvents: the Dimerisation of Nitric Acid in the Organic Solvent.*

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The extraction of nitric acid from aqueous solution (6—16M) into benzene and into toluene, and the infrared spectrum of the benzene phase, have been measured. It appears that the nitric acid in the organic phase is present as a monohydrated dimer.

During investigations[1] on the extraction of nitric acid from aqueous solution by dialkyl hydrogen phosphates in the diluents toluene, kerosene, n-dodecane, and carbon tetrachloride, it was observed that a little nitric acid is extracted by the diluents alone. As the nature of this extraction appears to be unknown we have examined in greater detail the extraction of nitric acid by toluene and benzene.

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[1] Hardy and Greenfield, unpublished work.

Values of C_a and C_o, the equilibrium concentrations of nitric acid in the aqueous and the organic phase respectively, and C_{H_2O}, the equilibrium concentration of water in the toluene phase, are given in Table 1 for certain solvents. The value of $C_{o,\,calc.}$ was calculated from

$$C_o = D \,.\, C_{u,a} + 2KD^2 \,.\, C_{u,a}{}^2$$

in which $C_{u,a}$ is the equilibrium concentration of the un-ionised nitric acid in the aqueous phase (taken from the data of Krawetz kindly made available by Hesford and McKay [2] from their original graphs), D is the distribution coefficient of un-ionised nitric acid between the two phases ($C_{u,o}/C_{u,a}$), and K is the stoicheiometric equilibrium constant given by $[(HNO_3)_2]_o/[HNO_3]_{u,o}{}^2$ for the equilibrium $2HNO_{3u,o} \rightleftharpoons (HNO_3)_{2,o}$. Values of $D = 1{\cdot}2 \times 10^{-3}$, and $K = 590$ mole^{-1}, were derived for this equation from the plot of $C_o \,.\, C_{u,a}{}^{-1}$ against $C_{u,a}$, a straight line of slope $2KD^2$ with intercept D at $C_{u,a} = 0$.

TABLE 1. *Values of* C_a, $C_{u,a}$, C_o, *and* C_{H_2O}.

Solvent	C_a (M)	$C_{u,a}$ (M) (from ref. 2)	C_o (M) exptl.	C_o (M) calc.	C_{H_2O} (M)	Solvent	C_a (M)	$C_{u,a}$ (M) (from ref. 2)	C_o (M) exptl.	C_o (M) calc.
Toluene	6·16	1·58	0·0062	0·0061		Kerosene ...	9·2	4·05	0·0010	0·0007
	9·20	4·05	0·0334	0·0323			12·2	7·75	0·0020	0·0023
	10·15	5·20	0·0505	0·0518			16·1	—	0·0064	0·0064
	12·10	7·65	0·108	0·108		CCl_4	14·1	10·7	0·0145	
	13·90	10·4	0·210	0·195			16·1	—	0·027	
	13·75	10·1	0·248		0·124	Cyclohexane	12·2	7·75	0·0016	
	15·12	—	0·86		0·425		13·9	10·4	0·0034	
Benzene	14·1	10·7	0·22			n-Dodecane	8·1	3·0	0·034	
	15·6	—	0·47				14·1	10·7	0·080	

TABLE 2. *Infrared difference spectrum of* 0·2M-*nitric acid in benzene against benzene.*

Peak max. (cm.$^{-1}$)	Assignment	Peak max. (cm.$^{-1}$)	Assignment
768w	ν_6 NO_3 out-of-plane	1401m	? NO_3^- ion
894s 929s	ν_2 NO stretch	1595w	Water H–O–H bend
		1668s	ν_4 NO_2 antisym. stretch
1299vs	ν_1 NO_2 sym. stretch	2703w	? combination band
~1340 *	ν_8 H-bend	3215m 3495w 3571m	ν_7 OH stretch

* Shoulder on 1299 band.

Similar calculations on the results for kerosene give approximately $D = 6 \times 10^{-5}$ and $K = 4 \times 10^3$ mole^{-1}, which were inserted in the equation to obtain the values of $C_{o,calc.}$ in Table 1.

The frequencies and intensities of the bands in the infrared difference spectrum between benzene, and of benzene containing 0·2M-nitric acid (extracted from 14M-nitric acid), are given in Table 2. Similar results were obtained in carbon tetrachloride and n-dodecane. The assignments of the frequencies of the bands due to the nitric acid molecule are those of Cohn, Ingold, and Poole.[3] The spectrum was not measured in toluene because significant attack on the toluene would have occurred during the measurements.

DISCUSSION

The above evidence strongly supports the idea that a dimer of nitric acid is the predominant species in solvents such as toluene, benzene, and kerosene, in contact with aqueous nitric acid under the range of conditions studied. Since the molar concentration of water in the toluene phase is approximately one-half the molar concentration of nitric acid in that phase, the dimer probably exists as the monohydrate, $(HNO_3)_2,H_2O$. This

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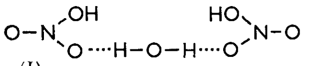
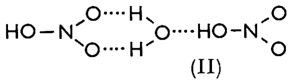
[2] Hesford and McKay, *Trans. Faraday Soc.*, 1958, **54**, 573.

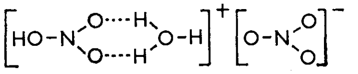
[3] Cohn, Ingold, and Poole, *J.*, 1952, 4272.

composition is the same as that of the hemihydrate of nitric acid found by Erdmann[4] and confirmed by Chédin[5] in an aqueous nitric acid containing $>90\%$ of HNO_3, and also postulated by Gillespie, Hughes, and Ingold[6] to interpret their freezing point results for $>95\%$ HNO_3.

The infrared spectrum of the $(HNO_3)_2,H_2O$ species in benzene has the interesting features (i) that the normal NO stretching band, ν_2, is split into two strong bands at 894 and 929 cm.$^{-1}$, comparable with the values 886 cm.$^{-1}$ found in the infrared spectrum[3] of the vapour (presumably non-H-bonded) and 925 cm.$^{-1}$ in the Raman[7] and infrared[8] spectra of the liquid (presumably H-bonded), and (ii) that there are two main bands and a subsidiary band in the OH stretching region (3200—3600 cm.$^{-1}$).


(I)


(II)


(III)

Structure (I), proposed by Chédin[5] for the hemihydrate in concentrated nitric acid solution, does not satisfy the first feature of the spectrum because both N–OH groups would be expected to be equivalent to each other. Accordingly we suggest structure (II) for the $(HNO_3)_2,H_2O$ species under the present conditions, and recognise that there may be some contribution from an ionic structure (III) to account for the 1401 cm.$^{-1}$ (possibly nitrate) band in the spectrum. At high concentrations of nitric acid in the organic phase the non-hydrogen-bonded N–OH group may be expected to form larger aggregates with other monomers or dimers and thus to cause deviations from the proposed equation at $C_a > 14$M.

Experimental.—The initial aqueous nitric acid concentration, C_i, was determined by titrating an aliquot part with standard alkali against Methyl Orange. Equal volumes of the nitric acid (diluted "AnalaR" grade) and toluene (sulphur-free "AnalaR" grade) were stirred together for 2 or 10 min. at 20°, the phases were separated by centrifugation, and an aliquot part of the organic phase was titrated electrometrically with standard alkali. The equilibrium aqueous nitric acid concentration, C_a, was calculated by difference for initial concentrations of less than 14M-nitric acid. Toluene slowly became coloured in contact with 16M-nitric acid, and titrations showed a gradual loss of acid amounting to 0·1M after 2 min. and ~1M after 10 min. No loss of acid, even at 16M, occurred with "AnalaR" benzene, n-dodecane, odourless kerosene, cyclohexane (Spectrosol), and "AnalaR" carbon tetrachloride. Water in the toluene phase was determined by the Karl Fischer method.

Infrared spectra of nitric acid extracted from aqueous 14M-nitric acid into benzene, carbon tetrachloride, and n-dodecane were measured from 2 to 15 microns (on liquid films between silver chloride plates separated by an ~10 μ Polythene spacer) on a Hilger H.800 double-beam spectrometer with a rock-salt prism. Silver chloride plates have been shown[8] to be satisfactory for use with concentrated nitric acid solutions.

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[4] Erdmann, *Z. anorg. Chem.*, 1902, **32**, 431.
[5] Chédin, *J. Chim. phys.*, 1952, **49**, 109.
[6] Gillespie, Hughes, and Ingold, *J.*, 1950, 2552.
[7] Ingold and Millen, *J.*, 1950, 2612.
[8] Marcus and Fresco, *J. Chem. Phys.*, 1957, **27**, 564.