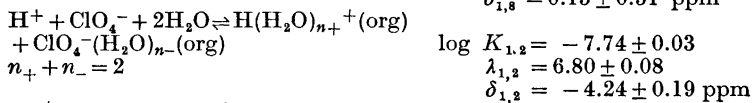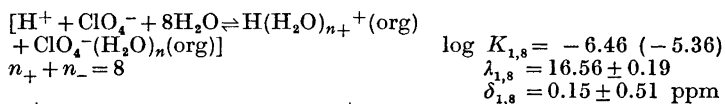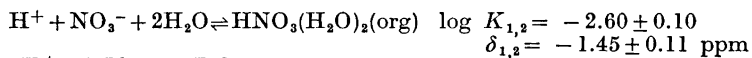# The Extraction of Water, Nitric and Perchloric Acids by Nitrobenzene

ERIK HÖGFELDT,[a] FOLKE FREDLUND,[a] LARS ÖDBERG[b] · and GABOR MERENYI[b]

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The extraction of water, nitric and perchloric acids by nitrobenzene has been studied at 25°C using partition, NMR, and conductivity methods. The results can be described by the following set of complexes, equilibrium constants, chemical shifts (relative to $H_2O(l)$) and equivalent conductivities.

$H^+ + NO_3^- + 2H_2O \rightleftharpoons HNO_3(H_2O)_2(org)$ 　$\log K_{1,2} = -2.60 \pm 0.10$
$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad \delta_{1,2} = -1.45 \pm 0.11$ ppm

$2H^+ + 2NO_3^- + 2H_2O \rightleftharpoons$
$\rightleftharpoons (HNO_3.H_2O)_2(org)$ 　$\log K_{2,2} = -5.37 \pm 0.24$
$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad \delta_{2,2} = -7.59 \pm 0.73$ ppm

$[H^+ + ClO_4^- + 8H_2O \rightleftharpoons H(H_2O)_{n_+}^+(org)$
$+ ClO_4^-(H_2O)_n(org)]$
$n_+ + n_- = 8$ 　　$\log K_{1,8} = -6.46 \ (-5.36)$
$\qquad\qquad\qquad\qquad\qquad\qquad\quad \lambda_{1,8} = 16.56 \pm 0.19$
$\qquad\qquad\qquad\qquad\qquad\qquad\quad \delta_{1,8} = 0.15 \pm 0.51$ ppm

$H^+ + ClO_4^- + 2H_2O \rightleftharpoons H(H_2O)_{n_+}^+(org)$
$+ ClO_4^-(H_2O)_{n_-}(org)$
$n_+ + n_- = 2$ 　　$\log K_{1,2} = -7.74 \pm 0.03$
$\qquad\qquad\qquad\qquad\qquad\qquad\quad \lambda_{1,2} = 6.80 \pm 0.08$
$\qquad\qquad\qquad\qquad\qquad\qquad\quad \delta_{1,2} = -4.24 \pm 0.19$ ppm

$3H^+ + 3ClO_4^- + 6H_2O \rightleftharpoons$
$\rightleftharpoons (HClO_4)_3(H_2O)_6(org)$ 　$\log K_{3,6} = -17.94 \pm 0.07$
$\qquad\qquad\qquad\qquad\qquad\qquad\quad \delta_{3,6} = -3.71 \pm 1.27$ ppm

In the reaction put within brackets there is a large uncertainty in the number of water molecules involved in the reaction.

From the chemical shifts some indications of the structure of the complexes are obtained.

In our first paper on the extraction of water and acids by aromatic hydrocarbons, the extraction of water and nitric acid by nitrobenzene from aqueous solutions of the acid was also included.[1] Although the data indicated formation of mixed nitric acid-water complexes, measurements at high acidities showed some inconsistencies. For that reason no attempts were made to evaluate the composition of the species present in the organic phase. In the present study

we have reexamined the extraction of nitric acid and also included perchloric acid. In addition to the titrimetric analysis, NMR and conductivity methods have been used.

EXPERIMENTAL

Chemicals and solutions. The nitrobenzene from AB Kebo was found to be at least 99.9 % pure by gaschromatography. The nitric (100 %) and perchloric (70 %) acids were of Merck *p.a.* quality and used as such. Various mixtures of nitric acid and water were prepared in the range $0-12$ M and of perchloric acid and water in the range $0-10$ M (mol l^{-1}) They were standardized against standard sodium hydroxide using methyl red as indicator. The chemicals and solutions prepared for the Karl Fischer titrations have been reported elsewhere.[1]

Experiments. Samples containing 15 ml nitrobenzene and 10 ml acid-water mixture were shaken in glass-stoppered bottles either overnight or for at least 1 h in a room kept at $25.0 \pm 0.3°C$. It was checked that 1 h was sufficient time for equilibrium to be reached. At least two samples were prepared for each concentration of acid. Actually, many extraction experiments have been performed in this laboratory by several investigators during the past ten years and an acceptable agreement has been obtained between the various studies. After equilibration the samples were centrifuged at 3500 rpm for $5-10$ min. Aliquot portions were drawn from both phases for determination of their acid concentration. For the organic phase, water concentration, conductivity, NMR chemical shift, and viscosity (HClO$_4$ system) were also determined.

The acid concentration in both phases was determined by titrating with standard alkali using methyl red as indicator. Water in the organic phase was determined by a modification of the Karl Fischer method.[1]

The conductivity measurements on the organic phase were carried out in a paraffin oil thermostat kept in a constant temperature room. The equipment used was a commercial WTW bridge type LBR and a standard conductivity cell. The temperature in the oil thermostat was kept at $25.00 \pm 0.02°C$. The cell constant was determined by measuring the resistance of 0.0100 M KCl. The reproducibility of the conductance measurements was about ± 0.1 %. The NMR measurements were carried out on a Varian A-60A apparatus equipped with a Varian variable temperature controller V-6040. The chemical shifts were determined by means of the side-band technique using a Hewlett-Packard 202 A audio oscillator and a Hewlett Packard 5512 A frequency counter. The temperature was checked with a standard methanol sample (Varian 943346-06). The temperature was always well within $\pm 1°C$ of 25°C. The shift determination was made $3-5$ times for each sample, resulting in a standard deviation of $\pm 0.1 - 0.2$ c/s. Benzene was used as an external standard. All shifts reported in this paper are relative to water as external reference with positive shifts upfield from the reference. The chemical shift between water and benzene was determined in a separate experiment. The susceptibility of the nitrobenzene changes slightly when water and acid are dissolved. This effect is, however, well below 1 Hz and is negligible compared to the very large shift changes reported here.

The viscosity measurements (perchloric acid only) were made with a capillary viscosimeter, Ostwald No. 5253. Two samples were prepared for each acid concentration and about 10 determinations were made for each sample.

Selection of thermodynamic data

In order to evaluate the composition of the various complexes present, the activities of water and acid are required.

Nitric acid. Densities of HNO$_3$ solutions at 25°C have been taken from the International Critical Tables.[2a] For the activities we have in all studies including this one used the data given by Redlich in Landolt-Börnstein.[3] However, in recent years new data have appeared.[4-7] These data were tested for thermodynamic consistency by Redlich *et al.*[8] They also compiled a set of best values. The data we have been using [1,3] are found to agree with the nitric acid activities reported by Redlich *et al.*[8] while the water activities

used by us are about 0.06 logarithmic units larger than their values in the concentration range used, i.e. < 7 M HNO_3. This difference will only influence the values of equilibrium constants, but not the description given in this paper. It will be shown below, that the data by Redlich et al.[8] are consistent with our model. We have therefore not found it necessary to recalculate our data.

Perchloric acid. Densities of $HClO_4$ solutions at 25°C have been taken from Markham [9] for high concentrations and from the International Critical Tables for low concentrations.[2b] This acid was also discussed by Redlich et al.[8] Using the data of Robinson and Baker,[10] Dücker,[11] and Mascherpa,[12] they compiled a set of best values. We have used the data by Robinson and Baker,[10] which are in good agreement with those given by Redlich et al.[8]

RESULTS

The system $C_6H_5NO_2 - HNO_3 - H_2O$

This system has previously been studied by Högfeldt and Bolander.[1] We have redetermined the system and obtained results in agreement with those obtained nearly 10 years ago by other workers in our laboratory. In Fig. 1 are given both acid (●) and water (○) concentration in M (mol l^{-1}) as a function of the stoichiometric molarity of HNO_3 in the aqueous phase at equilibrium, C_{HNO_3}. At high concentrations the curves for water and acid approach each other, and one can expect the main complex to have the composition $HNO_3 \cdot H_2O$. However, at high concentrations of water and acid in the organic phase, the assumption of constant activity coefficients in this phase may not be justified. For this reason we have restricted the treatment of data to the range $C_{HNO_3} < 7$ M.
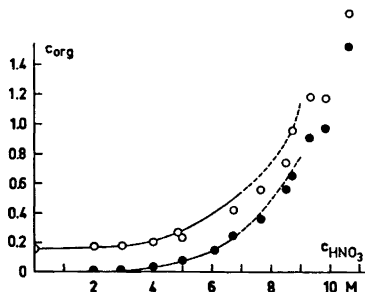
Fig. 1. The concentrations of water (○) and nitric acid (●) in nitrobenzene versus acid concentration in the aqueous phase for some representative points. The full-drawn curve has been calculated using the constants given in the abstract. The dashed part is an extension of the calculations above the concentration range used in the determination of the equilibrium constants.
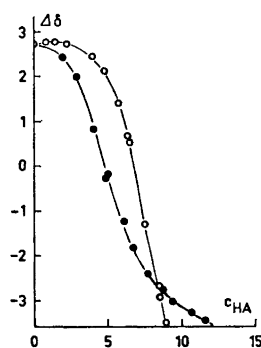
Fig. 2. The chemical shift of the water and acid protons in nitrobenzene for HNO_3(●) and $HClO_4$(○) versus acid concentration in the aqueous phase. The full-drawn curves have been calculated using the equilibrium constants and shifts given in the abstract.

The conductivity of this system was found to be so small that ionic species can certainly be neglected. In the NMR spectrum water and acid protons give rise to one signal only. The chemical shift is given in Fig. 2 (●) together with the same data for $HClO_4$ (○). The shifts are given in ppm with water as reference.

Treatment of data. Complexes present. The basic assumption is that the activity coefficients of the various species are constant in the organic phase.[14] For the aqueous phase the solubility of nitrobenzene can be expected to be negligible in the acidity range used for calculations [15] and we can use the activities of water and acid known from the binary system $HNO_3 - H_2O$. In the calculations the dimerization equilibrium of water in nitrobenzene has to be taken into account.[16]

For the reactions (where H^+ stands for H^+ in the aqueous phase *etc.*)

$$pH^+ + pA^- + qH_2O \rightleftharpoons (HA)_p(H_2O)_q(org) \tag{1}$$
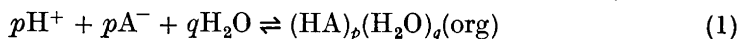
we have the following material balances in the organic phase:

$$[H_2O]_{org} = \sum_{p_i q_i} q_i[(HA)_{p_i}(H_2O)_{q_i}] \tag{2a}$$

$$[HA]_{org} = \sum_{p_i q_i} p_i[(HA)_{p_i}(H_2O)_{q_i}] \tag{2b}$$
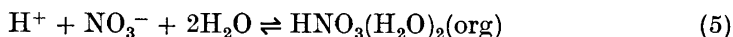
where HA in this case stands for HNO_3.

If constant activity coefficients in the organic phase are assumed and included in the equilibrium constants, eqns. (2a) and (2b) can be rewritten:

$$[H_2O]_{org} = \sum_{p_i, q_i} q_i K_{p_i, q_i}\{H^+\}^{p_i}\{A^-\}^{p_i}\{H_2O\}^{q_i} \tag{3}$$

$$[HA]_{org} = \sum_{p_i, q_i} p_i K_{p_i, q_i}\{H^+\}^{p_i}\{A^-\}^{p_i}\{H_2O\}^{q_i} \tag{4}$$

[ ] denotes concentration and { } activity.

The constants $K_{0,1}$ and $K_{0,2}$ are known from previous work.[16] As in previous papers [14,16] we have used the version of the computer program LETAGROP suitable for the treatment of NMR and extraction data.[17,18] A natural start was to try to fit our data with the extraction of $HNO_3.H_2O$ besides H_2O and $(H_2O)_2$. However, the fit was bad and when minimizing either on $[H_2O]_{tot}$ or $[HNO_3]_{tot}$ the equilibrium constant $K_{1,1}$ differed by about 50 % and it was obvious that $HNO_3.H_2O$ could not be the only species present. The next step was to try $HNO_3.H_2O$ together with other complexes, but in no case a good fit was obtained. After systematically trying various combinations of complexes the following two equilibria:

$$H^+ + NO_3^- + 2H_2O \rightleftharpoons HNO_3(H_2O)_2(org) \tag{5}$$

and

$$2H^+ + 2NO_3^- + 2H_2O \rightleftharpoons (HNO_3.H_2O)_2(org) \tag{6}$$

gave a consistent picture as illustrated in Fig. 3, where the quantity Y defined by

$$Y = \frac{[HNO_3]_{org}}{\{H^+\}\{NO_3^-\}\{H_2O\}^2} \times 10^3$$

is plotted against $\{H^+\}\{NO_3^-\}$. A straight line is obtained both when our activities and those of Redlich et al.[8] are used. The latter data are used in Fig. 3 giving $K_{1,2} = 2.7 \times 10^{-3}$ and $K_{2,2} = 2.4 \times 10^{-6}$. These values were used as input values for the computer calculations. The results of the computer calculations are given in Table 1.
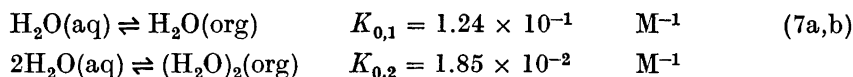
Table 1. Results of computer calculations on the system $C_6H_5NO_2 - HNO_3 - H_2O$; $t = 25°C$.

Choice	$K_{1,2}$	$\log K_{1,2}$	$K_{2,2}$	$\log K_{2,2}$*	$\sigma(y)$	U
2	$(2.27 \pm 0.14) \times 10^{-3}$	-2.64 ± 0.08	$(1.55 \pm 1.13) \times 10^{-6}$	$-5.81(-5.31)$	0.013	3.02×10^{-3}
3	$(2.53 \pm 0.19) \times 10^{-3}$	-2.60 ± 0.10	$(4.30 \pm 0.80) \times 10^{-6}$	-5.37 ± 0.24	0.008	1.31×10^{-3}

* Here $\log (K + 3\sigma(K))$ is given within parentheses.

In Table 1, choice 2 means that we have minimized on $[H_2O]_{tot}$ and choice 3 that the minimization has been carried out on $[HNO_3]_{tot}$. $\sigma(y)$ is the standard deviation in $[H_2O]_{tot}$ and $[HNO_3]_{tot}$, respectively, and U is the error squares sum $\sum([H_2O]_{tot} - [H_2O]_{calc})^2$ or $\sum([HNO_3]_{tot} - [HNO_3]_{calc})^2$, the summation taken over all experimental points. The spread in $\log K$ is $\pm 3\sigma(\log K)$.

When evaluating the constants $K_{1,2}$ and $K_{2,2}$ the following constants for the distribution and association of water in nitrobenzene were used:[16]

$$H_2O(aq) \rightleftharpoons H_2O(org) \qquad K_{0,1} = 1.24 \times 10^{-1} \qquad M^{-1} \qquad (7a,b)$$

$$2H_2O(aq) \rightleftharpoons (H_2O)_2(org) \qquad K_{0,2} = 1.85 \times 10^{-2} \qquad M^{-1}$$

As seen in Table 1 the values obtained graphically are in good agreement with the values obtained in the computer calculations. Both sets of activity data thus support the same model.
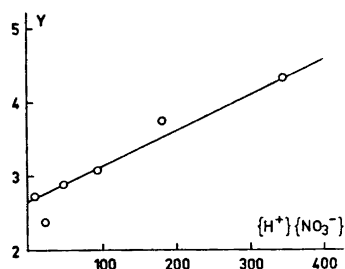

Fig. 3. The quantity $\dfrac{[HNO_3]_{org}}{\{H^+\}\{NO_3^-\}\{H_2O\}^2} \times$

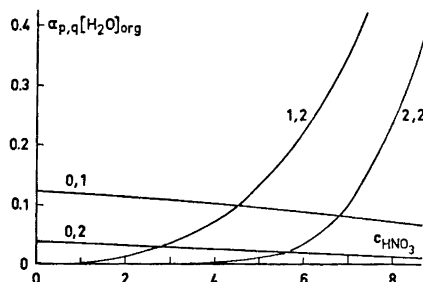$\times 10^3$ plotted against $\{H^+\}\{NO_3^-\}$ using the activity data given by Redlich et al.[8]

Fig. 4. The contribution from each species $(\alpha_{p,q}[H_2O]_{org})$ to the total amount of water present in the organic phase. $\alpha_{p,q}$ is the fraction of all water present in the species p,q. The water monomer is denoted 0,1, the dimer 0,2 etc.

From Table 1 it is evident that there is a good agreement between the values of $K_{1,2}$ obtained when minimizing on acid or water. The relative contribution from $(HNO_3.H_2O)_2$ to the total amount of water extracted is in the interval investigated very small and hence we get a very great uncertainty in $K_{2,2}$ as determined from choice 2 and can only expect a rough agreement obtained with $K_{2,2}$ from choice 3. The fit to the acid data is somewhat better than to the water data. This is expected since the water data have to be corrected for the water extracted as H_2O and $(H_2O)_2$.

As mentioned before attempts were made to incorporate $HNO_3.H_2O$ in the calculations, but the equilibrium constant came out as zero and does not need to be taken into account. Some other complexes with more water or acid were tried, but they all gave higher error square sums or larger discrepancies between choices 2 and 3. The values selected are those from choice 3. They are given in the abstract.

Fig. 4 gives the contribution from each species $(\alpha_{p,q}[H_2O]_{org})$ to the total amount of water in the organic phase. The water monomer is denoted 0,1, the dimer 0,2, etc. $\alpha_{p,q}$ is the fraction of all water present in the complex p,q.

Chemical shifts. The water and acid protons in the organic phase give rise to one resonance line only, *i.e.* the proton exchange between the various kinds of sites is too rapid for giving rise to several lines. In such a case the observed resonance frequency is given by:[13b]

$$\delta_{obs} = \sum \delta_{p_i,q_i} P_{p_i,q_i} \tag{8}$$

where δ_{p_i,q_i} is an average value of the resonance frequency of the various proton sites in the species $(HNO_3)_{p_i}(H_2O)_{q_i}$ relative to the chosen reference frequency and P_{p_i,q_i} is the proton fraction for that species, *i.e.*

$$P_{p_i,q_i} = \frac{(p_i + 2q_i)K_{p_i,q_i}\{H^+\}^{p_i}\{A^-\}^{p_i}\{H_2O\}^{q_i}}{\sum_{p_i,q_i}(p_i + 2q_i)K_{p_i,q_i}\{H^+\}^{p_i}\{A^-\}^{p_i}\{H_2O\}^{q_i}} \tag{9}$$

Using the same computer program, eqn. (8) has been used but now minimizing on $\sum(\delta_{obs} - \delta_{calc})^2$. In these calculations the complexes and K-values given for choice 3 in Table 1 have been used. For the species H_2O and $(H_2O)_2$ the following δ-values have been used:[16]

$$\delta_{0,1} = 2.94 \text{ ppm}; \quad \delta_{0,2} = 2.18 \text{ ppm} \tag{10a,b}$$

The following results were obtained:

$$\delta_{1,2} = -1.45 \pm 0.11 \text{ ppm}; \quad \delta_{2,2} = -7.59 \pm 0.73 \text{ ppm} \tag{11a,b}$$

The δ-values used in this paper are related to the ν-values given elsewhere [14,16] by $\delta = (\nu - \nu_{ref})/60 \times 10^6$ where $\nu_{ref} = \nu_{H_2O(l)}$.

The system $C_6H_5NO_2 - HClO_4 - H_2O$

This system has been studied by different workers in our laboratory by titrimetric analysis. They have all obtained consistent results. Fig. 5. gives the equilibrium molarity of H_2O in the organic phase, $[H_2O]_{org}$ (the open
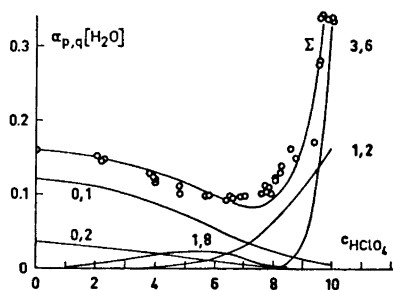
Fig. 5. The concentration of water in nitrobenzene *versus* concentration of HClO₄ in the aqueous phase for some representative points. The curve marked $\sum$ is the total concentration as calculated using the constants given in the abstract. Curves for (0,1), (0,2), (1,8), (1,2) and (3,6) are also drawn.
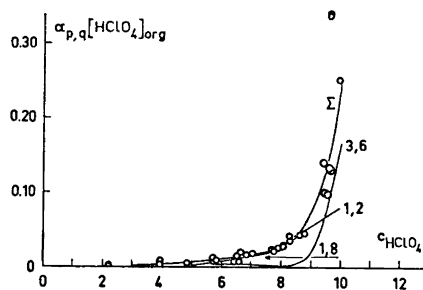

Fig. 6. The concentration of perchloric acid in nitrobenzene *versus* acid concentration in the aqueous phase for some representative points. The curve marked $\sum$ is the total concentration as calculated using the constants given in the abstracts. Curves for (1,8, (1,2) and (3,6) are also drawn.

circles) plotted against the stoichiometric molarity of HClO₄ in the aqueous phase, C_{HClO_4}, and Fig. 6 the equilibrium molarity of perchloric acid $[HClO_4]_{org}$ (the open circles) in the same phase also plotted against C_{HClO_4}. From these figures it is evident that at about 8 M HClO₄ an appreciable amount of acid is extracted. At the same time the water extraction increases, and acid-water complexes are obviously formed in the organic phase. In order to get an idea about the number of water molecules coextracted with HClO₄ the
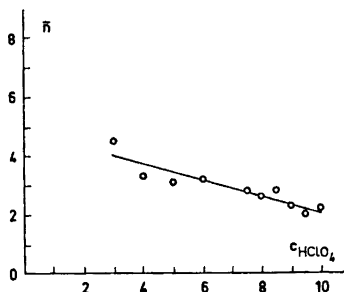

Fig. 7. The quantity $\bar{n}$ (eqn. 12) *versus* perchloric acid concentration in the aqueous phase.
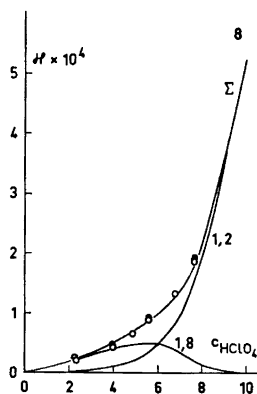

Fig. 8. The conductivity of the nitrobenzene phase *versus* the concentration of perchloric acid in the aqueous phase. Calculated values are denoted by the curve marked $\sum$. Curves for 1,8 and 1,2 are also marked out.

number of water molecules, $\bar{n}$, per acid molecule is plotted against C_{HClO_4} in Fig. 7. The quantity $\bar{n}$ is defined by

$$\bar{n} = ([H_2O]_{org} - [H_2O]_{\phi_{NO_2}})/[HClO_4]_{org} \qquad (12)$$

$[H_2O]_{\phi_{NO_2}}$ is computed with the aid of eqn. (7). From Fig. 7 it is seen that $\bar{n}$ decreases from 4 and seems to approach 2 at high acidities, $i.e.$ the composition $HClO_4.(H_2O)_2$. In order to check the possibility of extensive ionic dissociation, the conductivity ($\varkappa$) was measured in some representative solutions and the results are given in Fig. 8 where $\varkappa \times 10^4$ is plotted against C_{HClO_4}. Furthermore the viscosity (η) was also measured at various compositions. The results are given in Table 2. The chemical shift of the water and acid protons is plotted against C_{HClO_4} in Fig. 2 (O).

Treatment of data. Complexes present. (a). Conducting species. We begin by considering the following conducting species:

$$uH^+ + uClO_4^- + nH_2O \rightleftharpoons H_u(ClO_4)_{u-1}(H_2O)_{n+}{}^+(org) +$$
$$ClO_4(H_2O)_{n-}{}^-(org) \qquad (13)$$
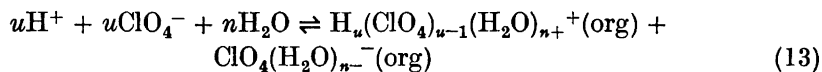
For the sake of simplicity only one multiple cation is indicated in eqn. (13) out of all possible species.

Application of the law of mass action to (13) gives under the assumption of ideal behavior in the organic phase

$$\log [H_u(ClO_4)_{u-1}(H_2O)_{n+}{}^+][ClO_4(H_2O)_{n-}{}^-] = \log K_{u,n} +$$
$$u \log \{H^+\}\{ClO_4^-\} + n \log \{H_2O\} \qquad (14)$$

where $n = n_+ + n_-$.

The requirement of electroneutrality in the organic phase gives

$$[H_u(ClO_4)_{u-1}(H_2O)_{n+}{}^+] = [ClO_4(H_2O)_{n-}{}^-] = C_{u,n} \qquad (15)$$

$C_{u,n}$ is the molarity in the organic phase of the completely dissociated complex containing n water molecules. Thus

$$\log C_{u,n} = \tfrac{1}{2} \log K_{u,n} + \tfrac{u}{2} \log \{H^+\}\{ClO_4^-\} + \tfrac{n}{2} \log \{H_2O\} \qquad (16)$$

Between $C_{u,n}$ and the conductivity ($\varkappa$) the following relation holds

$$\varkappa = 10^{-3} C_{u,n} \lambda_{u,n} \qquad (17)$$

Table 2. Viscosities in nitrobenzene-perchloric acid-water mixtures at 25°C.

C_{HClO_4}	η_{25} cP	Number of determinations
(Dry nitrobenzene)	1.3438	17
0	1.3223	9
0	1.3220	11
3.948	1.3240	11
3.939	1.3243	11
6.387	1.3372	10
6.391	1.3382	8
8.079	1.3523	11
8.075	1.3530	11
9.589	1.3943	10
9.571	1.3939	11

where $\lambda_{u,n}$ is the equivalent conductivity of the ion pair under consideration (u,n). From Table 2 it is seen that η varies only a few per cent in the concentration range of interest while $\varkappa$ has a fiftyfold variation. We now make the assumption that $\lambda_{u,n}$ is constant in the range where (u,n) makes a noticeable contribution to $\varkappa$.

By combining (16) and (17) we get

$$\log \varkappa - \frac{u}{2} \log \{H^+\}\{ClO_4^-\} = -3.00 + \tfrac{1}{2} \log K_{u,n} + \log \lambda_{u,n} + \frac{n}{2} \log \{H_2O\} \quad (18)$$

Setting $u=1$ in (18) implies that simple ions predominate in the system while $n=2$ means that triple ions containing cation, anion, and water predominate as conducting species. Triple ions are not unknown in either aqueous or organic solutions.[19-21]
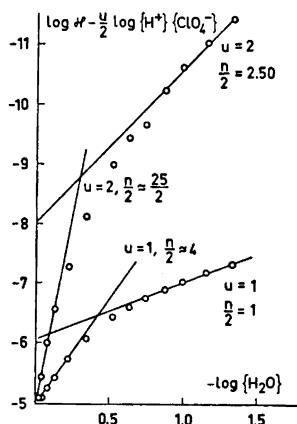
Fig. 9. $\log \varkappa - \frac{u}{2} \log \{H^+\} \{ClO_4^-\}$ (eqn. 18) versus the negative logarithm of the water activity for $u=1$ and $u=2$. Two linear asymptotes have been fitted to each curve.

In Fig 9, $\log \varkappa - \frac{u}{2} \log \{H^+\} \{ClO_4^-\}$ is plotted against $\log \{H_2O\}$ for $u=1$ (simple ions) and $u=2$ (triple ions). In both cases two linear asymptotes can be fitted to the data. The slopes of these lines give, according to (18), the number of water molecules belonging to the conducting species. The results are given in Table 3.

Table 3. Determination of n in eqn. (18)

u	n_1	n_2
1	8	2
2	25	5

For $u=1$ we find that at high acidities the conducting pair of ions has $n=\bar{n}=2$ in agreement with Fig. 7. For $u=2$ we get much higher values for $\bar{n}$, from $25-5$. The value of 25 is unreasonably high and multiple ions can hardly be expected

to predominate at low acidities. At high acidities triple ions cannot be excluded. However, the agreement between the limiting value in Fig. 7 and Table 3 makes it very tempting to assume simple ions only.

We first determine approximate equilibrium constants by simple calculations. The constants obtained are then refined by the computer program LETAGROP.

From Fig. 9 it is seen that in the range where the data can be approximated by the asymptote with a slope of unity the complex 1,2 predominates in the system. In order to obtain an approximate value for $K_{1,2}$ in (16) we make the following approximation:

$$C_{1,2} \approx [HClO_4]_{org} \qquad (19)$$

Using eqns. (16) and (19) with $u = 1$, $n = 2$, $K_{1,2}$ was found to be approximately constant in the range $7 - 8.5$ M $HClO_4$ as shown in Table 4.

Table 4. Evaluation of $K_{1,2}$ from eqns. (16) and (19).

C_{HClO_4}	$[HClO_4]_{org}$ interpolated	log $[HClO_4]_{org}$	log $\{H^+\}\{ClO_4^-\}$	log $\{H_2O\}$	$\frac{1}{2}$ log $K_{1,2}$
7	0.016	-1.80	5.14	-0.52	-3.85
7.5	0.021	-1.68	5.66	-0.63	-3.88
8	0.030	-1.52	6.19	-0.74	-3.88
8.5	0.041	-1.39	6.70	-0.87	-3.87
				Average:	-3.87 ± 0.02

With knowledge of $K_{1,2}$ it is possible to determine $\lambda_{1,2}$. From (18) and Fig. 9 we have with $u = 1$ and $n = 2$

$$\lim_{\log\{H_2O\} \to 0} (\log \varkappa - \tfrac{1}{2} \log \{H^+\}\{ClO_4^-\}) = -3.00 + \tfrac{1}{2} \log K_{1,2} + \log \lambda_{1,2} = -6.06$$

With $\frac{1}{2}$ log $K_{1,2} = -3.87$ we find:

$$\lambda_{1,2} = 6.5 \text{ cm}^2 \text{ ohm}^{-1} \text{ mol}^{-1} \qquad (20)$$

From Fig. 9 it is seen that at least one more conducting ion pair carrying about 8 water molecules is needed to account for the conductivity data. We assume that all acid in the organic phase below 7 M $HClO_4$ is due to (1,2)

Table 5. Evaluation of $K_{1,8}$ from eqn. (16).

C_{HClO_4} M	$[HClO_4]_{org}$ interpolated	$C_{1,2}$	$C_{1,8}$	log $C_{1,8}$	log $\{H^+\}\{ClO_4^-\}$	log $\{H_2O\}$	$\frac{1}{2}$ log $K_{1,8}$
4	0.003$_8$	0.0014	0.0024	-2.62	2.30	-0.13	-3.25
5	0.006$_2$	0.0030	0.0032	-2.49	3.13	-0.22	-3.18
6	0.010$_0$	0.0072	0.0028	-2.55	4.13	-0.34	-3.26
						Average:	-3.23 ± 0.05

and (1,8) and compute the contribution from (1,2) from (16) with $u = 1$ and $n = 2$ and $\frac{1}{2} \log K_{1,2} = -3.87$. This amount is subtracted from $[\text{HClO}_4]_{\text{org}}$ and the difference is attributed to (1,8). $\frac{1}{2} \log K_{1,8}$ is now computed from (16) with $u = 1$ and $n = 8$. The results are given in Table 5.

With knowledge of $K_{1,8}$ we can compute $\lambda_{1,8}$ from (18) and find from Fig. 9:

$$\lim_{\log\{H_2O\} \to 0} [\varkappa - \frac{1}{2} \log \{H^+\} \{ClO_4^-\}] = -3.00 + \frac{1}{2}\log K_{1,8} + \log \lambda_{1,8} = -5.00 \quad (21)$$

$$\lambda_{1,8} = 17 \text{ cm}^2\text{ohm}^{-1}\text{mol}^{-1} \quad (22)$$

(b). *The nonconducting species.* At concentrations above 9 M HClO_4 in the aqueous phase the material balances indicate further species in addition to the conducting ones. $C_{1,2}$ and $C_{1,8}$ are computed and subtracted from $[\text{HClO}_4]_{\text{org}}$ in the range $9 \leq C_{\text{HClO}_4} \leq 10$. We also employ the results of Fig. 7, and assume that we have two water molecules per acid in the complex. We assume the reaction to be the following:

$$u\text{H}^+ + u\text{ClO}_4 + 2u\text{H}_2\text{O} \rightleftharpoons (\text{HClO}_4(\text{H}_2\text{O})_2)_u(\text{org}) \quad (23)$$

$$\log [(\text{HClO}_4(\text{H}_2\text{O})_2)_u] = \log K_{u,2u} + u \log \{H^+\} \{ClO_4\} + 2u \log \{H_2O\} \quad (24)$$

In Table 6 $\log K_{u,2u}$ has been computed for $u = 2$ and 3.

Table 6. Evaluation of $K_{u,2u}$ from eqn. (24).

C_{HClO_4}	$[\text{HClO}_4]_{u,2u}$	$\log [\text{HClO}_4]_{u,2u}$	$\log \{H^+\} \{ClO_4^-\}$	$\log \{H_2O\}$	$\log K_{2,4}$	$\log K_{3,6}$
9.0	0.019	-1.72	7.20	-0.99	-12.46	-17.86
9.5	0.056	-1.25	7.71	-1.15	-12.37	-17.96
10	0.149	-0.83	8.22	-1.33	-12.25	-17.99
				Average:	-12.36 ± 0.12	-17.94 ± 0.08

From Table 6 it is seen that a trimer seems to fit the data better than a dimer.

As with nitric acid we have made a computer refinement with LETAGROP which has been extended to encompass also conductivity data. As starting values for the complexes the values given by Tables 4 − 6 have been used. The results are collected in Table 7 together with the results obtained in Tables 4 − 6. In the column for $\log \lambda$ the values given within parentheses have been obtained by computer and using the constants given in Tables 4 − 6. The agreement with the values obtained by extrapolation in Fig. 9 is satisfactory.

For the water equilibria the constants given by (7) have been used. As for the nitric acid case, the equilibrium constants determined from the water analysis (choice 2) are rather uncertain compared to choice 3 (acid analyses) since most of the water is involved in the equilibria (7). The agreement must, however, be regarded as rather satisfactory.

Table 7.

Choice	Complex	log K Tables 4 – 6	log K LETAGROP	log λ graphical	log λ computer	$\sigma(y)$	U
	[1,8	− 6.46	− 6.77(− 6.38)*	1.23 (1.22 ± 0.15)	0.99 ± 0.15]		
2	1,2	− 7.74	− 7.52 ± 0.10	0.81 (0.83 ± 0.02)	0.47 ± 0.02	0.007	4.81 × 10⁻⁴
	3,6	− 17.94	− 17.99 Not varied	—	—		
	[1,8	− 6.46	− 5.36 ± 0.28	1.23 (1.22 ± 0.15)	0.88 ± 0.15]		
3	1,2	− 7.74	− 7.76 ± 0.03	0.81 (0.83 ± 0.02)	0.54 ± 0.02	0.0005	1.84 × 10⁻⁶
	3,6	− 17.94	− 17.94 ± 0.07	—	—		

* Here log $(K + 3\sigma(K))$ is given. In other cases log $K \pm 3\sigma(\log K)$.

Table 8.

Equilibrium constants	$\delta_{1,8}$	$\delta_{1,2}$	$\delta_{3,6}$	$\sigma(y)$	U
Tables 4 – 6	0.15 ± 0.51	− 4.24 ± 0.19	− 3.71 ± 1.17	0.18	0.97 × 10³
Choice 3	0.26 ± 0.50	− 4.33 ± 0.20	− 3.47 ± 1.27	0.20	1.16 × 10³

A dimer (2,4) instead of a trimer gives an error squares sum 50 times larger than that in Table 7 and can thus be excluded. Besides 1,2 many different complexes (1,3) (1,4) (1,5), *etc.*, up to (1,18) were tried but the best fit was found with (1,8). However, this complex is very uncertain, and can only be taken to indicate the presence of hydrated ions with more than two water molecules per acid. For that reason this species is put within brackets in Table 7.

Chemical shifts. Finally the chemical shifts have been computed with LETAGROP employing eqns. (8) and (9) and the constants given in Tables 4 – 6 as well as for choice 3. The results given in Table 8 were obtained.

For the two water species the shifts given by (10) have been used. As seen in Tables 7 and 8 both equivalent conductivities as well as the shifts values are somewhat dependent on the equilibrium constants used; these quantities might thus change with an improved set of equilibrium constants.

As seen in Table 7 the values obtained in Tables 4 – 6 agree well with the values obtained by computer for 1,2 and 3,6, while the obtained value for 1,8 in Table 5 falls between the values from choices 2 and 3. For that reason we have given the values from Tables 4 – 6 in the abstract with limits found by comparing data in Table 7. The fit to the data in the water extraction could be improved by introducing further species, *cf.* Fig. 6. However, we do not feel that the present data permit more than a minimum description, fairly well satisfying all three kinds of experimental data used.

DISCUSSION

$C_6H_5NO_2 - HNO_3 - H_2O$. The reason that in the previous study [1] no definite water acid complexes were reported for the organic phase was that we were not fully convinced of the reliability of the Karl Fischer method for this system. In the present study we have used the possibility to integrate the NMR signal from acid and water in the organic phase. The concentration determined from NMR agrees to within 10 % with the analytically determined one, which is as good as can be expected considering the low intensity of the NMR signal. We thus have little reason to doubt the correctness of the water analysis in the concentration range used in our calculations.

The chemical shifts determined for the species in the interval $0-7$ M are $\delta_{HNO_3(H_2O)_2} = -1.45$ ppm and $\delta_{(HNO_3H_2O)_2} = -7.59$ ppm. In the system $C_6H_6 - HNO_3 - H_2O$ [14] we found evidence for the complexes $HNO_3.H_2O$ and $(HNO_3)_2.H_2O$. The chemical shifts for these species are close to that of the water reference, $i.e. \approx 0$ ppm. The water resonance in nitrobenzene is ≈ 2 ppm shifted towards negative values as compared to water in benzene. It can thus be seen that the shift for $HNO_3(H_2O)_2$ in nitrobenzene is in agreement with the shifts determined for similar complexes in benzene. The shift for $(HNO_3.H_2O)_2$ is on the other hand much more removed towards lower values. It is in fact so much shifted that one is tempted to compare it with the shift of H_3O^+ (-11 ppm in aqueous solutions).[18a] We can thus not exclude the possibility that $(HNO_3.H_2O)_2$ is better represented by $(H_3O^+NO_3^-)_2$.

At higher acid activities (> 8 M) the chemical shifts measured have a tendency to level off and not to approach the low negative value given above. The reason for this is that at these higher concentrations the dissociation of nitric acid in the aqueous phase is no longer complete. This will favour the extraction of further non ionic species into the organic phase and since these species have considerably more positive shifts the leveling off is easily rationalized.

$C_6H_5NO_2 - HClO_4 - H_2O$. The chemical shifts for this system are $\delta_{HClO_4(H_2O)_8} = 0.2$ ppm, $\delta_{HClO_4(H_2O)_2} = -4.2$ ppm and $\delta_{(HClO_4)_3(H_2O)_6} = -3.7$ ppm. We can make some approximate estimates to investigate whether these shifts are reasonable. Assume that the 1,8 complex "consists of" H^+ (-33 ppm) and $(H_2O)_8$. Take for the shift of $(H_2O)_8$ the mean of the monomer H_2O and liquid H_2O

$$\delta_{HClO_4(H_2O)_8} = \tfrac{16}{17} \times \frac{2.94+0}{2} + \tfrac{1}{17}(-33) = -0.6 \text{ ppm} \tag{25}$$

The 1,2 complex "consists of" $(H_2O)_2$ and H^+ giving

$$\delta_{HClO_4(H_2O)_2} = \tfrac{4}{5} \times 2.18 + \tfrac{1}{5}(-33) = -4.9 \text{ ppm} \tag{26}$$

It is thus seen that these estimates can account approximately for the chemical shifts observed, and are in agreement with the observation of dissociated species in the organic phase. The shift of the trimer is rather close to that of the 1,2 complex of the same composition. This leads one to suspect that the trimer should rather be written $(H(H_2O)_2^+ClO_4^-)_3$.

The equivalent conductivity in nitrobenzene of the 1,8 complex is found to be larger than of the 1,2 complex. This might at first sight seem surprising.

It must, however, be emphasized that we have not considered the interaction between the complexes and the nitrobenzene. It might very well be so that the 1,2 ions interact more strongly with the nitrobenzene and hence exhibit a lower mobility. Finally, it should once again be emphasized that the minimum number of complexes needed to fit the three kinds of experimental data have been used. We feel that at present no complexes can be added with a reasonable significance.

Added in proof. According to recent measurements by Walter the solubility of nitrobenzene in $HClO_4 - H_2O$ is larger than we expected making the distinction between dimers, trimers *etc.* less certain, because of unknown influence on the activity coefficients.

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