

NMR and Equilibrium Investigations on the Benzene Phase of the Systems $C_6H_6-HCl-H_2O$ and $C_6H_6-HNO_3-H_2O$

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The chemical shift of the proton resonance signal due to the water and acid present in the benzene phase of the ternary systems $C_6H_6-HCl-H_2O$ and $C_6H_6-HNO_3-H_2O$ has been determined as a function of the acid strength. The interpretation of the NMR-data is discussed on the basis of available distribution measurements. It is confirmed that complex formation between HCl and H_2O is negligible in benzene whereas in the $C_6H_6-HNO_3-H_2O$ system the equilibrium and NMR-data indicate the existence of complexes with the probable composition $HNO_3 \cdot H_2O$ and $(HNO_3)_2 \cdot H_2O$ in addition to the species HNO_3 and H_2O .

The extraction by hydrocarbons of hydrochloric acid, nitric acid, and water from aqueous solutions of the acids has been studied by a number of authors.¹⁻⁶ The solubility of mineral acids in hydrocarbons was first studied by Grinberg *et al.*¹ In investigations of the extraction of HNO_3 by amines dissolved in hydrocarbons, empirical corrections have been made for the amounts of HNO_3 extracted by the diluents.^{2,3} Hardy *et al.*⁴ studied the distribution of HNO_3 between nitric acid and benzene and between nitric acid and toluene and concluded that HNO_3 was extracted as the complex $(HNO_3)_2 \cdot H_2O$. Högfeldt and Bolander,⁵ however, were able to account for the extraction results for the same systems by assuming a distribution equilibrium of monomeric HNO_3 between the two phases, although the possible existence of mixed acid water complexes could not be excluded.

In the present paper we describe the results obtained in a high resolution NMR-investigation of samples drawn from the benzene phase of the systems $C_6H_6-HCl-H_2O$ and $C_6H_6-HNO_3-H_2O$. The purpose has been to try to resolve the discrepancies between the earlier investigations.

EXPERIMENTAL

The samples were prepared and analyzed as described previously by Högfeldt and Bolander.⁵ The benzene was checked by VPC and found to be 99.9 %. We are indebted to Gösta Lindgren for making this purity control. Since benzene samples with a high HNO₃-content undergo nitration fairly rapidly, the NMR-measurements and the analyses were carried out as soon as possible after the preparation. The NMR-measurements were made on a Varian A-60 spectrometer equipped with a Hewlett-Packard 202A audio oscillator and a Hewlett-Packard 5512A electronic frequency counter.

BENZENE—HYDROCHLORIC ACID—WATER

Activity coefficients. If the species H₂O, C₆H₆, and HCl are regarded as the independent components of the system we have to take into account the following equilibria:



In the subsequent study the interest will be focused mainly on the first and third of these reactions. At equilibrium we have

$$a_A/\{A\} = K_D \quad (4)$$

where a_A and $\{A\}$ are the activities of any of the compounds in the organic and aqueous phase respectively. K_D is the thermodynamic distribution coefficient, the value of which is dependent upon the choice of standard states. For the acid component, for water in the benzene phase, and for benzene in the aqueous phase, the hypothetical 1 M solution is taken as the standard state. For water in the aqueous phase and benzene in the benzene phase the pure substances are chosen as the standard states. By introducing:

$$[A] \cdot \gamma_A = a_A \quad (5)$$

where $[A]$ is the concentration of A in the benzene phase (in moles/l) and γ_A the corresponding activity coefficient we get from eqn. (4)

$$\gamma_A = \frac{K_D \cdot \{A\}}{[A]} \quad (6)$$

K_D was calculated for HCl by extrapolating $[A]/\{A\}$ to $[A] = 0$. For H₂O K_D was put equal to the solubility of water in benzene. From these distribution constants we obtain the values of $\gamma_{\text{H}_2\text{O}}$ and γ_{HCl} which have been plotted in Fig. 1 against the stoichiometric acid concentration in the aqueous phase, C_{HCl} . The activity data used for the system H₂O—HCl have been discussed elsewhere.⁷ It appears that the evaluated activity coefficients remain constant at different compositions and that they have values approximately equal to unity, except for the highest acid concentrations for which at least the water determinations are somewhat uncertain. These results are equivalent to the finding^{8ab} that the amounts of water and hydrochloric

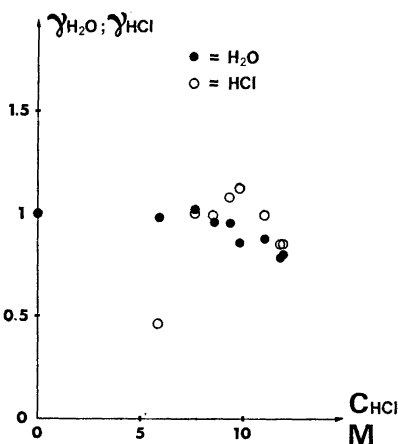


Fig. 1. The activity coefficient for water in the organic phase γ_{H_2O} (●) and the activity coefficient for hydrochloric acid in the organic phase γ_{HCl} (○) at 25°C versus the stoichiometric hydrochloric acid concentration in the aqueous phase, C_{HCl} .

acid in the organic phase are proportional to the corresponding activities in the aqueous phase.

NMR-measurements. The NMR-spectra of the benzene phase were recorded at 32°C whereas the equilibration of the two phases was carried out at 25°C. This temperature difference is neglected as a first approximation, *i.e.* the relative amounts of the various species are assumed to be unchanged. Only one resonance peak was found for the H_2O, HCl protons. The observed line width of this peak is approximately independent of the composition of the benzene phase. These findings indicate that a rapid exchange of protons takes place between the different available sites in the organic phase. The observed resonance line frequency should therefore be determined by the relation⁹

$$\nu_{obs} = \sum_i p_i \nu_i \quad (7)$$

ν_i is the resonance frequency for the protons at the site "i" and p_i is the proton fraction for that site. The resonance line position of the H_2O, HCl protons

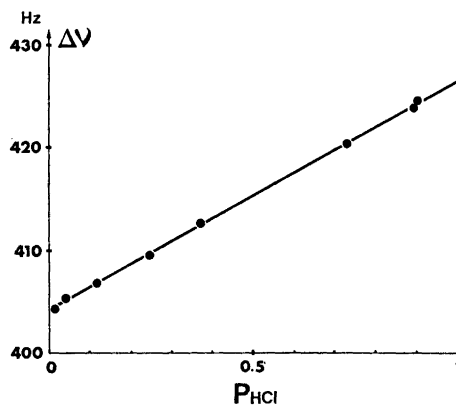


Fig. 2. The H_2O, HCl proton chemical shift $\Delta\nu$ measured relative to C_6H_6 as internal standard against the stoichiometric proton fraction of HCl , P_{HCl} .

was determined, at different compositions of the organic phase, using C_6H_6 as an internal standard. In separate experiments we verified that the resonance line position for the C_6H_6 hydrogens is independent of the acid concentration when determined against chloroform as an external standard. In Fig. 2 the chemical shift, $\Delta\nu$, of the H_2O, HCl hydrogens (relative to benzene) is plotted against the stoichiometric proton fraction P_{HCl} defined by

$$P_{HCl} = \frac{[HCl]}{[HCl] + 2[H_2O]} \quad (8)$$

If there is no complex formation between HCl and H_2O in the benzene phase, there are only two kinds of proton sites, namely the HCl - and the H_2O -sites. In such a case we can expect $\Delta\nu$ to vary linearly with P_{HCl} , since then $p_{HCl} = P_{HCl}$, and thus we have according to eqn. (7)

$$\nu_{obs} = P_{HCl}\nu_{HCl} + (1 - P_{HCl})\nu_{H_2O} \quad (9)$$

Such a linear variation of $\Delta\nu$ with P_{HCl} was found as shown in Fig. 2.

We have compared the resonance line positions of HCl and H_2O in benzene with the line positions for the same compounds in the gas phase. For H_2O the resonance line is shifted 25 c/s towards higher field relative to gaseous H_2O whereas for HCl the shift is 17 c/s towards lower field. These shifts are corrected for the bulk susceptibility differences. The data required for these calculations were taken from Refs. 10 and 11.

Self-association of H_2O and HCl in the organic phase would presumably cause large downfield shifts and can therefore hardly be of importance. Formation of strong π -electron complexes with benzene should give rise to shifts towards higher field. The order of magnitude of this shift would be 100 c/s.¹² Such a strong interaction can thus be excluded.

BENZENE—NITRIC ACID—WATER

The dependence of the activity coefficients γ_{H_2O} and γ_{HNO_3} on the acid concentration in the aqueous phase is given in Fig. 3. The variation of γ_{HNO_3} is

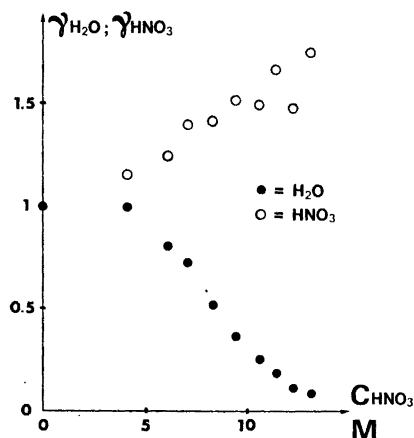


Fig. 3. The activity coefficient for water in the organic phase γ_{H_2O} (●) and the activity coefficient for nitric acid in the organic phase γ_{HNO_3} (○) at 25°C against the stoichiometric nitric acid concentration in the aqueous phase, C_{HNO_3} .

relatively small, neglecting the very uncertain measurements for the two lowest concentrations, supporting the preliminary description⁵ of a simple distribution equilibrium for HNO_3 , while $\gamma_{\text{H}_2\text{O}}$ drops significantly to about 0.1. The activity coefficients were evaluated from the activity data for the $\text{H}_2\text{O}-\text{HNO}_3$ system given by Redlich¹³ in the same way as described above for the $\text{C}_6\text{H}_6-\text{HCl}-\text{H}_2\text{O}$ system. The solubility of benzene in water is small¹⁴ and no detectable amounts of C_6H_6 are dissolved in the aqueous phase as checked by NMR for the most concentrated acid solutions studied. Thus the activity data in question should be applicable for the aqueous phase of the $\text{C}_6\text{H}_6-\text{HNO}_3-\text{H}_2\text{O}$ system. More recent activity data are available for the $\text{H}_2\text{O}-\text{HNO}_3$ system.^{15,16} In a future paper we want to make an attempt to evaluate an improved set of activities from these measurements.

As for the $\text{C}_6\text{H}_6-\text{HCl}-\text{H}_2\text{O}$ system only one resonance line was found and was attributed to the H_2O and HNO_3 protons in the benzene phase. However, in the case of the $\text{C}_6\text{H}_6-\text{HNO}_3-\text{H}_2\text{O}$ system, the position of this line is rapidly shifted towards lower field when the HNO_3 -content of the benzene phase is increased. In fact the entire measured shift amounts to about 350 c/s as shown in Fig. 4 where $\Delta\nu$ is plotted against the stoichiometric proton fraction of HNO_3 , P_{HNO_3} .

$$P_{\text{HNO}_3} = \frac{[\text{HNO}_3]}{[\text{HNO}_3] + 2[\text{H}_2\text{O}]} \quad (10)$$

The value 350 c/s should be compared with the shift of 10 c/s towards higher field obtained for the HCl system. Another important difference is that the line width exhibits a significant variation with P_{HNO_3} in the HNO_3 system.

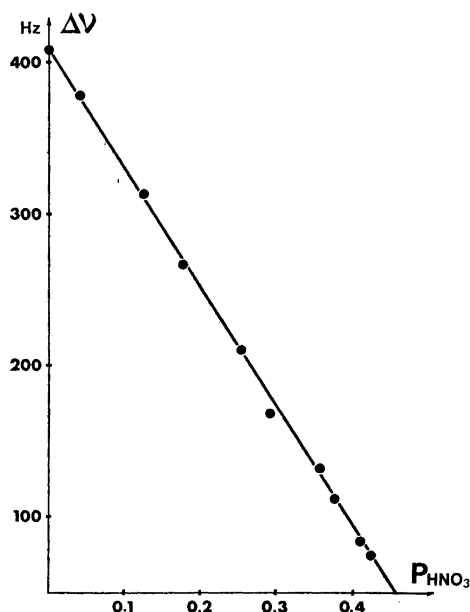
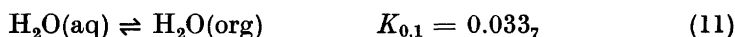


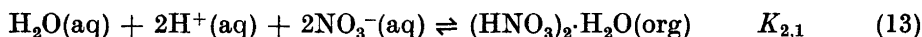
Fig. 4. The $\text{H}_2\text{O}, \text{HNO}_3$ proton chemical shift $\Delta\nu$ measured relative to C_6H_6 as internal standard against the stoichiometric proton fraction of HNO_3 , P_{HNO_3} .

Evaluation of possible complexes from activity coefficients. The activity coefficient determinations as well as the NMR-measurements indicate formation of complexes between water and acid in the organic phase. A likely complex would be $\text{HNO}_3 \cdot \text{H}_2\text{O}$ found in several organic systems.^{17,18} As already mentioned Hardy *et al.*⁴ suggested that all HNO_3 is extracted into the benzene phase in the form of $(\text{HNO}_3)_2 \cdot \text{H}_2\text{O}$.

As a starting point we assume the following molecular species to be present in the benzene phase: H_2O , $\text{HNO}_3 \cdot \text{H}_2\text{O}$ and $(\text{HNO}_3)_2 \cdot \text{H}_2\text{O}$. For the system $\text{C}_6\text{H}_6 - \text{HCl} - \text{H}_2\text{O}$ the activity coefficients are constant for the two components H_2O and HCl . It is thus reasonable to assume that they are constant also for the species in the present system. The concentration of H_2O is known from the experiments of the preceding section and previous investigations^{5,8a} and has here been calculated from the previously determined equilibrium constant $K_{0,1}$ for the reaction



The concentration of the other species are given by the following equilibria:



The quantity Y given by:

$$Y = \frac{[\text{H}_2\text{O}]_{\text{org}}^{\text{tot}} - [\text{H}_2\text{O}]_{\text{org}}}{\{\text{H}^+\}\{\text{NO}_3^-\}\{\text{H}_2\text{O}\}} = K_{1,1} + K_{2,1}\{\text{H}^+\}\{\text{NO}_3^-\} \quad (14)$$

was plotted against $\{\text{H}^+\}\{\text{NO}_3^-\}$. From the resulting straight line we found:

$$\begin{aligned} K_{1,1} &\sim 1 \times 10^{-4} \text{ M}^{-1} \\ K_{2,1} &\sim 2 \times 10^{-8} \text{ M}^{-3} \end{aligned} \quad (15a, b)$$

Starting from these preliminary values of $K_{1,1}$ and $K_{2,1}$ and the constant $K_{0,1}$ (eqn. 11), the computer program LETAGROPVRID,¹⁹ adopted to the present problem by Warnqvist,²⁰ was used to find the "best" constants $K_{1,1}$ and $K_{2,1}$. In this variation values for the equilibrium constants are sought which give a minimum in the error square sum

$U = \sum_1^{18} ([\text{H}_2\text{O}]_{\text{tot}}^{\text{calc}} - [\text{H}_2\text{O}]_{\text{tot}}^{\text{exp}})^2$ (18 experimental points). The following result was obtained:

$$\begin{aligned} K_{1,1} &= (9.85 \pm 0.23) \times 10^{-5} \text{ M}^{-1} \\ K_{2,1} &= (1.70 \pm 0.11) \times 10^{-8} \text{ M}^{-3} \end{aligned} \quad (16a, b)$$

The uncertainty given in (16) is $\pm \sigma$, the standard deviation. Moreover, the following additional complexes were tried but did not improve the fit:



When trying to describe the extraction of the nitric acid with the two complexes $\text{HNO}_3 \cdot \text{H}_2\text{O}$ and $(\text{HNO}_3)_2 \cdot \text{H}_2\text{O}$ and the constants given by eqn. (16) too low values were obtained. Of course water-free species like HNO_3 do not contribute to the mass balance for H_2O and no information about such species can be obtained from that balance. By subtracting the amount of

nitric acid due to $\text{HNO}_3 \cdot \text{H}_2\text{O}$ and $(\text{HNO}_3)_2 \cdot \text{H}_2\text{O}$ from the total amount of nitric acid in the organic phase it was found that the difference was proportional to $\{\text{H}^+\}\{\text{NO}_3^-\}$ indicating the presence of HNO_3 in the organic phase. The equilibrium constant $K_{1,0}$ for the reaction



was evaluated by computer calculations minimizing

$$U = \sum_1^{18} ([\text{HNO}_3]_{\text{tot}}^{\text{calc}} - [\text{HNO}_3]_{\text{tot}}^{\text{exp}})^2$$

giving

$$K_{1,0} = (1.23 \pm 0.05) \times 10^{-5} \quad (18)$$

The other equilibrium constants were not varied.

The concentrations of the various species at different C_{HNO_3} , as determined by the above set of reactions and equilibrium constants are plotted (the dashed curves) in Fig. 5. It also appears that the calculated stoichiometric concentrations of water and acid as given by the full drawn curves agree well with the experimental results. Only one point at $C_{\text{HNO}_3} = 12.24$ is slightly off the curve probably because of nitration. All other points agree within the experimental uncertainty, estimated as ± 0.002 M.

NMR-measurements. The NMR-data also show that there is a strong interaction between HNO_3 and H_2O in the benzene phase. It is likely that this

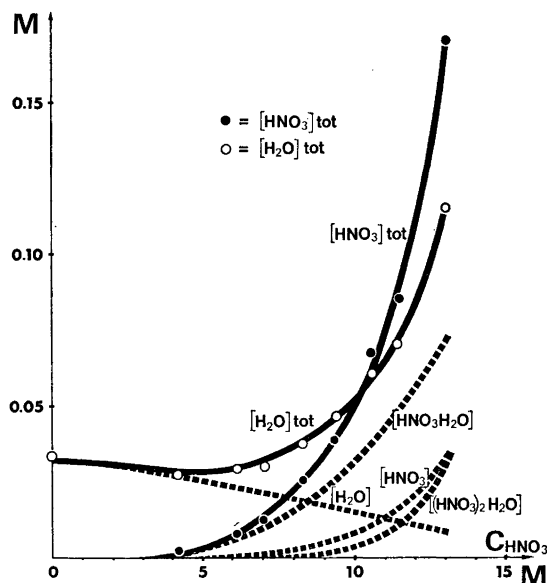


Fig. 5. The concentrations of the species H_2O , HNO_3 , $\text{HNO}_3 \cdot \text{H}_2\text{O}$, and $(\text{HNO}_3)_2 \cdot \text{H}_2\text{O}$ (dashed curves) as calculated from eqns. (11)–(13) and (17) together with the quantities $[\text{H}_2\text{O}]_{\text{tot}}$ and $[\text{HNO}_3]_{\text{tot}}$ against the stoichiometric acid concentration in the aqueous phase, C_{HNO_3} .

interaction involves a formation of hydrogen bonds, otherwise the large downfield shifts could hardly be explained. Furthermore, when the temperature of the sample corresponding to $C_{\text{HNO}_3} = 7.05 \text{ M}$ was raised 25°C , the shift changed from 268 c/s to 281 c/s. Thus the temperature dependence of the resonance frequency in question is about the same as for pure water (0.5 c/s $^\circ\text{C}$).¹¹

Using the knowledge obtained concerning the molecular composition of the benzene phase at different acid strengths, it is possible to account for the observed resonance frequency variation.

Consider first the interval $0 < P_{\text{HNO}_3} < 0.25$. In this range the protons originate almost exclusively from H_2O and $\text{HNO}_3 \cdot \text{H}_2\text{O}$. Thus the resonance frequency should be given by

$$\nu_{\text{obs}} = p_{\text{H}_2\text{O}} \cdot \nu_{\text{H}_2\text{O}} + p_{\text{HNO}_3 \cdot \text{H}_2\text{O}} \cdot \nu_{\text{HNO}_3 \cdot \text{H}_2\text{O}} \quad (19)$$

Since $p_{\text{HNO}_3 \cdot \text{H}_2\text{O}} = 3P_{\text{HNO}_3}$ in this interval, eqn. (19) means that ν_{obs} should vary linearly between $P_{\text{HNO}_3} = 0$ and $P_{\text{HNO}_3} = 1/3$. For values of $P_{\text{HNO}_3} > 0.25$ the situation becomes more complex since the concentrations of $(\text{HNO}_3)_2 \cdot \text{H}_2\text{O}$ and HNO_3 are no longer negligible. Eqn. (19) now has to be replaced by the expression

$$\begin{aligned} \nu_{\text{obs}} = & p_{\text{H}_2\text{O}} \cdot \nu_{\text{H}_2\text{O}} + p_{\text{HNO}_3 \cdot \text{H}_2\text{O}} \nu_{\text{HNO}_3 \cdot \text{H}_2\text{O}} + p_{(\text{HNO}_3)_2 \cdot \text{H}_2\text{O}} \nu_{(\text{HNO}_3)_2 \cdot \text{H}_2\text{O}} + \\ & + p_{\text{HNO}_3} \nu_{\text{HNO}_3} \end{aligned} \quad (20)$$

The observed resonance frequency for the protons in $(\text{HNO}_3)_2 \cdot \text{H}_2\text{O}$ should be lower than in $\text{HNO}_3 \cdot \text{H}_2\text{O}$ since in the first-mentioned complex half the protons are engaged in hydrogen bonding, whereas in $\text{HNO}_3 \cdot \text{H}_2\text{O}$ only one third of the protons are engaged. This can be verified by inspecting possible structures for the compounds, examples of which are shown in Fig. 6 (electrical charges omitted).

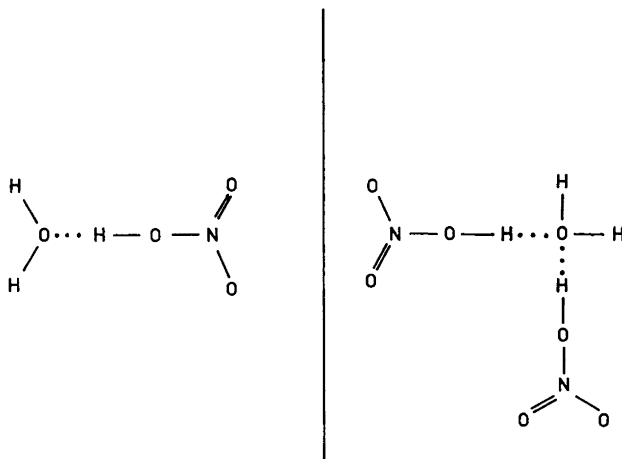


Fig. 6. Possible structures of the species $\text{HNO}_3 \cdot \text{H}_2\text{O}$ and $(\text{HNO}_3)_2 \cdot \text{H}_2\text{O}$.

Let us suppose that the proton resonance frequency in $(\text{HNO}_3)_2 \cdot \text{H}_2\text{O}$ is close to the frequency obtained by extending the straight line corresponding to eqn. (19) to $P_{\text{HNO}_3} = 0.5$. Such a situation would mean, as can be verified by eqn. (7), that all mixtures of H_2O , $\text{HNO}_3 \cdot \text{H}_2\text{O}$ and $(\text{HNO}_3)_2 \cdot \text{H}_2\text{O}$ would give a resonance frequency close to a straight line in accordance with our observations.

So far we have neglected the contribution from the HNO_3 -species. However, the actual proton fraction of HNO_3 never exceeds 0.075 and whatever value of $\Delta\nu_{\text{HNO}_3}$ we assume, a minor effect is obtained on the position of the resonance line as compared with the effect of $(\text{HNO}_3)_2 \cdot \text{H}_2\text{O}$ for which the proton fraction rises to 0.3.

Using the calculated equilibrium constants and keeping $\Delta\nu_{0,1}$ constant computer calculations minimizing $U = \sum_1^{18} (\Delta\nu_{\text{calc}} - \Delta\nu_{\text{exp}})^2$ gave the results shown in Table 1. In Table 1 we have also collected the equilibrium constants.

Table 1. Values for $K_{p,q}$ and $\Delta\nu_{p,q}$.

Complex	$K_{p,q}$ (25°C)	$\Delta\nu_{p,q}$ c/s (32°C)
H_2O	0.034 M (not varied)	405 (not varied)
$\text{HNO}_3 \cdot \text{H}_2\text{O}$	$(9.85 \pm 0.23) \times 10^{-5} \text{ M}^{-1}$	149 ± 25
$(\text{HNO}_3)_2 \cdot \text{H}_2\text{O}$	$(1.70 \pm 0.11) \times 10^{-8} \text{ M}^{-2}$	107 ± 61
HNO_3	$(1.23 \pm 0.05) \times 10^{-6} \text{ M}^{-1}$	—

The spread given is the standard deviation $\pm \sigma$.

For the interpretation of the uncertainty in $\Delta\nu$ it should be noted that the zero point of the $\Delta\nu$ -scale is arbitrary. As mentioned before the amount of HNO_3 is too small to allow $\Delta\nu_{\text{HNO}_3}$ to be determined with any reasonable accuracy.

The variation of the line width mentioned above can be interpreted as arising because of the exchange of protons between different sites. If this exchange is not rapid enough to give a complete collapse of the signals from the exchanging sites the obtained signal will have a line width given by:²¹

$$\frac{1}{T_2} = \frac{p_A}{T_{2A}} + \frac{p_B}{T_{2B}} + p_A^2 p_B^2 (\omega_A - \omega_B)^2 (\tau_A + \tau_B) \quad (21)$$

T_2 = effective transverse relaxation time
 T_{2A}, T_{2B} = transverse relaxation time at site A; B
 τ_A, τ_B = life time for a nucleus on site A; B
 $\omega = 2\pi\nu$

From eqn. (21) it can be understood that even if the life times for the protons at different sites are about the same in the HNO_3 -system as for the HCl -system, for the HNO_3 -system a line width broadening can arise due to the large separation of the resonance frequencies.

In Fig. 7 a theoretical curve obtained from eqn. (21) has been drawn under the assumption $T_{2A} = T_{2B}$ and putting $A = \text{H}_2\text{O}$ and $B = \text{HNO}_3 \cdot \text{H}_2\text{O}$.

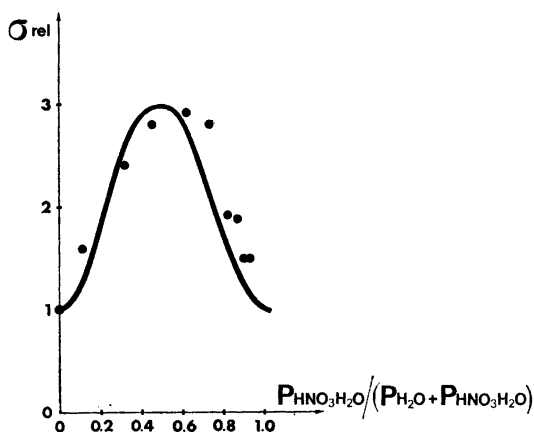


Fig. 7. The relative line width of the H_2O, HNO_3 signal σ_{rel} against $p_{HNO_3 \cdot H_2O} / (p_{H_2O} + p_{HNO_3 \cdot H_2O})$.

It can be seen that the experimental points fall on this curve when $p_{HNO_3 \cdot H_2O} / (p_{H_2O} + p_{HNO_3 \cdot H_2O})$ is less than 0.6 ($C_{HNO_3} = 8.3$). Above this value the amounts of $(HNO_3)_2 \cdot H_2O$ and HNO_3 are no longer negligible and the situation becomes more complex. Since the σ_{rel} -values are not very accurate (± 0.2) we only point out the two following features. At high acid concentrations ($C_{HNO_3} > 11$ M), $HNO_3 \cdot H_2O$ and $(HNO_3)_2 \cdot H_2O$ become the predominating species on the proton fraction scale and since $\nu_{HNO_3 \cdot H_2O} - \nu_{(HNO_3)_2 \cdot H_2O}$ is supposed to be less than $\nu_{H_2O} - \nu_{HNO_3 \cdot H_2O}$ we would, according to eqn. (21) expect a more narrow line. Eqn. (21) also predicts that as long as we have protons that exchange between different sites the line width will always be larger than the line width for pure water in benzene.

CONCLUDING REMARKS

Thus, for the $C_6H_6-HCl-H_2O$ system there is no complex formation in the organic phase whereas for the $C_6H_6-HNO_3-H_2O$ system we have found evidence for the existence of the complexes $HNO_3 \cdot H_2O$ and $(HNO_3)_2 \cdot H_2O$. In a further check we have made the tentative assumption that there is no complex formation in the case of the HNO_3 system. Such an assumption means that the analytical water determinations are entirely unreliable as was found to be the case in the system $C_6H_5NO_2-HNO_3-H_2O$.⁵ Using eqn. (11) "better" water concentrations were calculated and another set of P_{HNO_3} -values was obtained. When the observed resonance frequency was plotted against these P_{HNO_3} -values the linear relationship between ν_{obs} and P_{HNO_3} was definitely not preserved as would be required in accordance with eqn. (9) if the initial assumption was correct. We therefore prefer to believe in the correctness of the water determinations.

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