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Study of Hydration and Ionization of Nitric Acid in Benzene

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(Received November 18, 1993)

The hydration and ionization of nitric acid in benzene were examined at 298 K. The distribution of nitric acid and of water between aqueous solutions and benzene were determined as functions of water activity in the aqueous phase. Two hydrates, mono- and decahydrate, were found in addition to the anhydride in the organic phase by analyzing the distribution data on the basis of the stoichiometry of the acid hydration. The mono- and decahydrate were ascribed to molecular and ionized nitric acid, respectively, by means of spectrophotometry of the organic phase. By the analyses of the absorption spectra and the distribution data, the ionization of nitric acid by water in benzene was clarified and the equilibrium constant was determined.

Hydration of inorganic acids and ions in aqueous solutions has been determined by many methods.[1—4] However, the hydration number classically obtained depends on the employed method and is usually of unclear identity. On the contrary, X-ray and neutron diffraction methods give a well-defined hydration number which is for the number of water molecules closest to the central ion.[5—7] However, to determine the hydration number of a weakly hydrated ion, e.g., NO_3^-, in aqueous solution by means of the diffraction methods is difficult. In aqueous solution, the three dimensional network of water molecules often conceals such a weak interaction with water.

In a nonpolar solvent such as benzene, the network structure of water is absent and the free water around hydrated ion is in the mono-molecular form. Furthermore, no substitution by solvent molecules for water molecules of hydration occurs because of the inertness. Thus, the nature of hydration can be clarified in a nonpolar solvent. However, nonpolar solvents have been used little for such hydration studies of inorganic materials because of their low solubilities in nonpolar solvents and because of low water content; the diffraction methods cannot be employed for nonpolar solvent systems due to the solubility problem.

In the present study, ionization of nitric acid by water and the hydration of molecular and ionized acid in benzene were clarified by distribution and spectrophotometric methods. The present study has a methodological feature for the determination of hydration numbers. The experiments in the present study contain no procedure for keeping water activity constant, although such a procedure is conventionally often done. The water activity in the aqueous phase decreases with an increase in aqueous nitric acid concentration and the acid distribution is markedly affected by the water activity change. An apparent value from the acid distribution, which is a function of water activity, is used as an index of the acid hydration in benzene. The data of water distribution and of spectrophotometry are also analyzed as functions of water activity.

Experimental

All the chemicals are of reagent grade. Nitric acid (71% aqueous solution), lithium nitrate (purity > 99.0%), and benzene (purity > 99.7%, grade for spectrometry) were used without further purification. The nitric acid was standardized by titration. The experiments were carried out at 298 K.

Distribution of Nitric Acid. A certain volume of an aqueous nitric acid solution and the same volume of benzene were placed in a stoppered glass tube. The two phases were vigorously agitated for 15 min and then centrifuged. The concentration of nitric acid extracted into the organic phase was determined as follows. A portion of the organic phase was transferred into another tube and a certain volume of 1×10^{-3} mol dm^{-3} aqueous sodium hydroxide solution was added. The two phases were shaken vigorously for 15 min and then centrifuged; thus the acid was completely back-extracted into the aqueous phase. The concentration of aqueous nitrate was measured by ion chromatography using a 2.5×10^{-3} mol dm^{-3} aqueous potassium hydrogen phthalate solution as an eluent. The chromatographic system consists of a pump (Shimadzu, LC-9A), an automatic injector (SIL-6B) with 100 μl loop, an anion-separator column (Shim-Pack IC-A1: 10×0.46 cm) and a guard column (Shim-Pack IC-GA1) in an oven (HIC-6A), a pump controller (SCL-6B), a conductometric detector (CDD-6A) and a data analyzing computer (C-R4A Chromatopac). Eluent flow rate was 1.0 cm^3 min^{-1} for all the measurements. Water deionized by a milli.Q system was used for the preparation of eluent. The eluent was filtered on a membrane filter (Millipore type HA 0.45 μm) before use. The temperature in the oven was kept constant at 40 °C.

Distribution of Lithium Nitrate. The distribution of lithium nitrate between aqueous salt solutions and benzene was also measured in a similar manner to the measurements for nitric acid. The experiments were made separately; the distribution system of lithium nitrate contained no nitric acid and that of nitric acid contained no lithium nitrate.

Distribution of Water. The concentration of water in benzene equilibrated with aqueous HNO_3 or $LiNO_3$ solutions was measured by Karl–Fischer titration.

Spectrophotometry. For the spectrophotometry, the benzene solutions containing nitric acid and water were prepared by the distribution manner described above. The absorption of the organic phase in the ultraviolet range from 295 to 400 nm was measured by a spectrophotometer (Shimadzu UV-2200 Type) and recorded by a computer. Quartz cells of 1 and 10 cm optical path were used for the measurements.

Theoretical

Distribution of Nitric Acid. Extraction of nitric acid from an aqueous acid solution into benzene can be generally written as:

$$\mathrm{H^+ + NO_3^- \rightleftharpoons HNO_{3(o)}},$$

$$K_{\mathrm{ex(obs)}} = \frac{[\mathrm{HNO_3}]_{\mathrm{o,t}}}{\{\mathrm{H^+}\}\{\mathrm{NO_3^-}\}} = \frac{[\mathrm{HNO_3}]_{\mathrm{o,t}}}{\gamma_{\mathrm{s}}{}^2[\mathrm{HNO_3}]_{\mathrm{t}}^2}, \qquad (1)$$

where the subscript "o" denotes the species in the organic phase, while the lack of subscript denotes those in the aqueous phase, { } expresses the activity and γ_{s} is the stoichiometric activity coefficient. However, $K_{\mathrm{ex(obs)}}$ is not constant, but is a function of water activity; this observed value is an index for the acid hydration in the organic phase.

Total nitric acid concentration in the organic phase can be the sum of anhydrous acid and the hydrates.

$$[\mathrm{HNO_3}]_{\mathrm{o,t}} = [\mathrm{HNO_3(anhy)}]_{\mathrm{o}} + \sum_{n=1} [\mathrm{HNO_3(H_2O)}_n]_{\mathrm{o}}. \qquad (2)$$

The extraction constant of nitric acid hydrated with n water molecules can be written as:

$$K_{\mathrm{ex},n} = \frac{[\mathrm{HNO_3(H_2O)}_n]_{\mathrm{o}}}{\{\mathrm{H^+}\}\{\mathrm{NO_3^-}\}a_{\mathrm{w}}{}^n}, \qquad (3)$$

where a_{w} is relative water activity in the aqueous phase ($a_{\mathrm{w}}=1$ for pure water). Then, the value of $K_{\mathrm{ex(obs)}}$ can be written as:

$$K_{\mathrm{ex(obs)}} = K_{\mathrm{ex,0}} + \sum_{n=1}(K_{\mathrm{ex},n}\,a_{\mathrm{w}}{}^n), \qquad (4)$$

where $K_{\mathrm{ex,0}}$ is the anhydrous acid extraction constant:

$$K_{\mathrm{ex,0}} = \frac{[\mathrm{HNO_3(anhy)}]_{\mathrm{o}}}{\{\mathrm{H^+}\}\{\mathrm{NO_3^-}\}}. \qquad (5)$$

The $K_{\mathrm{ex(obs)}}$ can be written also by using the hydration constant from the anhydride:

$$K_{\mathrm{ex(obs)}} = K_{\mathrm{ex,0}}(1 + \sum_{n=1}(K'_{\mathrm{hy},n}a_{\mathrm{w}}{}^n)), \qquad (6)$$

where

$$K'_{\mathrm{hy},n} = \frac{[\mathrm{HNO_3(H_2O)}_n]_{\mathrm{o}}}{[\mathrm{HNO_3(anhy)}]_{\mathrm{o}}a_{\mathrm{w}}{}^n} = \frac{K_{\mathrm{ex},n}}{K_{\mathrm{ex,0}}}. \qquad (7)$$

Distribution of Water with Nitric Acid. Total water concentration in benzene equilibrated with an aqueous nitric acid solution is the sum of water free from the acid and water co-extracted with the acid. The concentration of water co-extracted with the acid into benzene can be written as:

$$\begin{aligned}[\mathrm{H_2O}]_{\mathrm{o,a}} &= [\mathrm{H_2O}]_{\mathrm{o,t}} - [\mathrm{H_2O(free)}]_{\mathrm{o}} \\ &= [\mathrm{H_2O}]_{\mathrm{o,t}} - K_{\mathrm{fw}}a_{\mathrm{w}} \\ &= \sum_{n=1}(n[\mathrm{HNO_3(H_2O)}n]_{\mathrm{o}}),\end{aligned} \qquad (8)$$

where

$$K_{\mathrm{fw}} = \frac{[\mathrm{H_2O(free)}]_{\mathrm{o}}}{a_{\mathrm{w}}} = 0.0321. \qquad (9)$$

K_{fw} (=0.0321) is the solubility of water in benzene at 25 °C in the molarity unit at $a_{\mathrm{w}}=1$; this value was obtained in the present study.

From Eqs. 3, 7, and 8,

$$\begin{aligned}\frac{[\mathrm{H_2O}]_{\mathrm{o,a}}}{\{\mathrm{H^+}\}\{\mathrm{NO_3^-}\}} &= \sum_{n=1}(nK_{\mathrm{ex},n}a_{\mathrm{w}}{}^n) \\ &= K_{\mathrm{ex,0}}\sum_{n=1}(nK'_{\mathrm{hy},n}a_{\mathrm{w}}{}^n).\end{aligned} \qquad (10)$$

Spectrophotometry. A part of nitric acid in benzene is ionized by water and an absorption peak of nitrate appears at around 350 nm (see Results).

The ionized nitric acid does not dissociate to free ions in benzene because of very low dielectric constant of the medium. Thus, the equilibrium can be written as:

$$\mathrm{HNO_3(H_2O)}_{p(\mathrm{o})} + (q-p)\mathrm{H_2O} \rightleftharpoons \mathrm{H^+NO_3^-(H_2O)}_{q(\mathrm{o})},$$

$$\begin{aligned}K'_{\mathrm{ion}} &= \frac{[\mathrm{H^+NO_3^-(H_2O)}_q]_{\mathrm{o}}}{[\mathrm{HNO_3(H_2O)}_p]_{\mathrm{o}}a_{\mathrm{w}}{}^{q-p}} \\ &= \frac{K'_{\mathrm{hy},q}}{K'_{\mathrm{hy},p}}(p \le q),\end{aligned} \qquad (11)$$

where $K'_{\mathrm{hy},p}$ and $K'_{\mathrm{hy},q}$ are the hydration constants for molecular and ionized nitric acid:

$$K'_{\mathrm{hy},p} = \frac{[\mathrm{HNO_3(H_2O)}_p]_{\mathrm{o}}}{[\mathrm{HNO_3(anhy)}]_{\mathrm{o}}a_{\mathrm{w}}{}^p}, \qquad (12)$$

$$K'_{\mathrm{hy},q} = \frac{[\mathrm{H^+NO_3^-(H_2O)}_q]_{\mathrm{o}}}{[\mathrm{HNO_3(anhy)}]_{\mathrm{o}}a_{\mathrm{w}}{}^q}. \qquad (13)$$

The absorbance of the organic phase at a certain wavelength can be written as:

$$\begin{aligned}Abs. = {}& \varepsilon_{\mathrm{mo,0}}[\mathrm{HNO_3(anhy)}]_{\mathrm{o}} + \sum_{p=1}(\varepsilon_{\mathrm{mo},p}[\mathrm{HNO_3(H_2O)}_p]_{\mathrm{o}}) \\ &+ \sum_{q=1}(\varepsilon_{\mathrm{ip},q}[\mathrm{H^+NO_3^-(H_2O)}_q]_{\mathrm{o}}),\end{aligned} \qquad (14)$$

where $\varepsilon_{\mathrm{mo,0}}$, $\varepsilon_{\mathrm{mo},p}$ and $\varepsilon_{\mathrm{ip},q}$ are the molar absorptivities of anhydrous molecular nitric acid (free acid), molecular and ionized acid hydrated with p and q water molecules, respectively.

The cumulative molar absorptivity can be written as:

$$\begin{aligned}\varepsilon &= \frac{Abs.}{[\mathrm{HNO_3}]_{\mathrm{o,t}}} \\ &= \frac{\varepsilon_{\mathrm{mo,0}}[\mathrm{HNO_3(anhy)}]_{\mathrm{o}} + \sum_{p=1}(\varepsilon_{\mathrm{mo},p}[\mathrm{HNO_3(H_2O)}_p]_{\mathrm{o}}) + \sum_{q=1}(\varepsilon_{\mathrm{ip},q}[\mathrm{H^+NO_3^-(H_2O)}_q]_{\mathrm{o}})}{[\mathrm{HNO_3(anhy)}]_{\mathrm{o}} + \sum_{p=1}[\mathrm{HNO_3(H_2O)}_p]_{\mathrm{o}} + \sum_{q=1}[\mathrm{H^+NO_3^-(H_2O)}_q]_{\mathrm{o}}} \\ &= \frac{\varepsilon_{\mathrm{mo,0}} + \sum_{p=1}(\varepsilon_{\mathrm{mo},p}K'_{\mathrm{hy},p}a_{\mathrm{w}}{}^p) + \sum_{q=1}(\varepsilon_{\mathrm{ip},q}K'_{\mathrm{hy},q}a_{\mathrm{w}}{}^q)}{1 + \sum_{p=1}(K'_{\mathrm{hy},p}a_{\mathrm{w}}{}^p) + \sum_{q=1}(K'_{\mathrm{hy},q}a_{\mathrm{w}}{}^q)},\end{aligned} \qquad (15)$$

where

$$\sum_{p=1}[\mathrm{HNO_3(H_2O)}_p]_o = \sum_{p=1}(K'_{\mathrm{hy},p}a_\mathrm{w}{}^p)[\mathrm{HNO_3(anhy)}]_o, \quad (16)$$

$$\sum_{q=1}[\mathrm{H^+NO_3{}^-(H_2O)}_q]_o = \sum_{q=1}(K'_{\mathrm{hy},q}a_\mathrm{w}{}^q)[\mathrm{HNO_3(anhy)}]_o. \quad (17)$$

Ionization Constant from Distribution Methods. The ionization constant defined in Eq. 11 can be obtained also from the distribution methods by the following simple equation:

$$K'_\mathrm{ion} = \frac{K_{\mathrm{ex},q}}{K_{\mathrm{ex},p}}, \quad (18)$$

where $K_{\mathrm{ex},p}$ and $K_{\mathrm{ex},q}$ are the extraction constants of the molecular and ionized nitric acid:

$$K_{\mathrm{ex},p} = \frac{[\mathrm{HNO_3(H_2O)}_p]_o}{\{\mathrm{H^+}\}\{\mathrm{NO_3{}^-}\}a_\mathrm{w}{}^p}, \quad (19)$$

$$K_{\mathrm{ex},q} = \frac{[\mathrm{H^+NO_3{}^-(H_2O)}_q]_o}{\{\mathrm{H^+}\}\{\mathrm{NO_3{}^-}\}a_\mathrm{w}{}^q}. \quad (20)$$

The K'_ion can be determined as a sole constant if only a molecular hydrate and an ionic one are present.

Hydration and Ionization Constants in Benzene. The hydrate-formation from free nitric acid (anhydrous acid) and free water can be defined as the equilibria in the sole medium of benzene by using the relation of Eq. 9. The hydration constants for the molecular and ionized acid in benzene can be written as:

$$K_{\mathrm{hy},p} = \frac{[\mathrm{HNO_3(H_2O)}_p]_o}{[\mathrm{HNO_3(anhy)}]_o[\mathrm{H_2O(free)}]_o^p} = \frac{K'_{\mathrm{hy},p}}{K_\mathrm{fw}{}^p}, \quad (21)$$

$$K_{\mathrm{hy},q} = \frac{[\mathrm{H^+NO_3{}^-(H_2O)}_q]_o}{[\mathrm{HNO_3(anhy)}]_o[\mathrm{H_2O(free)}]_o^q} = \frac{K'_{\mathrm{hy},q}}{K_\mathrm{fw}{}^q}. \quad (22)$$

Furthermore, the acid ionization constant in benzene can also be defined as:

$$K_\mathrm{ion} = \frac{[\mathrm{H^+NO_3{}^-(H_2O)}_q]_o}{[\mathrm{HNO_3(H_2O)}_p]_o[\mathrm{H_2O(free)}]_o^{q-p}} = \frac{K'_\mathrm{ion}}{K_\mathrm{fw}{}^{q-p}} = \frac{K_{\mathrm{hy},q}}{K_{\mathrm{hy},p}}. \quad (23)$$

Results

Distribution of Nitric Acid. Figure 1 gives total nitric acid concentration in the organic phase as a function of $\{\mathrm{H^+}\}\{\mathrm{NO_3{}^-}\}$ on a logarithmic scale; the stoichiometric activity coefficients for the acid at various concentrations were cited from literature.[8] If nitric acid in the organic phase is not hydrated, the value of $K_{\mathrm{ex,(obs)}}$ is constant and the slope of one is obtained. However, the experimental data do not show such a case.

The value of $K_{\mathrm{ex(obs)}}$ can be treated as an index of the acid hydration in the organic phase, as is described by Eq. 4. Figure 2(a) and (b) give $K_{\mathrm{ex(obs)}}$as a function of a_w on a logarithmic scale; the water activities in aqueous nitric acid solutions were cited from literature.[8] In the concentration range of aqueous nitric acid higher than 8 mol dm^{-3}, that is, $a_\mathrm{w} < 0.56$, the slope of the plots is between zero and one, as is seen in Fig. 2(a). The slope smaller than one implies the presence of anhydrous nitric acid in the organic phase. From this, the acid anhydride as well as some hydrates was taken into account in Eq. 4. The number of hydrates was assumed to be one, two or three in advance and the data were analyzed by a successive approximation method using a least squares computer program. The equations used for the analyses are as follows:

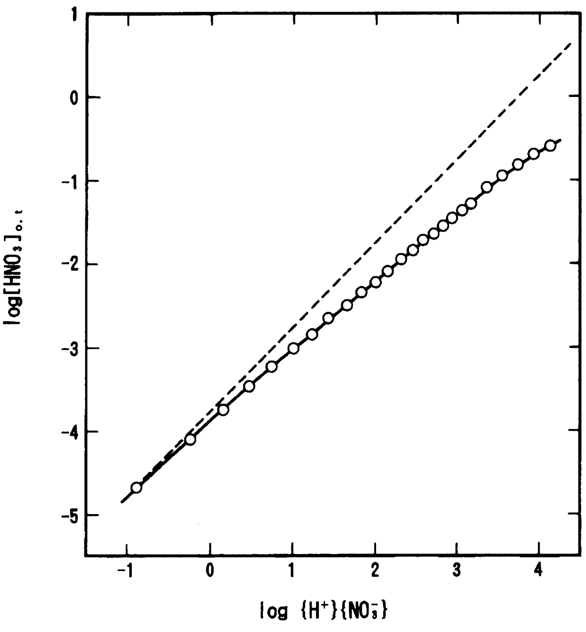

Fig. 1. Total nitric acid concentration in the organic phase as a function of $\{\mathrm{H^+}\}\{\mathrm{NO_3{}^-}\}$ on a logarithmic scale. The broken line is an asymptote to an infinite dilution of aqueous nitric acid where $a_\mathrm{w} \approx 1.000$; in the broken line, $K_{\mathrm{ex(obs)}}(=[\mathrm{HNO_3}]_{o,t}/\{\mathrm{H^+}\}\{\mathrm{NO_3{}^-}\}) = K_{\mathrm{ex},0}+K_{\mathrm{ex},1}+K_{\mathrm{ex},10} = 1.7\times10^{-4}$.

One hydrate assumed;

$$K_{\mathrm{ex(obs)}} = K_{\mathrm{ex},0} + K_{\mathrm{ex},n(1)}a_\mathrm{w}{}^{n(1)}, \quad (\mathrm{I})$$

Two hydrates assumed;

$$K_{\mathrm{ex(obs)}} = K_{\mathrm{ex},0} + K_{\mathrm{ex},n(1)}a_\mathrm{w}{}^{n(1)} + K_{\mathrm{ex},n(2)}a_\mathrm{w}{}^{n(2)}, \quad (\mathrm{II})$$

Three hydrates assumed;

$$K_{\mathrm{ex(obs)}} = K_{\mathrm{ex},0} + K_{\mathrm{ex},n(1)}a_\mathrm{w}{}^{n(1)} + K_{\mathrm{ex},n(2)}a_\mathrm{w}{}^{n(2)} + K_{\mathrm{ex},n(3)}a_\mathrm{w}{}^{n(3)}(n(1) \neq n(2) \neq n(3)). \quad (\mathrm{III})$$

Equation I can apply to the data in Fig. 2(a). The hydration number of $n(1)$ was treated as an unknown value set between 1 and 3 in this calculation; $K_{\mathrm{ex},0}$ and $K_{\mathrm{ex},n(1)}$ were also treated as unknown values. These

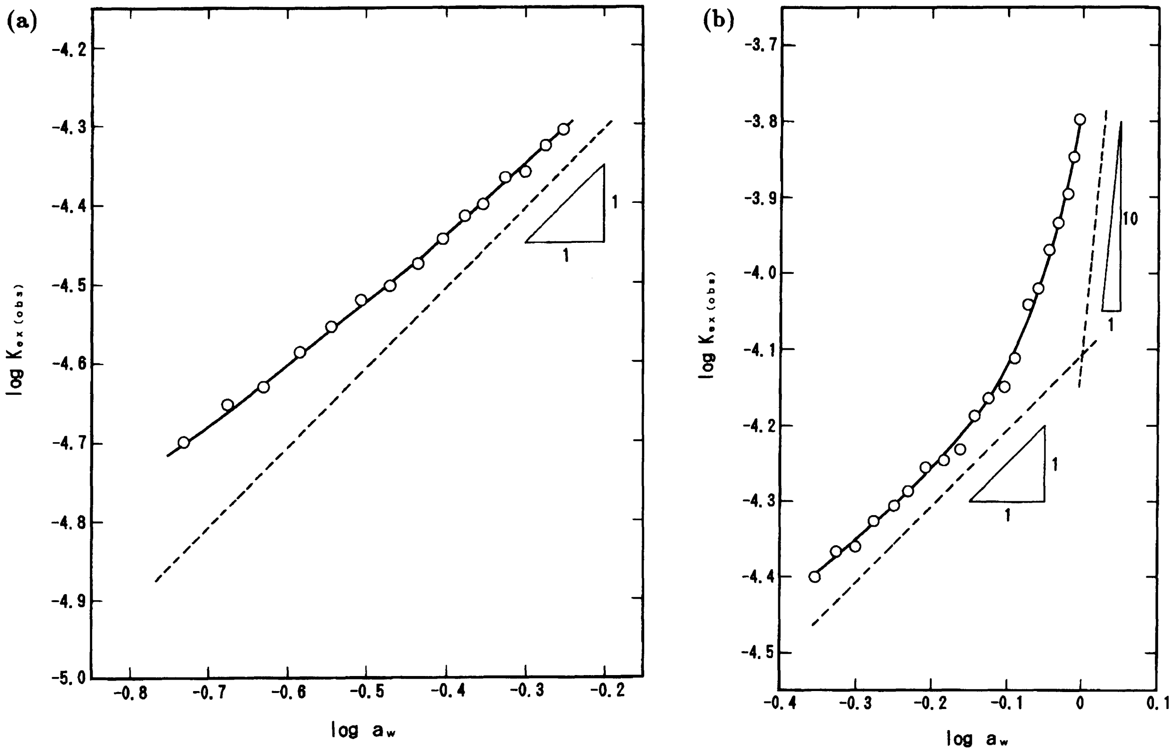

Fig. 2. $K_{\mathrm{ex(obs)}}$ of nitric acid as a function of a_{w} on a logarithmic scale; (a) $[\mathrm{HNO_3}]_{\mathrm{t}} \geq 8$ mol dm^{-3}, (b) $[\mathrm{HNO_3}]_{\mathrm{t}} \leq 10$ mol dm^{-3}. The solid line of each figure was calculated on the basis of Eq. 4 by introducing hydration numbers and equilibrium constants in Table 1. The asymptotic lines are also indicated.

values were precisely obtained with small 3σ errors and the optimum $n(1)$ was an integer of one. Thus, a monohydrate was postulated in the calculation. The results are shown in Table 1. However, in the $[\mathrm{HNO_3}]_{\mathrm{t}}$ lower than 8 mol dm^{-3}, that is, $a_{\mathrm{w}} > 0.56$, $K_{\mathrm{ex(obs)}}$ as a function of a_{w} increases drastically, as is seen in Fig. 2(b). The simple proportion is changed into a much higher order dependence. For the data analysis, at least one hydrate in addition to the monohydrate has to be taken into account. Equation II was applied first to the analysis of data in Fig. 2(b). In this calculation, $n(2)$ and $K_{\mathrm{ex},n(2)}$ were treated as unknown values, while $K_{\mathrm{ex,0}}$, $n(1)$ and $K_{\mathrm{ex},n(1)}$ were introduced as already-known values; the first guess for $n(2)$ was chosen between 2 and 15. These unknown values were obtained precisely and the optimum $n(2)$ was an integer of ten, as is shown in Table 1. Thus, the presence of the mono- and decahydrate in the organic phase interprets the experimental data very well. The analysis by using Eq. III was also made in order to confirm the results. In this analysis, $n(2)$, $K_{\mathrm{ex},n(2)}$, $n(3)$, and $K_{\mathrm{ex},n(3)}$ were treated as unknown values; $n(3)$ as well as $n(2)$ was set between 2 and 15. No combination of three different hydrates gave a standard deviation smaller than that obtained in the analysis assuming the two hydrates; first guessed values for $n(2)$ and $n(3)$ come to be close to the sole value of ten to give a better standard deviation in the course of the calculation. Then, the resulting standard deviation from the analysis by Eq. III was rather worse. From these, it is concluded that no hydrates other than the mono- and decahydrate are present practically in the organic phase. Similar calculations were made also for the data of water distribution and almost the same results were obtained.

Distribution of Water with Nitric Acid. The concentration of water actually co-extracted with nitric acid was also measured. The total water concentration in the organic phase as a function of a_{w} is shown in Fig. 3. In order to determine the concentration of water co-extracted with the acid, free water concentration in the organic phase must be known in advance. If the free water in benzene is monomeric like the water in the vapor state, the free water concentration is proportional to a_{w} obtained from vapor pressure measurements, which is expressed by Eq. 9. In fact, for example, in $\mathrm{LiNO_{3(aq)}}$–benzene system in which $[\mathrm{H_2O}]_{\mathrm{o,t}} \approx [\mathrm{H_2O(free)}]_{\mathrm{o}}$, the total water concentration in the organic phase was in proportion to a_{w}, as is seen in Fig. 4; the distribution ratio of lithium nitrate was extremely low and water co-extracted with the salt was in a negligible amount, which was also checked in the present study. Also in many other electrolytes and benzene systems, the distribution of water occurs on the basis of Eq. 9, which was reported in previous studies.[10,11] The stoichiometric data treatment shown in the present study is available on the condition that free water is in the monomolecular form. The broken line in Fig. 3 indicates the concentration of free water in the organic

Table 1. Hydration Numbers and Equilibrium Constants Obtained from Distribution Methods with 3σ Errors

Method	$n(1)$	$n(2)$	$K_{\mathrm{ex},0}$	$K_{\mathrm{ex},n(1)}$ $(=K_{\mathrm{ex},1})$	$K_{\mathrm{ex},n(2)}$ $(=K_{\mathrm{ex},10})$
Nitric acid Distribution	1.1 (± 0.1)	10.2 (± 0.9)	5.3×10^{-6} $(\pm 4\times10^{-7})$	7.8×10^{-5} $(\pm 4\times10^{-6})$	8.3×10^{-5} $(\pm 6\times10^{-6})$
Water Distribution	1.0 (± 0.2)	10.1 (± 0.5)	—	8.0×10^{-5} $(\pm 9\times10^{-6})$	8.3×10^{-5} $(\pm 5\times10^{-6})$

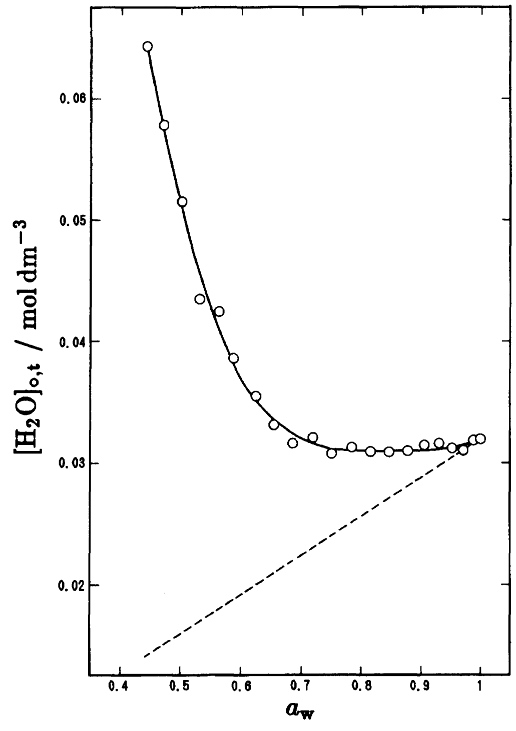

Fig. 3. Total water concentration in the organic phase as a function of a_{w} in $\mathrm{HNO_3}$–benzene system. The broken line indicates the concentration of acid-free water.

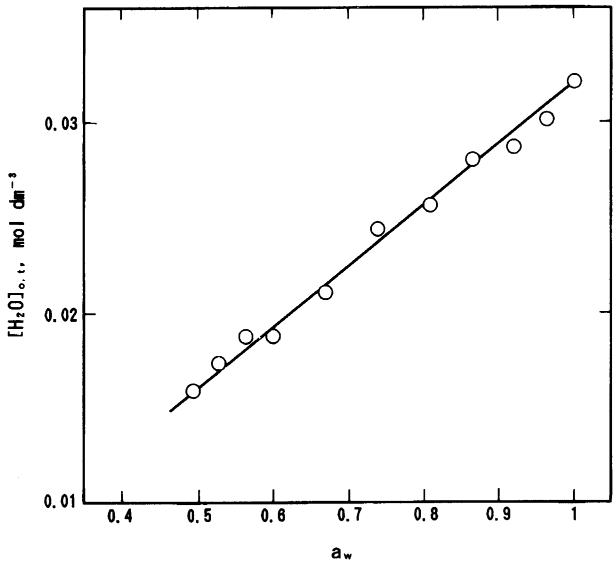

Fig. 4. Total water concentration in the organic phase as a function of a_{w} in $\mathrm{LiNO_3}$–benzene system. The values of a_{w} were calculated on the basis of vapor pressure data of aqueous lithium nitrate solutions in literature.[9] The slope corresponds with the solubility of water in benzene at $a_{\mathrm{w}}=1.000$.

phase. The very large discrepancy between the broken line and the experimental data in Fig. 3 shows that a considerable amount of water is co-extracted with nitric acid.

For the calculation, the experimental data in Fig. 3 were replotted as in Fig. 5. The data were analyzed on the basis of Eq. 10 by the successive approximation method. Also from the analysis of the water distribution data, the mono- and decahydrate of nitric acid in the organic phase were postulated. Furthermore, the equilibrium constants obtained from the water distribution were almost the same as those obtained from the acid distribution, as is seen in Table 1. Thus, the water measurements verified the hydration of nitric acid in benzene.

Spectrophotometry. Figure 6 gives the absorption spectra of the organic phase in the ultraviolet range in the molar absorptivity. A peak appears at around 350 nm, $\varepsilon_{\max}(\varepsilon$ at $\lambda_{\max})=6.2$ (calculated value); while a nitrate peak of $\mathrm{n}\rightarrow\pi^*$ transition appears at 303 nm in aqueous potassium nitrate solution, $\varepsilon_{\max}=6.9$.[12,13] From this, the peak at around 350 nm in benzene can be assigned to nitrate ion. It is reasonable that the nitrate peak in benzene is seen at a higher wavelength than in aqueous solution, because the $\mathrm{n}\rightarrow\pi^*$ transition peak is blue-shifted by an increase in medium polarity.[14] At aqueous acid concentrations higher than 8 mol dm^{-3}, that is, at a_{w} lower than 0.56, the absorption spectra have no peak around 350 nm and are not changed by any change in the acid concentration. From this, the spectrum at the higher $[\mathrm{HNO_3}]_{\mathrm{t}}$ can be attributed to the molecular acid. The absorbances from 295 to 400 nm at an interval of 1 nm were recorded and the data were analyzed by a computer.

Only two absorptive species, molecular and ionized acid, are seen in Fig. 6, because an isosbestic region appears below around 305 nm and the position of $\mathrm{NO_3}^-$ peak is hardly changed with any change in aqueous nitric acid concentration. Thus, Eq. 15 can be simplified to:

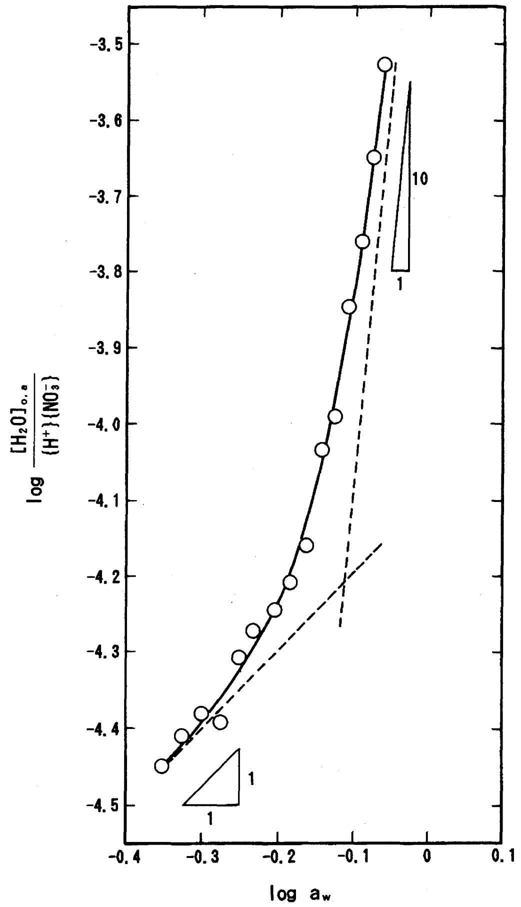

Fig. 5. $[H_2O]_{o,a}/\{H^+\}\{NO_3^-\}$ as a function of a_w on a logarithmic scale. The solid line was calculated by introducing hydration numbers and equilibrium constants in Table 1 into Eq. 10. The asymptotic lines are also indicated.

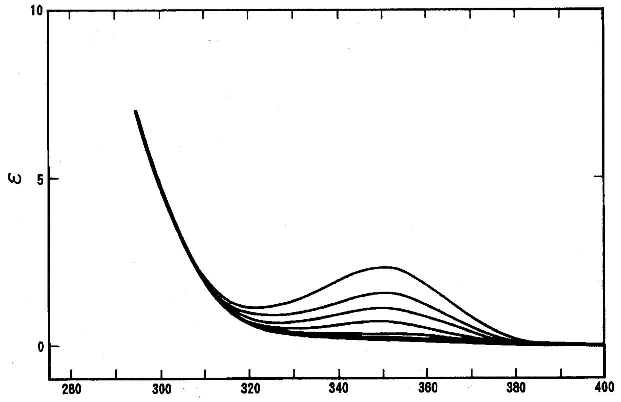

Fig. 6. Absorption spectra of the organic phase in the ultraviolet range; $[HNO_3]_t$=2, 3, 4, 5, 6, 7, 8, 9, 10 mol dm^{-3} from top to bottom.

$$\varepsilon = \frac{\varepsilon_{mo}(1+\sum_{p=1}(K'_{hy,p}a_w{}^p)) + \varepsilon_{ip}\sum_{q=1}(K'_{hy,q}a_w{}^q)}{1+\sum_{p=1}(K'_{hy,p}a_w{}^p)+\sum_{q=1}(K'_{hy,q}a_w{}^q)}, \tag{IV}$$

where ε_{mo} and ε_{ip} are independent of hydration number.

From the distribution methods, only the mono- and decahydrate were postulated in addition to the anhydride. The mono- and decahydrate can be attributed to the molecular and ionized acid, respectively. Because no absorption peak appears at around 350 nm until the decahydrate is partially formed, that is, until $[HNO_3]_t$ lower than 8 mol dm^{-3}, and the molar absorption around this wavelength is increased by an increase in a_w. By introducing the values of p (=1) and q (=10), Eq. 15 can be further simplified to:

$$\varepsilon = \frac{\varepsilon_{mo}(1+K'_{hy,1}a_w)+\varepsilon_{ip}(K'_{hy,10}a_w{}^{10})}{1+K'_{hy,1}a_w+K'_{hy,10}a_w{}^{10}}. \tag{V}$$

The above equation was, in fact, successfully applied to the analysis of data in Fig. 6. The absorption spectra in this figure were simultaneously analyzed as a function of a_w on the basis of this equation by the successive approximation method as was done in a previous study;[15] $K'_{hy,1}$, $K'_{hy,10}$ and ε_{ip} were treated as unknown values, while ε_{mo} was introduced as an already-known value. The analysis gave these unknown values precisely as constants at every wavelength. The spectrum of an ion-pair as the cumulation of ε_{ip} is shown in Fig. 7 and the values of $K'_{hy,1}$ and $K'_{hy,10}$ are shown in Table 2. These equilibrium constants obtained spectrophotometrically are in excellent agreement with those obtained from the distribution methods. Thus, the spectrophotometric measurements substantiated the acid ionization by water in benzene. The spectrophotometric data were also analyzed at individual wavelengths. Figure 8-(a), (b), and (c) give the representative data sets at λ=335, 350, and 365 nm. The analyses were made on the basis of the same equation as that used in the simultaneous analysis. The calculated constants at the respective wavelengths with 3σ errors are listed in Table 3.

Ionization Constant from Distribution Methods. The ionization constant of nitric acid can be also determined from the distribution results. The ionization constant of the acid can be simply obtained by Eq. 18. The value of K'_{ion} obtained from the distribution methods is in excellent agreement with that ob-

Table 2. Summary of Constants for Hydration and Ionization of Nitric Acid in the Liquid–Liquid System

Method	$K'_{hy,p}$ $(=K'_{hy,1})$	$K'_{hy,q}$ $(=K'_{hy,10})$	K'_{ion} $(=K'_{hy,q}/K'_{hy,p})$
Nitric acid Distribution	15 (±1)	16 (±1)	1.1
Water Distribution	15 (±2)	16 (±1)	1.1
Spectrophotometry[a]	16 (±2)	17 (±2)	1.1

a) Simultaneous analysis of absorption spectra in Fig. 6.

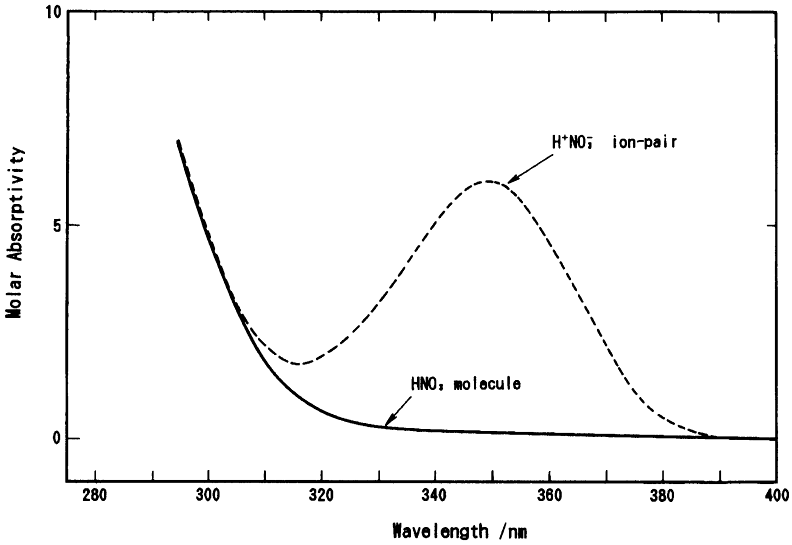

Fig. 7. Spectra of molecular (——) and ionized (- - -) nitric acid in the organic phase.

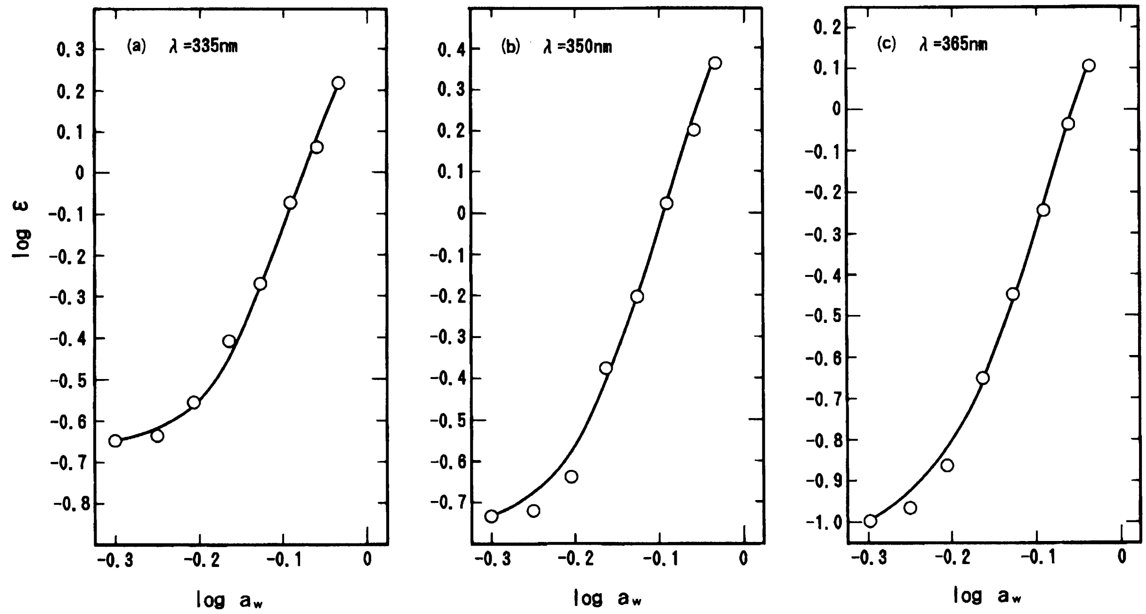

Fig. 8. ε as a function of a_w at certain wavelengths; (a) λ=335 nm, (b) λ=350 nm, (c) λ=365 nm. The solid line of respective figures was calculated by using the values of $K'_{\mathrm{hy},1}$, $K'_{\mathrm{hy},10}$, $\varepsilon_{\mathrm{mo}}$, and $\varepsilon_{\mathrm{ip}}$ in Table 3.

Table 3. Constants Obtained by Analyzing Spectrophotometric Data at Individual Wavelengths

Wavelength nm	$K'_{\mathrm{hy},1}$	$K'_{\mathrm{hy},10}$	$\varepsilon_{\mathrm{mo}}$ [a]	$\varepsilon_{\mathrm{ip}}$
335	16 (±2)	17 (±2)	0.225	4.1 (±0.3)
350	17 (±2)	17 (±2)	0.170	6.2 (±0.6)
365	15 (±2)	16 (±2)	0.100	3.5 (±0.3)

a) Already-known values obtained experimentally.

tained from the spectrophotometry, as is seen in Table 2.

The ratios of nitric acid species in benzene calculated by using a set of $K'_{\mathrm{hy},1}$ and $K'_{\mathrm{hy},10}$ are shown as functions of $[\mathrm{HNO_3}]_{\mathrm{o,t}}$ in Fig. 9. At very low nitric acid concentrations, i.e., $[\mathrm{HNO_3}]_{\mathrm{o,t}} \leq 10^{-6}$ mol dm^{-3}, the ratios are constant because a_w is a constant of unity.

Discussion

Hydration of Acid Molecules and Ion-Pairs. The molecular acid hydrate in benzene is a 1 : 1 complex. In the complex, the hydrogen atom of $\mathrm{HNO_3}$ molecule may combine with the oxygen atom of water molecule by a hydrogen bond. Such a monohydrate was proposed also in the hydration of carboxylic acids in benzene in previous water solubility studies; from acetic

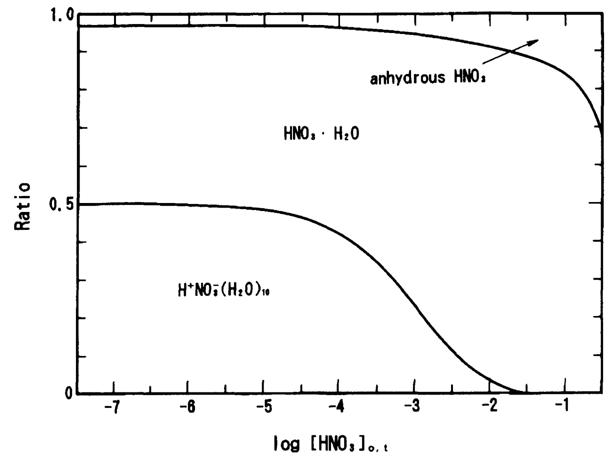

Fig. 9. The ratios of nitric acid species in the organic phase as functions of $[HNO_3]_{o,t}$.

to decanoic acid, only monohydrates of their monomers were reported.[16—18]

In contrast, the ion-pair of nitric acid in benzene is largely hydrated, that is, the decahydrate. The hydration number for lithium nitrate in benzene was also determined in the present study in a similar manner to that for the acid distribution method. The hydration number was twelve; the slope in Fig. 10 did not change from this value of twelve. The dodecahydrate should be also in the form of an ion-pair, as is the case for the decahydrate of nitric acid. The cations of H^+ and Li^+ are strongly hydrated ions and each ion has the primary hydration shell which is clearly observed by X-ray or neutron diffraction method in aqueous solution. The numbers of water molecules in the primary hydration shell for H^+ and Li^+ were reported in previous diffraction studies to be four[19)] and six[20)] (in 2.2 mol dm^{-3} LiCl), respectively; in an extremely concentrated solution of lithium salt, e.g., 10 mol dm^{-3} LiCl, enough ion-free water does not exist for the six-water-hydration of Li^+, and then smaller numbers of the water molecules for Li^+ are obtained.[21,22)] Previous molecular dynamics studies[21,23)] also revealed the primary hydration shell of these cations, which can be discriminated clearly from the secondary hydration shell. On the contrary, NO_3^- ion having negative hydration property in aqueous solution does not create a clear hydration structure in which the primary and secondary hydration shell can be distinguished. Therefore, the determination of the hydration number for NO_3^- in aqueous solution is not easy. Previously reported hydration numbers for NO_3^- by the diffraction methods in aqueous solution are distributed in a wide range from 4 to 14.[24—29)]

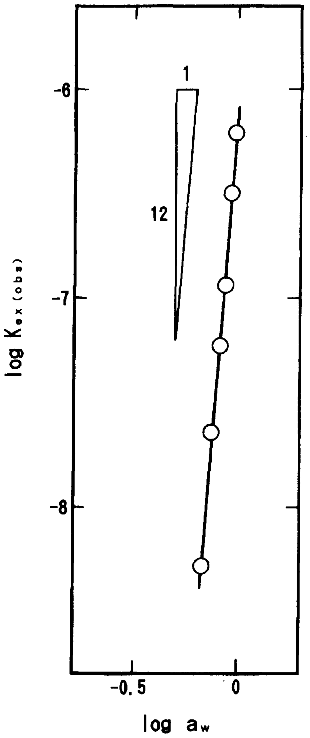

Fig. 10. $K_{ex(obs)}$ of lithium nitrate as a function of a_w on a logarithmic scale.

In benzene, the primary hydration shell for H^+ and for Li^+ can be reasonably regarded to be firm, as well as in aqueous solution, because no substitution by the benzene molecules for the water molecules of hydration occurs. The number of water molecules in the primary hydration shell for H^+ and Li^+ was subtracted from the hydration number for $H^+NO_3^-$ and $Li^+NO_3^-$, and a common value of six was obtained nevertheless the difference of cation. From this, the remaining six water molecules seem to belong to the anionic hydration shell rather than to the cationic secondary hydration shell. In aqueous solution, a buffer zone between the primary hydration shell and the water network is considered.[30)] However, since the water network is absent in benzene, the secondary hydration shell which cushions the incontinuity between the two differently structured water zones can be assumed also absent. On this hypothesis, the NO_3^- ion has six molecules of water of hydration.

The nitrate ion hydrated with six water molecules is considered to be reasonable structurally. Molecular orbital calculations for the hydrogen bonds between NO_3^- and water were carried out previously by Howell et al.[31)] and Shen et al.[32)] According to their calculations, the hydrogen-bonding water molecules lie in the plane of the planar triangular NO_3^- ion and each oxygen atom of NO_3^- can form two hydrogen bonds with water molecules; thus, six water molecules as a maximum can be combined with NO_3^- ion. This was derived by optimizing the geometry of the NO_3^-–water complexes and calculating the energy minima. The calculated values were in good agreement with the experimental data of clusters in the gas phase obtained from high pressure mass spectrometry.[33,34)] However, interaction of NO_3^- with more than three water molecules is not yet involved in the calculations.

Thus, the hydration number of NO_3^- ion can be clearly estimated in benzene, although no definitive answer has yet been given in aqueous solution.

Hydration and Ionization Constants in Benzene. The hydration constants of molecular and ionized nitric acid in benzene were obtained on the basis of Eqs. 21 and 22; these are listed in Table 4. The molecular acid hydration constant, $K_{\mathrm{hy},1}$, was compared with the results of the carboxylic acids.[16—18] The reported values for the carboxylic acids were between 6 and 13.5.[16—18] These are much smaller than the value for nitric acid, as is seen in Table 4.

The ionization constant of nitric acid in benzene was also obtained in the present study by using Eq. 23, which is also shown in Table 4.

Ionization of Nitric Acid. The molecular nitric acid monohydrate is ionized by the successive addition of nine water molecules to form an ion-pair hydrated with ten water molecules. Ionization ratio of nitric acid in benzene as a function of $[\mathrm{HNO_3}]_\mathrm{t}$ is shown in Fig. 11, which was calculated by using the ionization constant obtained from the acid distribution. The ionization of nitric acid is drastically promoted with an increase in a_w and, consequently, largely hydrated ion-pairs are formed in a considerable amount at high a_w, that is, at low $[\mathrm{HNO_3}]_\mathrm{t}$. About 44% of nitric acid in benzene is in the form of the ion-pair at $[\mathrm{HNO_3}]_\mathrm{t}=1$ mol dm^{-3}, whereas, at $[\mathrm{HNO_3}]_\mathrm{t}=10$ mol dm^{-3}, the ion-pair is under 1%, as is seen in Fig. 11.

Table 4. Summary of Constants for Hydration and Ionization of Nitric Acid in the Sole Medium of Benzene

Method	$K_{\mathrm{hy},p}$ $(=K_{\mathrm{hy},1})$	$K_{\mathrm{hy},q}$ $(=K_{\mathrm{hy},10})$	K_ion $(=K_{\mathrm{hy},q}/K_{\mathrm{hy},p})$
Nitric acid Distribution	460 (±30)	1.4×10^{16} $(\pm9\times10^{14})$	3.0×10^{13}
Water Distribution	470 (±60)	1.4×10^{16} $(\pm9\times10^{14})$	3.0×10^{13}
Spectrophotometry[a)]	500 (±60)	1.5×10^{16} $(\pm2\times10^{15})$	3.0×10^{13}

a) Simultaneous analysis of absorption spectra in Fig. 6.

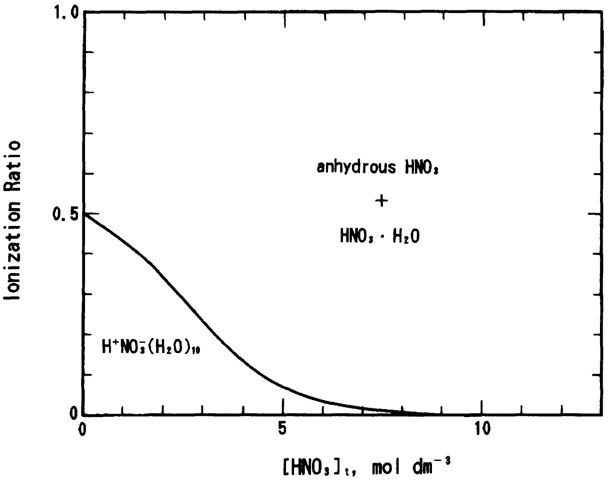

Fig. 11. Ionization ratio of nitric acid in the organic phase $(=[\mathrm{H^+NO_3}^-]_\mathrm{o}/[\mathrm{HNO_3}]_\mathrm{o,t})$ as a function of $[\mathrm{HNO_3}]_\mathrm{t}$, calculated by using the value of K'_ion from the acid distribution.

Conclusions

The following conclusions were obtained by use of benzene.

1. Nitric acid is partially ionized by water and the ionized acid is largely hydrated.
2. Nitric acid is in three forms; molecular anhydride and monohydrate, and ionic decahydrate.
3. Nitric acid forms the molecular monohydrate much more strongly than carboxylic acids (Refs. 16, 17, and 18).
4. The hydration number for $\mathrm{NO_3}^-$ ion in the ion-pair is estimated to be six.

These conclusions obtained in benzene may correspond to those obtained in the gas phase of $\mathrm{HNO_3}$–$\mathrm{H_2O}$. Such a study will give much fundamental information for the nature of hydration.

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