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Distribution Study of the Hydration of Nitric Acid in Dodecane

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The hydration of nitric acid in dodecane was determined on the basis of the acid and water distribution between aqueous acid solutions and dodecane at 298 K. By analyzing the distribution data, mono- and decahydrate of nitric acid in addition to the anhydrous acid were found in dodecane. The solvent influence on the formation of the acid hydrates in dodecane was also compared with the results obtained in benzene.

The hydration of electrolytes has been extensively studied, especially in aqueous solutions. However, a weak interaction with water, e.g., hydration of the NO_3^- ion, is often concealed by the bulk of water in the form of a three-dimensional network in aqueous solutions. In contrast, in nonpolar solvents, such as alkanes, (i) no substitution by solvent molecules for water molecules of hydration occurs, (ii) the network of water molecules is absent, and, water free from the electrolyte is in the mono-molecular form. From these factors, solutes in a nonpolar solvent are under a similar condition as those in a gas phase, and weak interactions with water, i.e., the hydrogen-bonding and ion–dipole interactions, can be estimated more clearly than in aqueous solutions. The information concerning the nature of the hydration of electrolytes obtained in nonpolar solvents should be fundamentally correlated with the massive accumulated data previously obtained in aqueous solutions.

Previously, the hydrogen-bonding interaction with water in nonpolar solvents was reported in many studies. For instance, tributyl phosphate (TBP) hydrated through hydrogen bonds was found in nonpolar solvents by IR,[1] NMR,[2,3] and distribution methods.[4—7] Carboxylic acids, hydrogen-bonding with water in benzene, were investigated based on water solubility measurements.[8—10] However, the hydration of electrolytes, such as nitric acid, in nonpolar solvents has never been studied because of their low solubilities in nonpolar solvents.

A liquid–liquid system was employed in the present study, and the distribution data of nitric acid and water were obtained. This is one of the most useful methods for such a hydration study in a nonpolar solvent where electrolytes dissolve only slightly. The distribution system comprising an aqueous nitric acid solution and dodecane is quite simple, and the data can be treated by a simple theory of the stoichiometry of hydration. Thus, this is the simplest and easiest method to clarify the nature of hydration, while spectroscopic methods, such as NMR, X-ray diffraction, EXAFS, etc. are often complicated in reading data, and some uncertainty remains; however, micro-phenomenal information can be directly obtained by various spectroscopies.[11—13]

The methodology proposed in the present study can be applied to any organic solvents immiscible with water. From this, the solvent influence on hydration, i.e., whether solvent molecules around a hydrate stabilize the hydration structure or not, can be easily estimated by the distribution method with a specific hydration constant. In the present study, dodecane and benzene as solvents were compared under the presence of an aqueous phase as a common reference to these solvents. The specific hydration constant ($K_{\mathrm{hy},n}^{\mathrm{solv}}$), defined as an index of the solvent influence on nitric acid hydration, was determined in dodecane and benzene.

Experimental

All of the chemicals were of reagent grade. Nitric acid (71% aqueous solution), lithium nitrate (purity > 99.0%), and dodecane (purity > 99.3%) were used without further purification. The nitric acid was standardized by titration. A certain volume of an aqueous nitric acid solution (or an aqueous lithium nitrate solution) and the same volume of dodecane were placed in a stoppered glass tube. The two phases were vigorously agitated by a mechanical shaker for 15 min and then centrifuged in a thermostated chamber at 298K. The concentration of nitric acid (or lithium nitrate) 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 (or water) was added. The two phases were shaken vigorously for 15 min and then centrifuged; thus, nitric acid (or lithium nitrate) was completely back-extracted into the aqueous phase. The concentration of nitrate in the aqueous phase was measured by ion chromatography using a 2.5×10^{-3} aqueous potassium hydrogen phthalate solution as an eluent. The chromatographic system used for the nitrate determination was the same as that used in a previous study.[14] The concentration of water in the organic phase was determined by coulometric Karl–Fischer titration (MKC-210 Type, Kyoto Electronics Manufacturing Co., Ltd., Japan). The extent of the distribution equilibrium was checked with various agitation times. The same experiments were repeated, at least three times, in order to confirm the reproducibility; the average values were shown in figures in the present study.

Theoretical

Distribution of Nitric Acid. The distribution of nitric acid between aqueous acid solutions and dodecane can be written as follows:

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

$$\begin{aligned} K_{\mathrm{ex(obs)}} &= \frac{[\mathrm{HNO_3}]_{\mathrm{o,t}}}{\{\mathrm{H^+}\}\{\mathrm{NO_3^-}\}} = \frac{[\mathrm{HNO_3}]_{\mathrm{o,t}}}{\gamma_{\mathrm{s}}^2\,[\mathrm{HNO_3}]_{\mathrm{t}}^2} \\ &= \frac{[\mathrm{HNO_3(anhy)}]_{\mathrm{o}} + \sum\limits_{n=1}[\mathrm{HNO_3\,(H_2O)}_n]_{\mathrm{o}}}{\gamma_{\mathrm{s}}^2\,[\mathrm{HNO_3}]_{\mathrm{t}}^2} \\ &= K_{\mathrm{ex,0}} + \sum_{n=1}(K_{\mathrm{ex},n}(a_{\mathrm{w}}^{\mathrm{aq}})^n), \end{aligned} \tag{1}$$

where subscript "o" denotes the species in the organic phase, while the lack of a subscript denotes the species in the aqueous phase. The activities for the dissociated ions from nitric acid are expressed by { }, and γ_{s} is the stoichiometric activity coefficient; $\gamma_{\mathrm{s}}=1$ at infinite dilution. The value of $K_{\mathrm{ex\,(obs)}}$ is not a constant, but an observed value which is a function of the water activity in the aqueous phase ($a_{\mathrm{w}}^{\mathrm{aq}}$); $a_{\mathrm{w}}^{\mathrm{aq}}=1$ for pure water. The hydration of nitric acid in the aqueous phase is not expressed in Eq. 1, because the stoichiometric activity coefficients obtained experimentally include the hydration terms by themselves.[15] $K_{\mathrm{ex,0}}$ and $K_{\mathrm{ex},n}$ are the extraction constants of anhydrous nitric acid and the acid hydrated with n water molecules, respectively:

$$K_{\mathrm{ex,0}} = \frac{[\mathrm{HNO_3(anhy)}]_{\mathrm{o}}}{\gamma_{\mathrm{s}}^2\,[\mathrm{HNO_3}]_{\mathrm{t}}^2}, \tag{2}$$

$$K_{\mathrm{ex},n} = \frac{[\mathrm{HNO_3(H_2O)}_n]_{\mathrm{o}}}{\gamma_{\mathrm{s}}^2\,[\mathrm{HNO_3}]_{\mathrm{t}}^2\,(a_{\mathrm{w}}^{\mathrm{aq}})^n}. \tag{3}$$

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

$$\begin{aligned} [\mathrm{H_2O}]_{\mathrm{o,HA}} &= [\mathrm{H_2O}]_{\mathrm{o,t}} - [\mathrm{H_2O(free)}]_{\mathrm{o}} \\ &= [\mathrm{H_2O}]_{\mathrm{o,t}} - K_{\mathrm{fw}}a_{\mathrm{w}}^{\mathrm{aq}} \\ &= \sum_{n=1}(n[\mathrm{HNO_3(H_2O)}_n]_{\mathrm{o}}), \end{aligned} \tag{4}$$

where K_{fw} is the distribution constant of the water free from nitric acid:

$$K_{\mathrm{fw}} = \frac{[\mathrm{H_2O(free)}]_{\mathrm{o}}}{a_{\mathrm{w}}^{\mathrm{aq}}} = 2.7\times10^{-3} \quad \text{(Ref. 7)}. \tag{5}$$

This value corresponds to the water solubility in dodecane at $a_{\mathrm{w}}^{\mathrm{aq}}=1$. From Eqs. 3 and 4,

$$\frac{[\mathrm{H_2O}]_{\mathrm{o,HA}}}{\gamma_{\mathrm{s}}^2\,[\mathrm{HNO_3}]_{\mathrm{t}}^2} = \sum_{n=1}(nK_{\mathrm{ex},\,n}(a_{\mathrm{w}}^{\mathrm{aq}})^n). \tag{6}$$

Hydration Constant in Dodecane. The hydration of nitric acid can be also defined as an equilibrium in the sole medium of dodecane:

$$\begin{aligned} K_{\mathrm{hy},n}^{\mathrm{org}} &= \frac{[\mathrm{HNO_3(H_2O)}_n]_{\mathrm{o}}}{[\mathrm{HNO_3(anhy)}]_{\mathrm{o}}[\mathrm{H_2O(free)}]_{\mathrm{o}}{}^n} \\ &= \frac{K_{\mathrm{ex},n}}{K_{\mathrm{ex,0}}K_{\mathrm{fw}}{}^n}. \end{aligned} \tag{7}$$

Solvation of Nitric Acid Hydrates. The solvent influence on the acid hydration in the organic phase cannot be distinctively discussed by comparing the $K_{\mathrm{hy},n}^{\mathrm{org}}$ values. Because anhydrous nitric acid and acid-free water themselves, as well as the acid hydrates, are partially "solvated" in the organic phase; the term "solvation" is used in the present study for convenience in discussing the solvent influence, although both dodecane and benzene are not in the category of solvating solvents, but of nonpolar ones. Thus, $K_{\mathrm{hy},n}^{\mathrm{org}}$ is the hydrate-formation constant from the components *solvated partially*; $\mathrm{HNO_3}$ (anhy) and $\mathrm{H_2O}$ (free) in the organic phase mean the nitric acid free from water and the water free from the acid, respectively, though they are not always free from the solvent. In order to determine whether the solvent molecules around an acid hydrate stabilize the hydration structure or not, the hydration constant from *solvent-free* nitric acid and *solvent-free* water to a *partially solvated* acid hydrate must be defined.

The rational activities of nitric acid and water, defined as the quantities proportional to their vapor pressures at equilibrium, are independent of the medium:

$$a_{\mathrm{HA}}^{\mathrm{aq}} = a_{\mathrm{HA}}^{\mathrm{org}}, \tag{8}$$

$$a_{\mathrm{w}}^{\mathrm{aq}} = a_{\mathrm{w}}^{\mathrm{org}}. \tag{9}$$

Thus, $a_{\mathrm{HA}}^{\mathrm{aq}}$ ($=a_{\mathrm{HA}}^{\mathrm{org}}$) and $a_{\mathrm{w}}^{\mathrm{aq}}$ ($=a_{\mathrm{w}}^{\mathrm{org}}$) should correspond to the *solvent-free* nitric acid and water, because of their independence from the solvent.

The activity, expressed by { }, is normalized at an infinite dilution, in which solute molecules are always surrounded (often interacted) with solvent molecules, and is thus naturally dependent on the medium and does not correspond to a *solvent-free* solute. Thus, the nitric acid activity based on infinite dilution must be converted into its rational activity. The conversion can be done by the following relation:

$$\begin{aligned} \frac{a_{\mathrm{HA}}^{\mathrm{aq}}}{\{\mathrm{H^+}\}\{\mathrm{NO_3^-}\}} &= \frac{a_{\mathrm{HA}}^{\mathrm{aq}}}{\gamma_{\mathrm{s}}^2\,[\mathrm{HNO_3}]_{\mathrm{t}}^2} \\ &= (\gamma_{\mathrm{s}}^0)^{-2}(C_{\mathrm{HA}}^0)^{-2} \\ &= 3.98\times10^{-6} \quad \text{(Ref. 16)}, \end{aligned} \tag{10}$$

where γ_{s}^0 is the activity coefficient for pure nitric acid and C_{HA}^0 is the molarity of pure nitric acid.

A specific equilibrium between the *solvent-free* components (nitric acid and water) and a *partially solvated* acid hydrate can be defined under the presence of an aqueous phase as a common reference to any organic solvents immiscible with water. Such a specific hydration constant for estimating the solvent influence on the stability of a hydrate can be written as:

$$K_{\mathrm{hy},n}^{\mathrm{solv}} = \frac{[\mathrm{HNO_3(H_2O)}_n]_{\mathrm{o}}}{a_{\mathrm{HA}}^{\mathrm{aq}}(a_{\mathrm{w}}^{\mathrm{aq}})^n} = \frac{[\mathrm{HNO_3(H_2O)}_n]_{\mathrm{o}}}{a_{\mathrm{HA}}^{\mathrm{org}}(a_{\mathrm{w}}^{\mathrm{org}})^n}. \tag{11}$$

This value is independent of the mass transfer between the aqueous and organic phases. The rational activities of the components are proportional to their vapor pressures in the equilibrated gas phase. Thus, in other words, the value of $K_{\mathrm{hy},n}^{\mathrm{solv}}$ corresponds to an equilibrium constant between the "free" components in the gas phase and a "solvated" product in the organic liquid phase.

The value of $K^{\mathrm{solv}}_{\mathrm{hy},n}$ can be easily obtained from $K_{\mathrm{ex},n}$:

$$K^{\mathrm{solv}}_{\mathrm{hy},n} = \frac{K_{\mathrm{ex},n}}{3.98 \times 10^{-6}}. \tag{12}$$

Solvation of Components. The distribution constant of anhydrous (free) nitric acid, defined in a similar manner to K_{fw}, can be written as:

$$K_{\mathrm{fHA}} = \frac{[\mathrm{HNO_3(anhy)}]_\mathrm{o}}{a^{\mathrm{aq}}_{\mathrm{HA}}}. \tag{13}$$

The rational activity ($a^{\mathrm{aq}}_{\mathrm{HA}}$) is defined on the basis of the partial vapor pressure of nitric acid over aqueous acid solutions;[16] $a^{\mathrm{aq}}_{\mathrm{HA}} = 1$ for pure nitric acid. K_{fHA} can be written as a value directly proportional to $K_{\mathrm{ex},0}$:

$$K_{\mathrm{fHA}} = \frac{K_{\mathrm{ex},0}}{3.98 \times 10^{-6}}. \tag{14}$$

K_{fHA} and K_{fw} are the characteristic values for a certain solvent. These values can also be defined as the equilibrium constants in the organic phase:

$$K_{\mathrm{fHA}} = \frac{[\mathrm{HNO_3(anhy)}]_\mathrm{o}}{a^{\mathrm{aq}}_{\mathrm{HA}}} = \frac{[\mathrm{HNO_3(anhy)}]_\mathrm{o}}{a^{\mathrm{org}}_{\mathrm{HA}}}, \tag{15}$$

$$K_{\mathrm{fw}} = \frac{[\mathrm{H_2O(free)}]_\mathrm{o}}{a^{\mathrm{aq}}_{\mathrm{w}}} = \frac{[\mathrm{H_2O(free)}]_\mathrm{o}}{a^{\mathrm{org}}_{\mathrm{w}}}. \tag{16}$$

Thus, they are independent of the interfacial mass transfer between the aqueous and organic phases. Each of the constants can be regarded as being an index for the "solvation" of these components. Since a_{HA} and a_{w} are obtained as quantities proportional to their vapor pressures, the values of K_{fHA} and K_{fw} are proportional to the vapor solubilities in an organic solvent. Since the vapors, which correspond to their *solvent-free* molecules, are dissolved by some sort of interactions with the solvent molecules, the values of K_{fHA} and K_{fw} reflect the "solvation" for the components.

In the present study, since the molarity unit is used, consistently, through all of the experiments and the data analyses, we always discuss *the "solvation" in 1 liter of solvent.* The values of $K^{\mathrm{solv}}_{\mathrm{hy},n}$, K_{fHA}, and K_{fw} do not mean the "solvation" by individual solvent molecules, but by the solvent having a certain bulk structure as a medium. These specific values for "solvation", which naturally reflect both the solute–solvent and solvent–solvent interactions, are indispensable for understanding the nature of the solvent influence; not only the solute–solvent, but also the solvent–solvent, interaction often affects on the solubility of solutes, e.g., the solvent network springs out of large solute molecules, in another case, the outer-sphere effect, i.e., pile-up and/or spill-over effect,[17] reinforces the solvation.

Results and Discussion

Distribution of Nitric Acid. Figure 1 gives the total nitric acid concentration in dodecane as a function of $\gamma_\mathrm{s}{}^2$ $[\mathrm{HNO_3}]_\mathrm{t}{}^2$; γ_s at various acid concentrations were taken from the literature.[16] The results obtained in the benzene–$\mathrm{HNO_{3\,(aq)}}$ system are also given in this figure. Each of these curves has a negative deviation from an asymptote having a slope of one to infinite dilution of aqueous nitric acid; $[\mathrm{HNO_3}]_{\mathrm{o,t}}/\gamma_\mathrm{s}{}^2\,[\mathrm{HNO_3}]_\mathrm{t}{}^2$ $(=K_{\mathrm{ex\,(obs)}}) = 8.23\times10^{-6}$ in the asymptotic line in dodecane, and 1.66×10^{-4} in that in benzene.

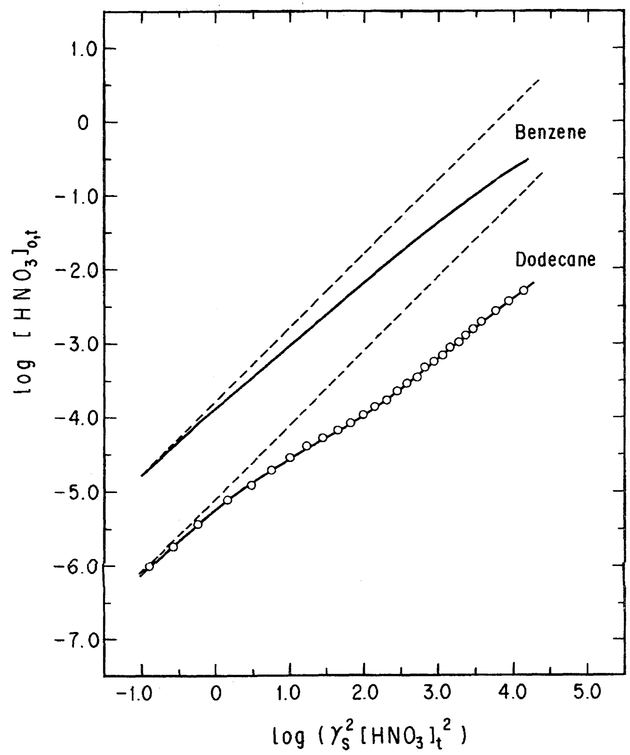

Fig. 1. Total nitric acid concentration in dodecane as a function of $\gamma_\mathrm{s}{}^2$ $[\mathrm{HNO_3}]_\mathrm{t}{}^2$. The values of γ_s at various acid concentrations were cited from literature.[16] The broken line indicates an asymptote to an infinite dilution of aqueous nitric acid where $a^{\mathrm{aq}}_{\mathrm{w}} \approx 1$. The results obtained in benzene–$\mathrm{HNO_{3\,(aq)}}$ system[14] are also shown.

The observed value ($K_{\mathrm{ex\,(obs)}}$) is not constant, but is a function of $a^{\mathrm{aq}}_{\mathrm{w}}$, as shown in Fig. 2; $a^{\mathrm{aq}}_{\mathrm{w}}$ for various aqueous nitric acid solutions were taken from literature.[16] The data in this figure were analyzed on the basis of Eq. 1 by a successive approximation method using a least squares computer program. The analysis was performed by assuming one, two, or three acid hydrates in addition to the anhydrous acid in the organic phase. That the slope of the plot is smaller than one on the left-hand side in this figure implies the presence the anhydrous acid. Although up to the middle range of $a^{\mathrm{aq}}_{\mathrm{w}}$ the slope steadily increases to one, a drastic change appears in the high-$a^{\mathrm{aq}}_{\mathrm{w}}$ range. In the range of $a^{\mathrm{aq}}_{\mathrm{w}}$ lower than 0.5, i.e., $[\mathrm{HNO_3}]_\mathrm{t} > 9$ mol dm^{-3}, fitting to the experimental data was successfully done by introducing a hydrate in addition to the anhydrous acid; in the calculation, the hydration number $(=n(1))$, as well as $K_{\mathrm{ex},0}$ and $K_{\mathrm{ex},n(1)}$, was treated as an unknown value, and was found to be one. The results are given in Table 1. When $a^{\mathrm{aq}}_{\mathrm{w}} \geq 0.5$, i.e., $[\mathrm{HNO_3}]_\mathrm{t} \leq 9$ mol dm^{-3}, the dependence is drastically changed into a much higher power. At least, another hydrate in addition to the monohydrate

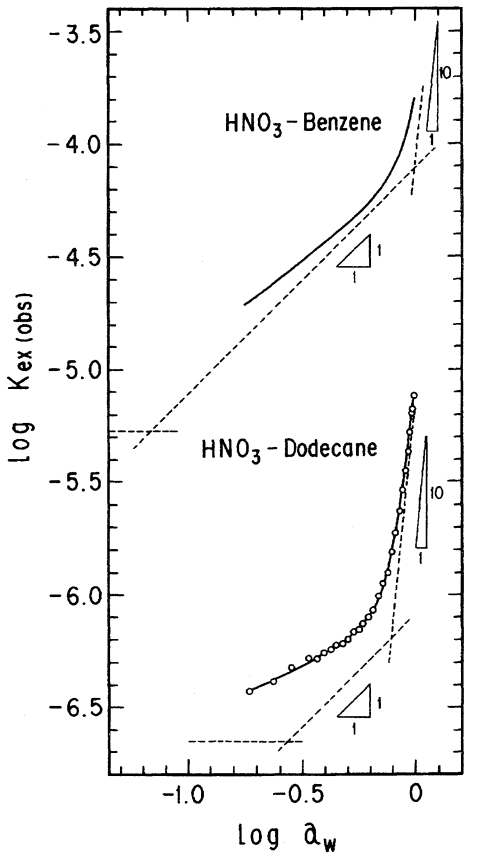

Fig. 2. $K_{ex\,(obs)}$ of nitric acid in dodecane as a function of a_w^{aq}. The values of a_w^{aq} at various acid concentrations were cited from literature.[16] Three asymptotic lines whose slopes are zero, one, and ten, respectively, are also indicated. The results obtained in benzene–$HNO_{3\,(aq)}$ system[14] are also shown.

Table 1. Summary of Acid Hydration Numbers and Equilibrium Constants in Dodecane

Method	$n(1)$	$n(2)$	$K_{ex,0}$	$K_{ex,n(1)}$	$K_{ex,n(2)}$
Acid Distribution	1.0 (±0.1)	10.0 (±0.4)	2.2×10^{-7} ($\pm1\times10^{-8}$)	8.1×10^{-7} ($\pm4\times10^{-8}$)	7.2×10^{-6} ($\pm3\times10^{-7}$)
Water Distribution	1.0 (±0.2)	10.0 (±0.5)	—	8.2×10^{-7} ($\pm4\times10^{-8}$)	7.1×10^{-6} ($\pm4\times10^{-7}$)

should be present in the higher a_w^{aq} region. An additional hydrate ($n(2)$-hydrate) to the monohydrate was first assumed in the data analysis; $n(2)$ and $K_{ex,n(2)}$ were treated as unknown values, while $K_{ex,0}$, $n(1)$, and $K_{ex,n(1)}$ were introduced as already known values. The values of $n(2)$ and $K_{ex,n(2)}$ were obtained with small 3σ errors, which are given in Table 1. Since the value of $n(2)$ was an integer of ten, a decahydrate as well as the monohydrate was found. In order to confirm the results, an analysis by introducing three hydrates ($n(2)$- and $n(3)$-hydrate in addition to the monohydrate) was also made. In this analysis, four unknown values ($n(2)$, $K_{ex,n(2)}$, $n(3)$, and $K_{ex,n(3)}$) and three already known values ($K_{ex,0}$, $n(1)$, and $K_{ex,n(1)}$) were introduced into Eq. 1. By a calculation, it was found that there is no combination of three different hydrates which gives a standard deviation better than that obtained by introducing the mono- and decahydrate. The first guesses for $n(2)$ and $n(3)$ turned out to be close to each other to give a better standard deviation in the course of the calculation; finally, these values were converged into certain decimals which were approximately the same as the value of ten. Therefore, hydrates other than mono- and decahydrate were concluded to be absent in the organic phase.

The hydration number of ten was checked again from the view point of its reliability. Calculation curves with a variation in the hydration number ($n(2)$; nine, ten, and eleven) are shown in Fig. 3; $K_{ex,0}$, $n(1)$, and $K_{ex,n(1)}$ were introduced as already-known values. The experimental data obtained from $[HNO_3]_t=3\ \mathrm{mol\,dm^{-3}}$ to $10\ \mathrm{mol\,dm^{-3}}$ are also given together with the calculated curves; the circle key in this figure, which indicates the experimental points and their average errors, is a 3% (±1.5%) error-circle corresponding to the experimental errors of the anion chromatography derived from its reproducibility. The calculation curves best fitted to the experimental data for the respective hydration numbers are indicated by the dotted, solid, and chain line,

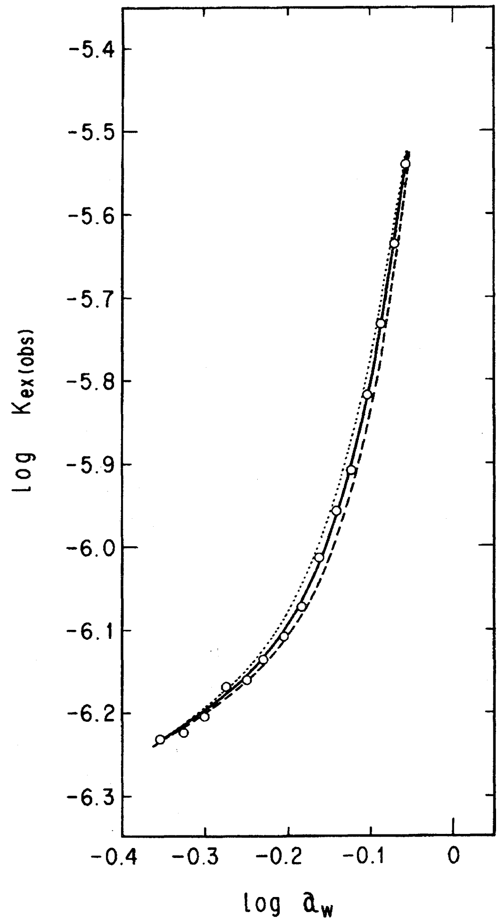

Fig. 3. Calculation curves best fitted to the experimental data when $n(2)$ is assumed to be nine, ten, and eleven, respectively; $K_{ex,0}$ ($=2.2\times10^{-7}$), $n(1)$ ($=1.0$), and $K_{ex,n(1)}$ ($=8.1\times10^{-7}$) are introduced as fixed values. $\cdots$: $n(2)=9$, $K_{ex,9}=6.6\times10^{-6}$, —: $n(2)=10$, $K_{ex,10}=7.2\times10^{-6}$, - - -: $n(2)=11$, $K_{ex,11}=7.8\times10^{-6}$.

respectively. The equilibrium constants ($K_{\mathrm{ex},n(2)}$) for $n(2)=9$, 10, and 11 were calculated to be 6.6×10^{-6} ($\pm8\times10^{-7}$), 7.2×10^{-6} ($\pm3\times10^{-7}$), and 7.8×10^{-6} ($\pm1\times10^{-6}$), respectively. Obviously, the best-fitted curve with the least error was obtained when $n(2)=10$; thus, the value of ten was precisely determined by the data analysis. If the decahydrate is ionic, the number of ten is also reasonable based on a structural consideration; the details are discussed again later.

Distribution of Water. The concentration of water actually co-extracted with nitric acid into the organic phase was also measured in order to verify the results from the acid distribution data. Figure 4A gives the total concentration of water extracted from aqueous nitric acid solutions into the organic phase as a function of $a_{\mathrm{w}}^{\mathrm{aq}}$. The dotted line in this figure indicates the concentration of water free from nitric acid in the organic phase. In nonpolar solvent, where no polymerization of water by itself occurs, the free-water concentration is in proportion to $a_{\mathrm{w}}^{\mathrm{aq}}$ on the basis of Eq. 5.[7,14,18,19] The discrepancy between the dotted line and the experimental data shows the presence of water coextracted with nitric acid in a measurable amount. In contrast, the total water concentration in the organic phase equilibrated with aqueous lithium nitrate solution was quite completely proportional to $a_{\mathrm{w}}^{\mathrm{aq}}$, as can be seen from Fig. 4B. This is because the concentration of co-extracted water with lithium nitrate is quite negligible against the free water concentration; e.g., the concentration of lithium nitrate extracted from a 6.0 mol dm^{-3} aqueous lithium nitrate solution into dodecane was only 9.7×10^{-8} mol dm^{-3}.

The concentration of water co-extracted with the acid ($[H_2O]_{\mathrm{o,HA}}$) was obtained by subtracting $[H_2O(\mathrm{free})]_{\mathrm{o}}$ from $[H_2O]_{\mathrm{o,t}}$. The value of $[H_2O]_{\mathrm{o,HA}}/\gamma_{\mathrm{s}}^2\,[HNO_3]_{\mathrm{t}}^2$ was plotted as a function of $a_{\mathrm{w}}^{\mathrm{aq}}$ (Fig. 5). These data were analyzed on the basis of Eq. 6 by the successive approximation method. The results obtained from the water distribution data were almost the same as those obtained from the acid distribution data (Table 1). Thus, the formation of the mono- and decahydrate in dodecane was verified by water distribution measurements.

Equilibrium Constants in Dodecane. The hydration constants, defined as the equilibrium constants in a sole medium of dodecane ($K_{\mathrm{hy,1}}^{\mathrm{org}}$ and $K_{\mathrm{hy,10}}^{\mathrm{org}}$), were obtained (Table 2). The values obtained in dodecane were larger than those in benzene, as can be seen in Table 2.

Solvation of Nitric Acid Hydrates. The values of $K_{\mathrm{hy,1}}^{\mathrm{solv}}$ and $K_{\mathrm{hy,10}}^{\mathrm{solv}}$, which reflect the "solvations" for the respective acid hydrates, were determined in dodecane and compared with those in benzene. As can be seen from Table 3, both $K_{\mathrm{hy,1}}^{\mathrm{solv}}$ and $K_{\mathrm{hy,10}}^{\mathrm{solv}}$ in dodecane are smaller than those in benzene, which is quite the inverse to the comparison of $K_{\mathrm{hy},n}^{\mathrm{org}}$ values. Thus, both mono- and decahydrate are more stable in benzene than in dodecane. This can be due to the difference in the chemical properties, especially the basicity,

Table 2. Hydration and Ionization Constants in Dodecane and Those in Benzene Obtained from Nitric Acid Distribution

Solvent	$K_{\mathrm{hy,1}}^{\mathrm{org}}$	$K_{\mathrm{hy,10}}^{\mathrm{org}}$	$K_{\mathrm{ion}}^{\mathrm{org}}$
Dodecane	1.4×10^{3}	1.6×10^{27}	1.1×10^{24}
	(±90)	($\pm9\times10^{25}$)	
Benzene[a)]	4.6×10^{2}	1.4×10^{16}	3.0×10^{13}
	(±30)	($\pm9\times10^{14}$)	

a) Ref. 14.

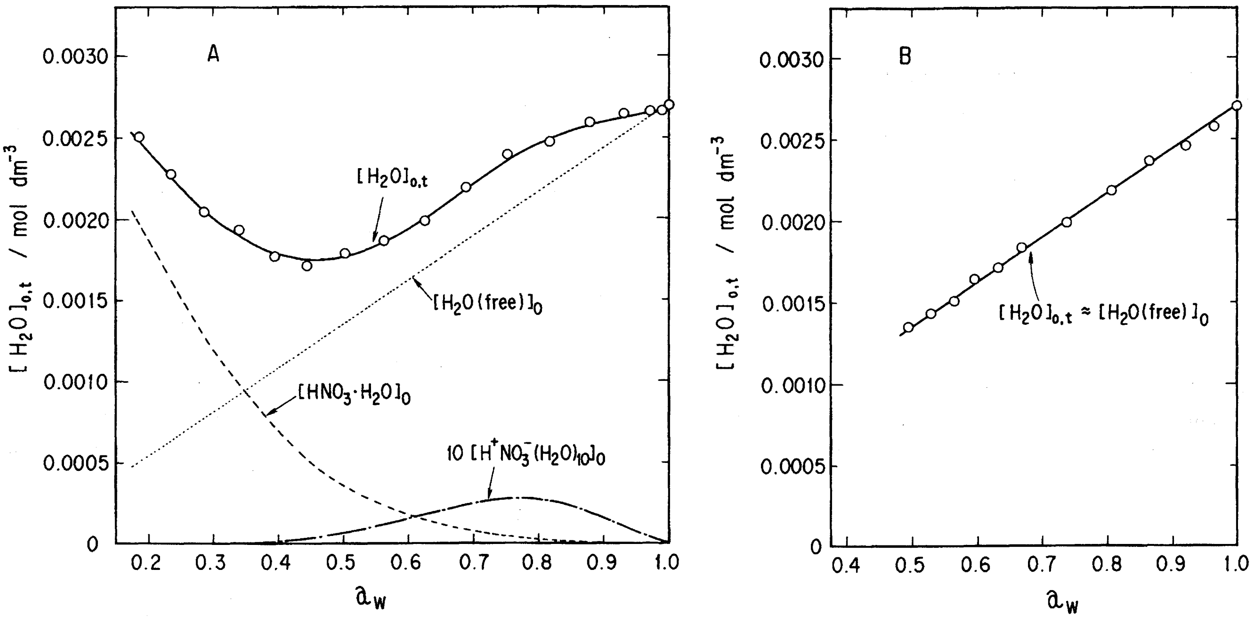

Fig. 4. (A) Total water concentration in the organic phase in dodecane–$HNO_{3\,(\mathrm{aq})}$ system, which is the sum of free water (···) and water co-extracted with the monohydrate (- - -) and with the decahydrate (– • –), as a function of $a_{\mathrm{w}}^{\mathrm{aq}}$. (B) Total water concentration in the organic phase in dodecane–$LiNO_{3\,(\mathrm{aq})}$ system, which is quite equal to free water concentration. The values of $a_{\mathrm{w}}^{\mathrm{aq}}$ were calculated on the basis of vapor pressure data of aqueous lithium nitrate solutions in literature.[20)]

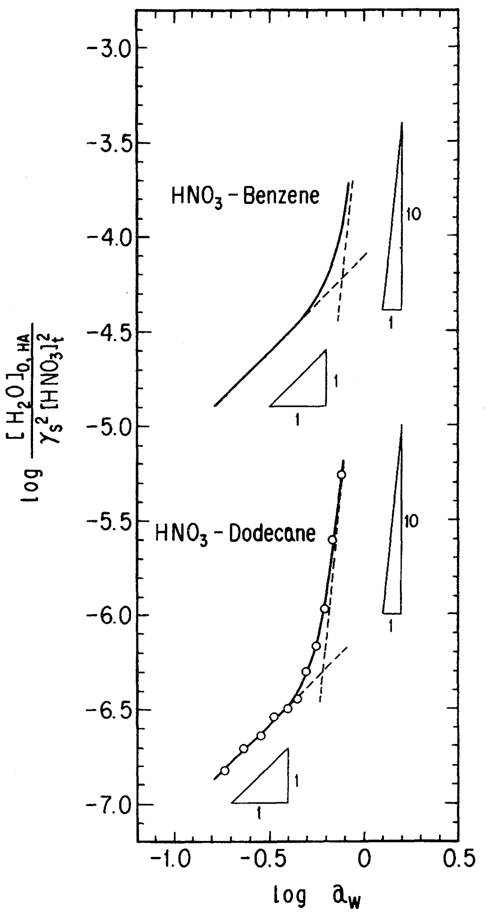

Fig. 5. $[H_2O]_{o,HA}/\gamma_s^2\ [HNO_3]_t^2$ in dodecane as a function of a_w^{aq}. Two asymptotic lines whose slopes are one and ten are also indicated. The results obtained in benzene–$HNO_{3\,(aq)}$ system[14] are also shown.

Table 3. Specific Constants for Solvent Influence

Solvent	$K_{hy,1}^{solv}$	$K_{hy,10}^{solv}$	K_{ion}^{solv}	K_{fw}	K_{fHA}
Dodecane	0.3	1.7	8.8	2.7×10^{-3}	5.5×10^{-2}
	$(\pm2\times10^{-2})$	$(\pm7\times10^{-2})$			$(\pm3\times10^{-3})$
Benzene	19[a)]	21[a)]	1.1	3.2×10^{-2}	1.3[b)]
	(±1)	(±2)			(±0.1)

a) Calculated by Eq. 12 using $K_{ex,1}$ and $K_{ex,10}$ obtained in our previous report.[14)] b) Calculated by Eq. 14 using $K_{ex,0}$ obtained in the previous report.[14)]

between the two solvents. Dodecane is one of the most inert solvents, in which only the van der Waals force works among the solute and the solvent molecules. In contrast, benzene has some basic property as a π-electron donor; e.g., benzene forms charge-transfer complexes with halogen diatomic molecules, which are π–σ complexes.[21)] Since, in general, both dodecane and benzene are classified in the category of nonpolar solvents, the differences in their chemical properties have not been of concern. However, the results obviously show a difference, i.e., benzene, which is not as inert as dodecane, stabilizes both of the hydrates.

Solvation of Components. By comparing the K_{fHA} and K_{fw} values in dodecane with those in benzene, the interactions of anhydrous nitric acid and free water with dodecane were found to be weaker than those with benzene, as is seen in Table 3. This can also be due to the basicity of benzene as a π-electron donor.

Ionization of Nitric Acid. Similarly to the dodecane system, such mono- and decahydrate of nitric acid were also found in benzene.[14)] The mono- and decahydrate in benzene were spectrophotometrically quite different, and were assigned to the molecular and ionized nitric acid, respectively; the absorption spectrum of the acid in the ultra-violet region in benzene changed as a function of the water activity (a_w), and the nitrate peak appeared at around 350 nm in high a_w.[14)] Unfortunately, in dodecane the absorption peak of nitrate could not be detected because of the very small amount of acid extracted into the organic phase. However, with due regard to the results obtained in benzene, the mono- and decahydrate found in dodecane are reasonably regarded as being the molecular and ionized nitric acid, respectively.

The equilibrium constant for the ionization of nitric acid by free water can be defined as:

$$K_{ion}^{solv} = \frac{[H^+NO_3^-(H_2O)_{10}]_o}{[HNO_3\cdot H_2O]_o(a_w^{aq})^9} = \frac{[H^+NO_3^-(H_2O)_{10}]_o}{[HNO_3\cdot H_2O]_o(a_w^{org})^9} = \frac{K_{ex,10}}{K_{ex,1}}. \tag{I}$$

This is the ionization constant from *partially solvated* molecular monohydrate to *partially solvated* ionic decahydrate by *solvent-free* water. If the molecular hydrate is strongly solvated, successive hydration to form the ionic hydrate does not effectively occur because the attack of free water molecules is often blocked by the solvent molecules. While, if the ionic hydrate produced by successive hydration is strongly solvated, ionization is promoted due to a stabilization of the ionic hydrate by the solvation. The value of K_{ion}^{solv} can give an evaluation for such a solvent influence on the ionization. The value of K_{ion}^{solv} in dodecane was larger than that in benzene, while both $K_{hy,1}^{solv}$ and $K_{hy,10}^{solv}$ in dodecane were smaller than those in benzene; thus, the acid ionization occurs in dodecane to a larger degree than in benzene, while both hydrates are less stable in dodecane than in benzene. This can be due to the "solvation" of the molecular monohydrate by benzene as a π-electron donor (a kind of base), which can interfere with the successive addition of water molecules to form the ionic decahydrate.

The ionization ratio of nitric acid in dodecane was calculated as a function of the aqueous nitric acid concentration, and compared with the results obtained in benzene (Fig. 6). The acid ionization in dodecane is drastically promoted by an increase in a_w^{aq}, that is, a decrease in $[HNO_3]_t$. It is surprising that about 85% of the nitric acid in dodecane is in the form of an ion-pair at $[HNO_3]_t=1$ mol dm^{-3} ($a_w^{aq}=0.970$), whereas less than 1% is ionic at $[HNO_3]_t=10$ mol dm^{-3} ($a_w^{aq}=0.444$).

Ionization Constant in Dodecane. The acid-ionization constant by water in the sole medium of dodecane can be written as:

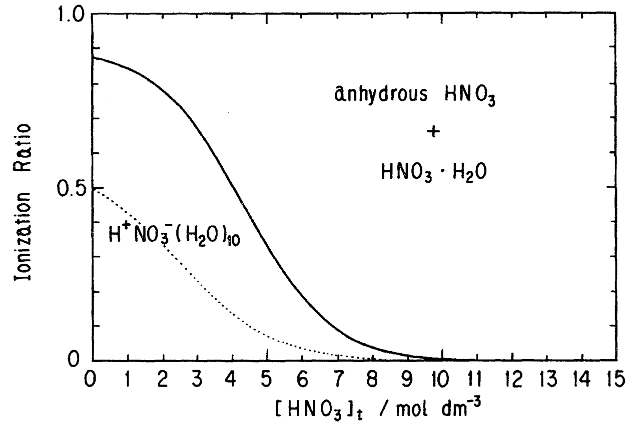

Fig. 6. Ionization ratio of nitric acid in dodecane as a function of nitric acid concentration in the aqueous phase, calculated by using the value of $K_{\text{ion}}^{\text{solv}}$ from the acid distribution data. The dotted line is the result obtained in benzene–HNO_3 (aq) system.[14]

$$K_{\text{ion}}^{\text{org}} = \frac{[H^+NO_3^-(H_2O)_{10}]_o}{[HNO_3 \cdot H_2O]_o[H_2O(\text{free})]_o{}^9} = \frac{K_{\text{ex},10}}{K_{\text{ex},1}K_{\text{fw}}{}^9}. \tag{II}$$

This was also obtained, and is given in Table 2.

Hydration of Lithium Nitrate. The hydration of lithium nitrate in dodecane was also determined by the distribution method of the salt in a similar manner to that of nitric acid. The results were compared with those obtained in benzene. The hydration number of lithium nitrate in dodecane was obtained to be twelve from the slope of $\log K_{\text{ex (obs)}}$ vs. $\log a_{\text{w}}^{\text{aq}}$ plot shown in Fig. 7. This is the same number as that obtained in benzene;[14] further, the dodecahydrate should also be an ion-pair, as is the case for the decahydrate of nitric acid. The extraction constants of dodecahydrate ($K_{\text{ex},12}$) were obtained to be 1.06×10^{-7} in dodecane and 8.32×10^{-7} in benzene, respectively. The "solvation" of the lithium hydrate can be estimated from $K_{\text{ex},12}$, because the value is directly proportional to $K_{\text{hy},12}^{\text{solv}}$; $K_{\text{hy},12}^{\text{solv}} = (\gamma_{\text{s}}^0)^2 (C_{\text{LiA}}^0)^2\ K_{\text{ex},12}$, where γ_{s}^0 and C_{LiA}^0 are the activity coefficient and the molarity of pure lithium nitrate, respectively (see Eqs. 10 and 12). From the results of the $K_{\text{ex},12}$ values, the lithium nitrate dodecahydrate, as well as nitric acid decahydrate, was found to be less solvated with dodecane than with benzene.

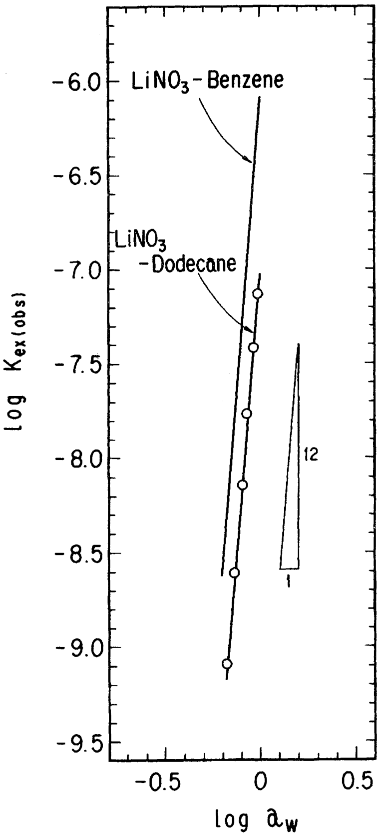

Fig. 7. $K_{\text{ex (obs)}}$ of lithium nitrate as a function of a_{w}^{aq}. The values of a_{w}^{aq} were calculated on the basis of vapor pressure data of aqueous lithium nitrate solutions in literature.[20] The results obtained in benzene–$LiNO_3$ (aq) system are also shown.[14]

Hydration Number of NO_3^-. In a nonpolar solvent, such as an alkane, an intrinsic hydration number for NO_3^- can be obtained, because solutes in a nonpolar solvent are under a similar condition as those in the gas phase; nothing but the van der Waals force concerns the solute–solvent interactions in an alkane. Thus, practically, nothing but water molecules interact with nitric acid in an alkane. Although this is similar to an aqueous solution, no secondary hydration shells, but only primary hydration shells, should be formed in a nonpolar solvent because of a shortage of water content; only those water molecules which directly interact with an ion can be seen as the water of hydration in a nonpolar solvent. The hydration number of NO_3^- was estimated to be six in dodecane, as well as in benzene,[14] as follows. Previously, the numbers of water molecules in the primary hydration shells for H^+ and Li^+ in aqueous solutions were obtained to be four[22] and six,[23] respectively, from X-ray and neutron-diffraction methods. The primary hydration shells should also be firm in dodecane, where no substitution by the solvent molecules for the water molecules of hydration occurs. By subtracting the number of water molecules in the primary hydration shell of the cations from the hydration number of their ion-pairs, a common value of six was obtained. The remaining six water molecules seem to belong to the anionic hydration shell rather than to the cationic secondary hydration shell. The respective primary hydration shells for the cation (H^+ or Li^+) and anion (NO_3^-) in the ion-pair form can be kept in dodecane and benzene, because the value of ten (or twelve) for $H^+NO_3^-$ (or $Li^+NO_3^-$) seems to be reasonable as the sum of the hydration numbers for the cation and anion; if the primary hydration shells in an ion-pair are broken by the Coulomb force working between the cation and anion, a smaller hydration number for the ion-pair should be obtained. On the other hand, the hydration of NO_3^- ion was previously studied with the molecular orbital calculations by Howell et al.[24] and Shen et al.[25] Their calculations indicate that each oxygen atom of the NO_3^- ion can form two hydrogen bonds with water molecules;[24,25] thus, six water molecules as a maximum can combine with the NO_3^- ion. The details were given in a previous paper.[14]

Conclusions

1. The mono- and decahydrate, which are regarded as the molecular and ionized acid, respectively, are present in addition to the anhydrous acid in dodecane, as well as in benzene (Ref. 14).
2. The "solvation" of these hydrates by dodecane is weaker than that by benzene.
3. The "solvation" of anhydrous nitric acid and that of acid-free water by dodecane are also weaker than by benzene.
4. Benzene, as well as dodecane, does not work for destroying the acid hydration structure itself. Benzene works for rather reinforcing the hydration structure by the outer-sphere "solvation" with the acid hydrates.
5. The ionization of molecular acid by the addition of water occurs in a larger degree in dodecane than in benzene, while both molecular and ionized nitric acid are "solvated" more weakly by dodecane than by benzene.
6. From 5, some benzene molecules "solvating" with the acid monohydrate can repel the attack of water molecules, consequently, the degree of ionization in benzene are smaller than in dodecane.
7. Lithium nitrate forms dodecahydrate in dodecane, as well as in benzene.
8. The dodecahydrate of lithium nitrate is also "solvated" by benzene more strongly than by dodecane.
9. The hydration number of NO_3^- is estimated to be six in dodecane, as well as in benzene (Ref. 14).

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