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Complex Formation between Tributyl Phosphate and Nitric Acid and the Hydration of the Complexes in Dodecane

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Complex-formation of nitric acid with tributyl phosphate (TBP) and the hydration of the complexes in dodecane were examined from the acid and water distribution data between the aqueous and organic phases at 298 K. The equilibrium constants were determined by analyzing the acid and water distribution data as functions of the TBP concentration in the organic phase, the aqueous acid activity, and the water activity. Three complexes ($TBP\cdot HNO_3$, $(TBP)_2\cdot HNO_3$, and $(TBP)_3\cdot HNO_3$) were found in the organic phase when the aqueous nitric acid concentration was not higher than 3 mol dm^{-3}. The hydration numbers for these complexes were also obtained. The $TBP\cdot HNO_3$ was chiefly anhydrous, but partially a monohydrate. In contrast, the $(TBP)_2\cdot HNO_3$ was only a monohydrate and $(TBP)_3\cdot HNO_3$ was only a tetrahydrate. The $TBP–HNO_3–H_2O$ stoichiometry, by taking account of these complexes in addition to the TBP hydrates and free nitric acid in the organic phase, applied very well, up to 2 mol dm^{-3} (54.6 vol%) TBP in dodecane without any activity correction.

The PUREX (Plutonium Uranium Recovery by Extraction) system has been studied for more than forty years and the extraction mechanism of nitric acid with tributyl phosphate (TBP) has been the subject of numerous studies.[1—20] Many complexes of TBP with nitric acid have been suggested in organic solvents. There is, however, still no definitive explanation for the liquid–liquid system.

The solvent extraction system for practical use in nuclear fuel reprocessing is always highly concentrated with an extractant and nitric acid. The liquid–liquid system containing TBP and nitric acid at high concentrations is too complicated to investigate all of the interactions working in the system at the same time; since numerous equilibria exist, such as $TBP–HNO_3$ complex-formation, TBP dimerization, hydration of these species, free nitric acid distribution, etc, in the organic phase, too many unknown values must be introduced in the data analysis. In many previous studies,[11,14,15,20] certain complexes were assumed in advance in a curve-fitting analysis for the data obtained in a highly concentrated system. However, such a fitting is apparently possible even when some complexes are erroneously assumed. A solution to these problems was suggested in the present study as follows. In the beginning, the condition of sufficiently low concentrations of TBP and/or aqueous nitric acid is chosen to be examined. Since, in a sufficiently low TBP concentration range, only lower order complexes of TBP can form predominantly in the organic phase, such complexes are first determined. Then, in a more complicated state of higher TBP concentration range, the composition of higher order complexes, which form in addition to the lower order complexes, is clarified. In a sufficiently low aqueous nitric acid concentration range, the acid distribution data can be simply analyzed without any consideration for the hydration of $TBP–HNO_3$ complexes, because the water activity (a_w) can be approximately regarded as being unity, e.g., $a_w = 0.9976 \approx 1$, in a 0.1 mol dm^{-3} aqueous nitric acid solution (Ref. 21). The results obtained in a low nitric acid concentration range are fed back to the analysis of the water distribution data obtained in a higher nitric acid concentration range, and the hydration numbers of $TBP–HNO_3$ complexes are determined. In these data analyses the number of $TBP–HNO_3$ complexes present in the organic phase is first set up arbitrarily. The combination numbers of TBP, nitric acid, and water molecules in a complex are treated as unknown values and optimized to give the best standard deviation for fitting to the experimental data. If a sufficient number of complexes is not assumed, at least one of these combination numbers is not obtained as being an integer. In such a case, other complexes are of necessity added to the analysis.

The methodology suggested in the present study is based on the stoichiometry started from sufficiently diluted organic solutions and extended to highly concentrated ones, over a check on the limitation of stoichometry; however, a stoichiometric approach has generally been believed to be unavailable to such a system that is highly concentrated by an extractant because of the lack of a theory for the activity correction in the organic phase. In the present study, an important direction for the treatment of the activity in the highly concentrated organic solutions is given.

Experimental

All of the chemicals were of reagent grade. Nitric acid was used without further purification, and standardized by titration. Tributyl phosphate (TBP) was purified in the same manner as that described in previous papers.[22,23] Dodecane was washed with distilled water two times. The experiments were carried out at 298 K. An aqueous nitric acid solution and the same volume of a TBP–dodecane solution were placed in a stoppered glass tube; the two phases were agitated vigorously for 15 min and then centrifuged. The change in the volume of both phases was also checked. The concentration of nitric acid in the organic phase was determined as follows. A portion of the organic phase was transferred into another tube and a certain volume of aqueous sodium hydroxide solution was added. After the two phases were shaken the acid was completely back-extracted into the aqueous phase as nitrate ion; the complete back-extraction was confirmed, i.e., no nitrate ion was found in the aqueous phase of the second back-extraction. For determining the back-extracted nitric acid, anion chromatography was employed. The chromatographic system comprised an anion-separator column (Shimadzu Shim-Pack IC-Al; 10×0.46 cm) and its guard column (Shim-Pack IC-GA1) in an oven (HIC-6A), a pump (LC-9A), a pump controller (SCL-6B), a conductometric detector (CDD-6A), an automatic injector (SIL-6B) with 100 μl loop, and a data analyzing computer (C-R4A Chromatopac). A 2.5×10^{-3} mol dm^{-3} aqueous potassium hydrogenphthalate solution was used as an eluent, and the flow rate was fixed at 1.0 ml min^{-1} for all of the measurements. Deionized water by a milli.Q system was used for preparing the eluent. The eluent was filtered on a membrane filter (Millipore Type HA 0.45 μm) before use. The temperature in the oven was kept at 40 °C.

The concentration of water in the organic phase was measured by Karl–Fischer titration (MKC-210 Type, Kyoto Electronics Manufacturing Co., Ltd., Japan).

The distribution of TBP was also determined. The TBP concentration in the aqueous phase was measured by ICP-MS (FISONS Instruments, VG PQ Ω, England) as the phosphorus concentration.

Theoretical

Complex-Formation between TBP and Nitric Acid. The equilibrium for TBP–HNO_3 complex-formation can be generally written as:

$$n\,\mathrm{TBP(ah)}_{(o)} + \mathrm{H}^+ + \mathrm{NO_3}^- + h\,\mathrm{H_2O} \rightleftharpoons \mathrm{(TBP)}_n\cdot\mathrm{HNO_3}\cdot\mathrm{(H_2O)}_{h(o)}$$
$$(n = 1,2,3,\cdots,\ \ h = 0,1,2,\cdots),$$

$$K_{n1,h} = \frac{[\mathrm{(TBP)}_n\cdot\mathrm{HNO_3}\cdot\mathrm{(H_2O)}_h]_o}{[\mathrm{TBP(ah)}]_o{}^n\{\mathrm{H}^+\}\{\mathrm{NO_3}^-\}\,a_w{}^h},$$
$$= \frac{[\mathrm{(TBP)}_n\cdot\mathrm{HNO_3}\cdot\mathrm{(H_2O)}_h]_o}{[\mathrm{TBP(ah)}]_o{}^n\,\gamma_s{}^2[\mathrm{HNO_3}]_t{}^2\,a_w{}^h}, \tag{1}$$

where subscript "o" denotes the species in the organic phase, while the lack of a subscript denotes the species in the aqueous phase. TBP(ah) is an anhydrous TBP molecule (free TBP). The activity for nitric acid and that for water in the aqueous phase are expressed by { } and a_w ($a_w=1$ for pure water), respectively, and γ_s is the stoichiometric activity coefficient for nitric acid. The hydration of nitric acid in the aqueous phase is not expressed in Eq. 1, because the stoichiometric activity coefficients, which were obtained experimentally, include the hydration terms by themselves.[24]

Species Other Than TBP–HNO_3 Complexes. For a stoichiometric treatment, chemical species other than TBP–HNO_3 complexes, such as TBP hydrates, TBP dimer, nitric acid hydrates, etc, must also be taken into account in the mass-balance equations. In previous studies in our laboratory,[22,23,25] such species were determined in simple liquid–liquid systems, separately from the TBP–dodecane–$HNO_{3(aq)}$ system.

A TBP molecule (TBP monomer) simply forms a monohydrate,

$$\mathrm{TBP(ah)}_{(o)} + \mathrm{H_2O} \rightleftharpoons \mathrm{TBP}\cdot\mathrm{H_2O}_{(o)}$$

$$K_{m,1} = \frac{[\mathrm{TBP}\cdot\mathrm{H_2O}]_o}{[\mathrm{TBP(ah)}]_o\,a_w} = 0.11\ \text{(Refs. 22,23)}. \tag{2}$$

The dimerization of TBP with two water molecules and its trimerization with six water molecules also occur in a high TBP concentration range in dodecane, as follows:

$$2\,\mathrm{TBP(ah)}_{(o)} + 2\,\mathrm{H_2O} \rightleftharpoons \mathrm{(TBP)_2}\cdot\mathrm{(H_2O)}_{2(o)}$$

$$K_{d,2} = \frac{[\mathrm{(TBP)_2}\cdot\mathrm{(H_2O)_2}]_o}{[\mathrm{TBP(ah)}]_o{}^2\,a_w{}^2} = 0.22\ \text{(Refs. 22,23)}. \tag{3}$$

$$3\,\mathrm{TBP(ah)}_{(o)} + 6\,\mathrm{H_2O} \rightleftharpoons \mathrm{(TBP)_3}\cdot\mathrm{(H_2O)}_{6(o)}$$

$$K_{t,6} = \frac{[\mathrm{(TBP)_3}\cdot\mathrm{(H_2O)_6}]_o}{[\mathrm{TBP(ah)}]_o{}^3\,a_w{}^6} = 0.037\ \text{(Ref. 23)}. \tag{4}$$

When the TBP concentration is very low, the extraction of nitric acid free from TBP is not negligible. The free nitric acid, extracted into dodecane, is in two forms (molecular and ion-pair form),[25] i.e., the molecular HNO_3 hydrate extraction:

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

$$K_{f,1} = \frac{[\mathrm{HNO_3}\cdot\mathrm{H_2O}]_o}{\{\mathrm{H}^+\}\{\mathrm{NO_3}^-\}\,a_w} = 8.1\times10^{-7}\ \text{(Ref. 25)}, \tag{5}$$

and the ion-pair hydrate extraction:

$$\mathrm{H}^+ + \mathrm{NO_3}^- + 10\,\mathrm{H_2O} \rightleftharpoons \mathrm{H^+NO_3}^-\cdot\mathrm{(H_2O)}_{10(o)}$$

$$K_{f,10} = \frac{[\mathrm{H^+NO_3}^-\cdot\mathrm{(H_2O)_{10}}]_o}{\{\mathrm{H}^+\}\{\mathrm{NO_3}^-\}\,a_w{}^{10}} = 7.2\times10^{-6}\ \text{(Ref. 25)}. \tag{6}$$

The free nitric acid concentration in the organic phase is the sum of the two forms:

$$[\mathrm{HNO_3(free)}]_o = [\mathrm{HNO_3}\cdot\mathrm{H_2O}]_o + [\mathrm{H^+NO_3}^-\cdot\mathrm{(H_2O)_{10}}]_o$$
$$= \{\mathrm{H}^+\}\{\mathrm{NO_3}^-\}(K_{f,1}a_w + K_{f,10}a_w{}^{10}). \tag{7}$$

Stoichiometric Treatment. The total concentration of TBP, nitric acid, and water in the organic phase can be written as follows:

$$\begin{aligned}[\mathrm{TBP}]_{o,t} &= [\mathrm{TBP(ah)}]_o + [\mathrm{TBP}\cdot\mathrm{H_2O}]_o + 2[\mathrm{(TBP)_2}\cdot\mathrm{(H_2O)_2}]_o\\ &\quad +3[\mathrm{(TBP)_3}\cdot\mathrm{(H_2O)_6}]_o\\ &\quad +\sum_{n=1}\sum_{h=0}(n[\mathrm{(TBP)}_n\cdot\mathrm{HNO_3}\cdot\mathrm{(H_2O)}_h]_o)\\ &= (1+K_{m,1}a_w)[\mathrm{TBP(ah)}]_o + 2K_{d,2}a_w{}^2[\mathrm{TBP(ah)}]_o{}^2\\ &\quad +3K_{t,6}a_w{}^6[\mathrm{TBP(ah)}]_o{}^3\\ &\quad +\{\mathrm{H}^+\}\{\mathrm{NO_3}^-\}\sum_{n=1}\sum_{h=0}(nK_{n1,h}a_w{}^h[\mathrm{TBP(ah)}]_o{}^n).\end{aligned} \tag{8}$$

$$\begin{aligned}[\mathrm{HNO_3}]_{o,t} &= [\mathrm{HNO_3}\cdot\mathrm{H_2O}]_o + [\mathrm{H^+NO_3}^-\cdot\mathrm{(H_2O)_{10}}]_o\\ &\quad +\sum_{n=1}\sum_{h=0}[\mathrm{(TBP)}_n\cdot\mathrm{HNO_3}\cdot\mathrm{(H_2O)}_h]_o\\ &= \{\mathrm{H}^+\}\{\mathrm{NO_3}^-\}[K_{f,1}a_w + K_{f,10}a_w{}^{10}\\ &\quad +\sum_{n=1}\sum_{h=0}(K_{n1,h}a_w{}^h[\mathrm{TBP(ah)}]_o{}^n)].\end{aligned} \tag{9}$$

$$\begin{aligned}[\mathrm{H_2O}]_{\mathrm{o,t}} &= [\mathrm{H_2O(free)}]_{\mathrm{o}} + [\mathrm{TBP{\cdot}H_2O}]_{\mathrm{o}} + 2[(\mathrm{TBP})_2{\cdot}(\mathrm{H_2O})_2]_{\mathrm{o}} \\ &\quad +6[(\mathrm{TBP})_3{\cdot}(\mathrm{H_2O})_6]_{\mathrm{o}} \\ &\quad +[\mathrm{HNO_3{\cdot}H_2O}]_{\mathrm{o}} + 10[\mathrm{H^+NO_3^-}{\cdot}(\mathrm{H_2O})_{10}]_{\mathrm{o}} \\ &\quad +\sum_{n=1}\sum_{h=0}(h[(\mathrm{TBP})_n{\cdot}\mathrm{HNO_3}{\cdot}(\mathrm{H_2O})_h]_{\mathrm{o}}) \\ &= K_{\mathrm{fw}}a_{\mathrm{w}} + K_{\mathrm{m,1}}a_{\mathrm{w}}[\mathrm{TBP(ah)}]_{\mathrm{o}} \\ &\quad +2K_{\mathrm{d,2}}a_{\mathrm{w}}^2[\mathrm{TBP(ah)}]_{\mathrm{o}}^2 + 6K_{\mathrm{t,6}}a_{\mathrm{w}}^6[\mathrm{TBP(ah)}]_{\mathrm{o}}^3 \\ &\quad +\{\mathrm{H^+}\}\{\mathrm{NO_3^-}\}[K_{\mathrm{f,1}}a_{\mathrm{w}} + 10K_{\mathrm{f,10}}a_{\mathrm{w}}^{10} \\ &\quad +\sum_{n=1}\sum_{h=0}(hK_{n1,h}a_{\mathrm{w}}^h[\mathrm{TBP(ah)}]_{\mathrm{o}}^n)], \end{aligned} \tag{10}$$

where K_{fw} is distribution constant of free water; this corresponds to the solubility of water in dodecane ($=2.7\times10^{-3}$ mol dm^{-3}) at $a_{\mathrm{w}}=1$.[22,23]

Under the condition of an aqueous nitric acid concentration not higher than 0.1 mol dm^{-3}, a_{w} is approximately regarded as being unity; e.g., $a_{\mathrm{w}}=0.9976\approx1$ at $[\mathrm{HNO_3}]_{\mathrm{t}}=0.1$ mol dm^{-3} (Ref. 21). Thus,

$$a_{\mathrm{w}} \approx a_{\mathrm{w}}^2 \approx a_{\mathrm{w}}^6 \approx a_{\mathrm{w}}^{10} \approx a_{\mathrm{w}}^h \approx 1\,. \tag{11}$$

Furthermore, on this condition, always $[\mathrm{TBP}]_{\mathrm{o,t}} \gg [\mathrm{HNO_3}]_{\mathrm{o,t}}$ and $[\mathrm{H_2O}]_{\mathrm{o,t}} \gg [\mathrm{HNO_3}]_{\mathrm{o,t}}$ (see Results). From these, Eqs. 8, 9, and 10 can be very much simplified, as follows:

$$[\mathrm{TBP}]_{\mathrm{o,t}} \approx (1+K_{\mathrm{m,1}})[\mathrm{TBP(ah)}]_{\mathrm{o}} + 2K_{\mathrm{d,2}}[\mathrm{TBP(ah)}]_{\mathrm{o}}^2 + 3K_{\mathrm{t,6}}[\mathrm{TBP(ah)}]_{\mathrm{o}}^3, \tag{12}$$

$$[\mathrm{HNO_3}]_{\mathrm{o,t}} \approx \{\mathrm{H^+}\}\{\mathrm{NO_3^-}\}[K_{\mathrm{f,1}} + K_{\mathrm{f,10}} + \sum_{n=1}\sum_{h=0}(K_{n1,h}[\mathrm{TBP(ah)}]_{\mathrm{o}}^n)], \tag{13}$$

$$\begin{aligned}[\mathrm{H_2O}]_{\mathrm{o,t}} &\approx K_{\mathrm{f,w}} + K_{\mathrm{m,1}}[\mathrm{TBP(ah)}]_{\mathrm{o}} + 2K_{\mathrm{d,2}}[\mathrm{TBP(ah)}]_{\mathrm{o}}^2 \\ &\quad +6K_{\mathrm{t,6}}[\mathrm{TBP(ah)}]_{\mathrm{o}}^3. \end{aligned} \tag{14}$$

The acid distribution data can be analyzed on the basis of Eqs. 12 and 13 by a successive approximation method using a least-squares computer program, and the unknown values of $\sum_{h(1)=0} K_{11,h(1)}$, $\sum_{h(2)=0} K_{21,h(2)}$, $\cdots$ can be obtained.

By analyzing the water distribution data obtained in $[\mathrm{HNO_3}]_{\mathrm{t}}$ higher than 0.1 mol dm^{-3}, the hydration numbers ($h(1)$, $h(2)$, $\cdots$) can also be determined on the basis of Eqs. 8 and 10; the complex-formation constants cumulating their hydrates ($\sum_{h(1)=0} K_{11,h(1)}$, $\sum_{h(2)=0} K_{21,h(2)}$, $\cdots$) are fed back to these equations as already known values.

Results and Discussion

Analysis of Data Obtained in $[\mathrm{HNO_3}]_{\mathrm{t}} \le 0.1$ mol dm^{-3}. In the low aqueous nitric acid concentration range, the acid distribution data can be analyzed without any consideration for the hydration of TBP–HNO$_3$ complexes, by using the simplified Eqs. 12 and 13. Figure 1A gives $[\mathrm{HNO_3}]_{\mathrm{o,t}}$ as a function of $[\mathrm{TBP}]_{\mathrm{o,t}}$ at various $[\mathrm{HNO_3}]_{\mathrm{t}}$. The experimental results can be replotted against $[\mathrm{TBP(ah)}]_{\mathrm{o}}$, as shown in Fig. 1B; since always $[\mathrm{TBP}]_{\mathrm{o,t}} \gg [\mathrm{HNO_3}]_{\mathrm{o,t}}$, as can be seen from Fig. 1A, $[\mathrm{TBP(ah)}]_{\mathrm{o}}$ can be easily calculated on the basis of Eq. 12. The slope of the plots in Fig. 1B is directly concerned with the order of TBP in the TBP–HNO$_3$ complexes. When the TBP concentration is sufficiently low, e.g., $[\mathrm{TBP}]_{\mathrm{o,t}} \le 0.03$ mol dm^{-3}, the slope at every $[\mathrm{HNO_3}]_{\mathrm{t}}$ is approximately one. Thus, the 1 : 1 complex forms predominantly in the low TBP concentration range. The value of $\sum_{h(1)=0} K_{11,h(1)}$ was first determined in the low TBP concentration range by a simultaneous analysis of data obtained at various $[\mathrm{HNO_3}]_{\mathrm{t}}$; $[\mathrm{HNO_3(free)}]_{\mathrm{o}}$, calculated on the basis of Eq. 7, was negligible. In the calculation, the activity coefficients of nitric acid, taken from the literature,[21] were introduced into Eq. 13. In the higher TBP concentration range, the slope increases drastically. This means that other complex-formations take place in addition to the 1 : 1 complex. The following equation was first employed for the analysis of data over the whole TBP concentration range in Fig. 1B:

$$\begin{aligned}[\mathrm{HNO_3}]_{\mathrm{o,t}} &\approx [\mathrm{TBP{\cdot}HNO_3}]_{\mathrm{o}} + [(\mathrm{TBP})_n{\cdot}\mathrm{HNO_3}]_{\mathrm{o}} \\ &= \{\mathrm{H^+}\}\{\mathrm{NO_3^-}\}\left(\sum_{h(1)=0} K_{11,h(1)}[\mathrm{TBP(ah)}]_{\mathrm{o}}\right. \\ &\quad \left. + \sum_{h(2)=0} K_{n1,h(2)}[\mathrm{TBP(ah)}]_{\mathrm{o}}^n\right), \end{aligned} \tag{I}$$

where $\sum_{h(2)=0} K_{n1,h(2)}$ and n were introduced as unknown values, while $\sum_{h(1)=0} K_{11,h(1)}$ was introduced as an already-known value. By the analysis n was obtained to be 2.30±0.24. Since this value was not an integer, but between 2 and 3, in the next stage 2 : 1 and 3 : 1 complex were taken into account in addition to the 1 : 1 complex:

$$\begin{aligned}[\mathrm{HNO_3}]_{\mathrm{o,t}} &\approx [\mathrm{TBP{\cdot}HNO_3}]_{\mathrm{o}} + [(\mathrm{TBP})_2{\cdot}\mathrm{HNO_3}]_{\mathrm{o}} + [(\mathrm{TBP})_3{\cdot}\mathrm{HNO_3}]_{\mathrm{o}} \\ &= \{\mathrm{H^+}\}\{\mathrm{NO_3^-}\}\left(\sum_{h(1)=0} K_{11,h(1)}[\mathrm{TBP(ah)}]_{\mathrm{o}}\right. \\ &\quad \left. + \sum_{h(2)=0} K_{21,h(2)}[\mathrm{TBP(ah)}]_{\mathrm{o}}^2 + \sum_{h(3)=0} K_{31,h(3)}[\mathrm{TBP(ah)}]_{\mathrm{o}}^3\right), \end{aligned} \tag{II}$$

where $\sum_{h(2)=0} K_{21,h(2)}$ and $\sum_{h(3)=0} K_{31,h(3)}$ were introduced as unknown values, while $\sum_{h(1)=0} K_{11,h(1)}$ was introduced as an already-known value. The calculated values were fitted very well to the experimental data, and a standard deviation better than that in the former analysis was obtained. The cumulative equilibrium constants with 3σ errors are shown in Table 1.

In most of the previous studies,[1—20] the 3 : 1 complex was not supposed. However, the fitting to the experimental data without assuming a 3 : 1 complex is unsatisfying, as can be seen from Fig. 1C. The dotted lines in this figure indicate the

Table 1. Complex-Formation Constants Cumulating Their All Hydrates with 3σ Errors

Complex	Cumulative constant
$\mathrm{TBP{\cdot}HNO_3{\cdot}(H_2O)}_{h(1)}$	$\sum_{h(1)=0} K_{11,h(1)}=0.198\ (\pm0.009)$
$(\mathrm{TBP})_2{\cdot}\mathrm{HNO_3{\cdot}(H_2O)}_{h(2)}$	$\sum_{h(2)=0} K_{21,h(2)}=0.484\ (\pm0.049)$
$(\mathrm{TBP})_3{\cdot}\mathrm{HNO_3{\cdot}(H_2O)}_{h(3)}$	$\sum_{h(3)=0} K_{31,h(3)}=0.333\ (\pm0.045)$

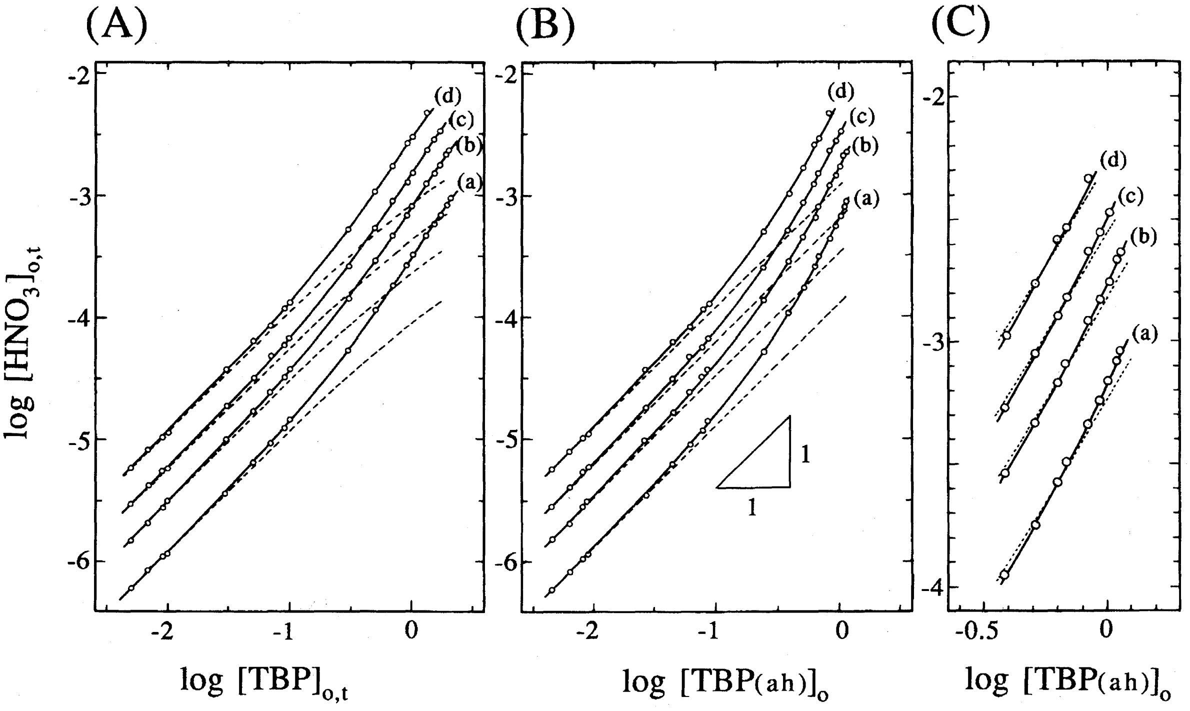

Fig. 1. [HNO$_3$]$_{o,t}$ as a function of [TBP]$_{o,t}$ (or [TBP(ah)]$_o$) at various [HNO$_3$]$_t$ on a logarithmic scale; [HNO$_3$]$_t$=(a) 0.03, (b) 0.05, (c) 0.07, and (d) 0.1 mol dm^{-3}.

(A) [HNO$_3$]$_{o,t}$ as a function of [TBP]$_{o,t}$.

—: calculated values by introducing $\sum_{h(1)=0} K_{11,h(1)}=0.198$, $\sum_{h(2)=0} K_{21,h(2)}=0.484$, and $\sum_{h(3)=0} K_{31,h(3)}=0.333$,

- - -: calculated values by introducing only $\sum_{h(1)=0} K_{11,h(1)}=0.198$, into Eq. 13.

(B) [HNO$_3$]$_{o,t}$ as a function of [TBP(ah)]$_o$; [TBP(ah)]$_o$ was calculated from [TBP]$_{o,t}$ on the basis of Eq. 12.

—: calculated values by introducing $\sum_{h(1)=0} K_{11,h(1)}=0.198$, $\sum_{h(2)=0} K_{21,h(2)}=0.484$, and $\sum_{h(3)=0} K_{31,h(3)}=0.333$,

- - -: calculated values by introducing only $\sum_{h(1)=0} K_{11,h(1)}=0.198$, into Eq. 13.

(C) [HNO$_3$]$_{o,t}$ as a function of [TBP(ah)]$_o$ in high TBP concentration range.

—: calculated values by introducing $\sum_{h(1)=0} K_{11,h(1)}=0.198$, $\sum_{h(2)=0} K_{21,h(2)}=0.484$, and $\sum_{h(3)=0} K_{31,h(3)}=0.333$,

····: calculated values by introducing $\sum_{h(1)=0} K_{11,h(1)}=0.198$ and $\sum_{h(2)=0} K_{21,h(2)}=0.703$ into Eq. 13.

optimal values calculated by assuming only the 2 : 1 complex in addition to the 1 : 1 complex.

Figure 2 gives [HNO$_3$]$_{o,t}$ as a function of {H$^+$}{NO$_3{}^-$} at various [TBP]$_{o,t}$. These lines are completely straight with a slope of one, which can be easily explained by Eq. 13; when [TBP]$_{o,t}$ is constant, [TBP(ah)]$_o$ is also constant because [TBP]$_{o,t}$$\gg$[HNO$_3$]$_{o,t}$.

Hydration of TBP–HNO$_3$ Complexes. To obtain the hydration numbers is not possible in the range of [HNO$_3$]$_t$$\leq$0.1 mol dm^{-3}, because of the low extraction of the acid complexes, resulting in low water co-extraction. Therefore, for this purpose, the water distribution was measured at high aqueous nitric acid concentrations. The data were analyzed as functions of [TBP]$_{o,t}$, {H$^+$}{NO$_3{}^-$}, and a_w; the a_w values were taken from the literature.[21]

When [TBP]$_{o,t}$ is sufficiently low, e.g., [TBP]$_{o,t}$$\leq$0.03 mol dm^{-3}, TBP·HNO$_3$ is predominantly formed in the organic phase, as can be seen from Fig. 1B. Figure 3 gives [H$_2$O]$_{o,t}$ vs. [HNO$_3$]$_t$ at [TBP]$_{o,t}$=0.005, 0.01, and 0.03 mol dm^{-3}. The hydration number for the 1 : 1 complex (h(1)) can be obtained stoichiometrically by analyzing the data in Fig. 3 on the basis of Eqs. 8 and 10. The dotted and chain lines in Fig. 3 were calculated by introducing h(1)=0 and 1, respectively, into these equations, while $\sum_{h(1)=0} K_{11,h(1)}$ (=$K_{11,0}$ or $K_{11,1}$) was introduced as an already-known value. Since the experimental data were between the dotted and chain lines, the data were analyzed again by taking account of both anhydrous TBP·HNO$_3$ and its monohydrate; $\sum_{h(1)=0} K_{11,h(1)}$ (=$K_{11,0}$+$K_{11,1}$) was introduced as an already-known value. By the data analysis, the values of $K_{11,0}$ and $K_{11,1}$ were obtained to be 0.180±0.0082 and 0.0180±0.0009, respectively. The solid lines, which agreed very well with the experimental data, were calculated by introducing these values.

In the next stage, the values of h(2) and h(3) are judged as to whether they are stoichiometric or not. Figure 4 gives [H$_2$O]$_{o,t}$ vs. [HNO$_3$]$_t$ at [TBP]$_{o,t}$=0.05, 0.1, 0.3, 0.5, 0.7, 0.9, 1.0, 1.3, 1.5, 1.7, 1.9, and 2.0 mol dm^{-3}; the change in the volume of the organic phase was quite negligible (maximum 3%). One hydrate for each of the 2 : 1 and 3 : 1 complex

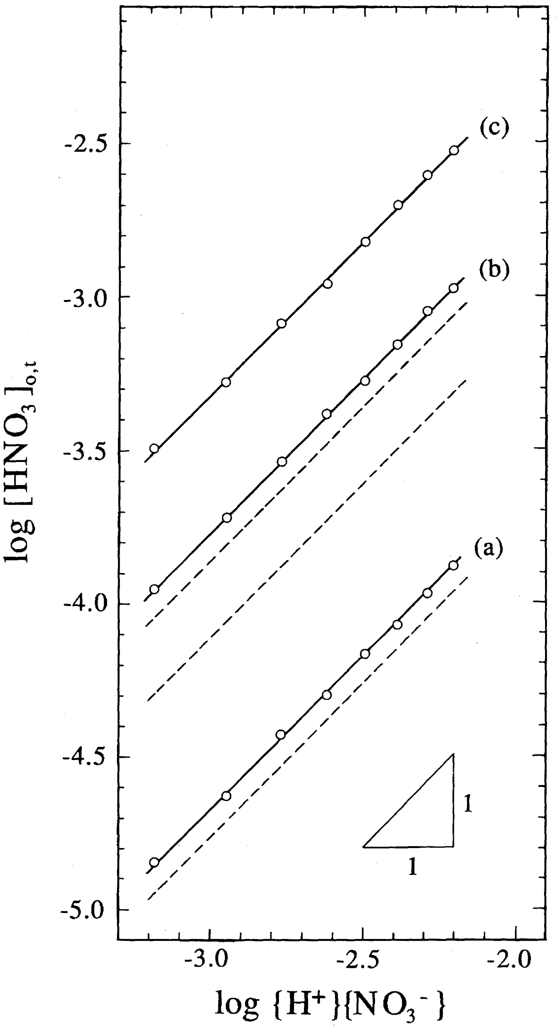

Fig. 2. $[HNO_3]_{o,t}$ as a function of $\{H^+\}\{NO_3^-\}$ at various $[TBP]_{o,t}$ on a logarithmic scale; $[TBP]_{o,t}$=(a) 0.10, (b) 0.50, and (c) 1.0 mol dm^{-3}.
—: calculated values by introducing $\sum_{h(1)=0} K_{11,h(1)}=0.198$, $\sum_{h(2)=0} K_{21,h(2)}=0.484$, and $\sum_{h(3)=0} K_{31,h(3)}=0.333$,
- - -: calculated values by introducing only $\sum_{h(1)=0} K_{11,h(1)}=0.198$, into Eq. 13.

was first assumed and the data in Fig. 4 were analyzed on the basis of Eqs. 8 and 10; $h(2)$ and $h(3)$ were introduced as unknown values, while $\sum_{h(2)=0} K_{21,h(2)}$ and $\sum_{h(3)=0} K_{31,h(3)}$ were introduced as already-known values. The values of $h(2)$ and $h(3)$, obtained at the respective TBP concentrations, are given in Table 2 along with their 3σ errors. They are independent of $[TBP]_{o,t}$, and precisely obtained as being integers (1 and 4). Thus, $h(2)$ and $h(3)$, as well as $h(1)$, are stoichiometric constants and each of the 2 : 1 and 3 : 1 complex is in the only one hydrate form.

The water distribution data, as well as the nitric acid distribution data, cannot be explained without assuming $(TBP)_3 \cdot HNO_3$ complex, as shown in Fig. 5. The calculated values were not suitable even when more than one hydrate for $(TBP)_2 \cdot HNO_3$ was assumed.

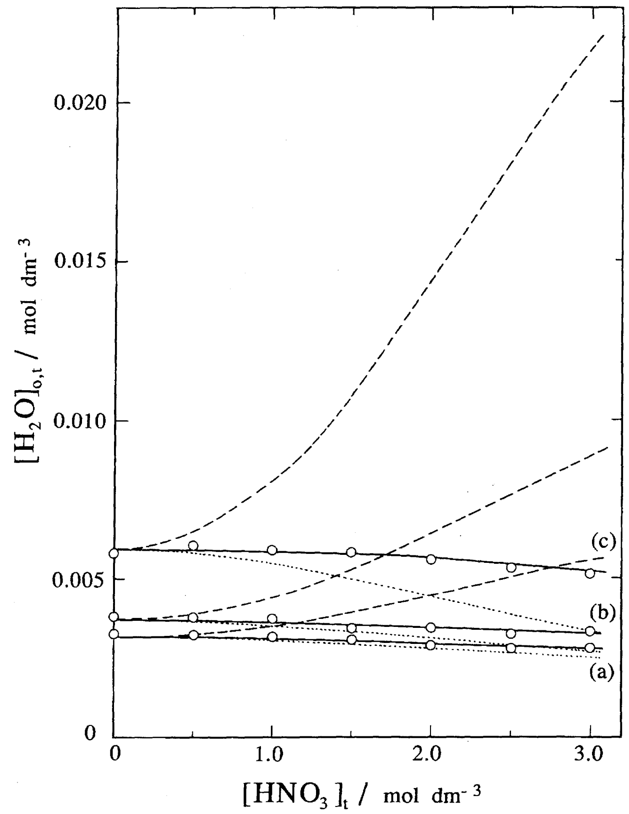

Fig. 3. $[H_2O]_{o,t}$ as a function of $[HNO_3]_t$ at low $[TBP]_{o,t}$; $[TBP]_{o,t}$=(a) 0.005, (b) 0.01, and (c) 0.03 mol dm^{-3}.
····: calculated values by introducing $h(1)=0$ and $K_{11,0}=0.198$,
- - -: calculated values by introducing $h(1)=1$ and $K_{11,1}=0.198$,
—: calculated values by introducing $h(1)=0$ and 1, $K_{11,0}=0.180$, $K_{11,1}=0.0180$ ($K_{11,0}+K_{11,1}=0.198$), into Eqs. 8 and 10.

Figures 6 and 7 give $[HNO_3]_{o,t}$ vs. $[TBP(ah)]_o$ at various $[HNO_3]_t$, and, $[HNO_3]_{o,t}$ vs. $\{H^+\}\{NO_3^-\}$ at various $[TBP]_{o,t}$, respectively. The solid lines in these figures were calculated by introducing all of the stoichiometric constants, summarized in Table 3, into Eqs. 8 and 9, while the chain lines were calculated by assuming TBP hydrates and only 1 : 1 TBP–HNO$_3$ complexes; the discrepancies between the solid and chain lines seen in the low TBP concentration range in these figures are due to the extraction of free nitric acid.

Distribution of TBP between Two Phases. The distribution of TBP between the two phases was also measured by means of ICP-mass spectrometry. For at least up to 3 mol dm^{-3} aqueous nitric acid, on the whole, the concentration of TBP in the aqueous phase was decreased by an increase in the aqueous acid concentration. For instance, the solubility of TBP in pure water was 1.5×10^{-3} mol dm^{-3}, while that in a 3 mol dm^{-3} aqueous nitric acid solution was 1.0×10^{-3} mol dm^{-3}; the results agreed very well with the data obtained in a previous study by using ^{32}P-labeled TBP.[1] In any case, the TBP concentration in the aqueous phase was negligible against that in the organic phase; thus, the TBP concentration initially added to the liquid–liquid system was

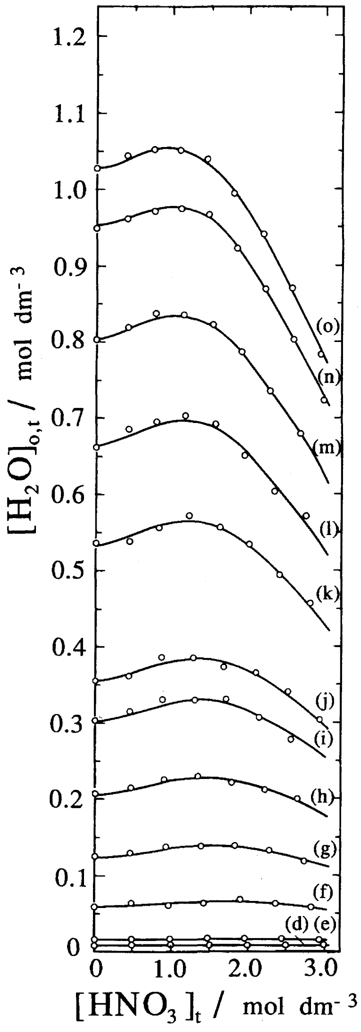

Fig. 4. $[H_2O]_{o,t}$ as a function of $[HNO_3]_t$ at high $[TBP]_{o,t}$; $[TBP]_{o,t}$=(d) 0.05, (e) 0.1, (f) 0.3, (g) 0.5, (h) 0.7, (i) 0.9, (j) 1.0, (k) 1.3, (l) 1.5, (m) 1.7, (n) 1.9, and (o) 2.0 mol dm^{-3}. —: calculated values by introducing $h(1)=0$ and 1, $h(2)=1$, $h(3)=4$, $K_{11,0}=0.180$, $K_{11,1}=0.0180$, $K_{21,1}=0.484$, and $K_{31,4}=0.333$ into Eqs. 8 and 10.

Table 2. Hydration Numbers for 2 : 1 and 3 : 1 Complex ($h(2)$ and $h(3)$) at Various TBP Concentrations with 3σ Errors

$[TBP]_{o,t}$ / mol dm^{-3}	$h(2)$	$h(3)$
0.005	—	—
0.010	—	—
0.030	—	—
0.050	1.02 (±0.35)	—
0.070	1.06 (±0.22)	—
0.090	0.98 (±0.12)	—
0.10	0.94 (±0.07)	—
0.30	1.00 (±0.08)	4.02 (±0.82)
0.50	0.93 (±0.07)	4.11 (±0.35)
0.70	1.03 (±0.07)	3.90 (±0.22)
0.90	1.04 (±0.06)	3.78 (±0.19)
1.00	1.05 (±0.06)	3.85 (±0.18)
1.30	1.08 (±0.05)	4.20 (±0.17)
1.50	1.02 (±0.06)	4.03 (±0.17)
1.70	1.01 (±0.08)	4.05 (±0.20)
1.90	1.00 (±0.07)	4.01 (±0.16)
2.00	1.00 (±0.06)	4.00 (±0.15)

Table 3. Summary of Stoichiometric Constants in TBP–Dodecane–HNO_3(aq) System

Species	Stoichiometric constant
TBP–HNO_3 complexes	
TBP·HNO_3	$h(1)=0$ $K_{11,0}=0.180$
TBP·HNO_3·H_2O	$h(1)=1$ $K_{11,1}=0.0180$
$(TBP)_2$·HNO_3·H_2O	$h(2)=1$ $K_{21,1}=0.484$
$(TBP)_3$·HNO_3·$(H_2O)_4$	$h(3)=4$ $K_{31,4}=0.333$
TBP hydrates	
TBP·H_2O $^{a)}$	$K_{m,1}=0.110$
$(TBP)_2$·$(H_2O)_2$ $^{a)}$	$K_{d,2}=0.220$
$(TBP)_3$·$(H_2O)_6$ $^{a)}$	$K_{t,6}=0.037$
HNO_3 hydrates	
HNO_3·H_2O $^{b)}$	$K_{f,1}=8.1\times10^{-7}$
$H^+NO_3^-$·$(H_2O)_{10}$ $^{b)}$	$K_{f,10}=7.2\times10^{-6}$
Free water	
H_2O (free) $^{a)}$	$K_{fw}=0.0027$

a) Refs. 22 and 23. b) Ref. 25.

almost equal to the TBP concentration in the organic phase.

TBP·$(HNO_3)_m$ ($m \geq 2$) Complexes. In many previous studies,[1,11,12,15,16,20] the formation of TBP–HNO_3 complexes including more than one nitric acid, TBP·$(HNO_3)_m$ ($m \geq 2$), was pointed out at high nitric acid concentrations. This was also examined in the present study by checking the data in Figs. 2 and 7. If TBP·$(HNO_3)_m$ forms in addition to the above-mentioned complexes in the organic phase, an m-order dependence of $[HNO_3]_{o,t}$ on $\{H^+\}\{NO_3^-\}$ should appear. However, in fact, the experimental data did not show this case, and were consistently explained without taking account of TBP·$(HNO_3)_m$. From this, at least up to $[HNO_3]_t$= 3 mol dm^{-3}, no TBP·$(HNO_3)_m$ was formed in the organic phase.

When $[HNO_3]_t \geq 7$ mol dm^{-3}, $(TBP)_2$·HNO_3 and $(TBP)_3$·HNO_3 disappear quite completely in the range of $[TBP]_{o,t} \leq 2$ mol dm^{-3}, and only TBP·HNO_3 and TBP·$(HNO_3)_m$ exist in the organic phase, which was confirmed experimentally and by a calculation. If TBP·$(HNO_3)_m$ forms stoichiometrically, the ratio of TBP·$(HNO_3)_m$ to TBP·HNO_3 is independent on TBP concentration, as can be seen from the following equation:

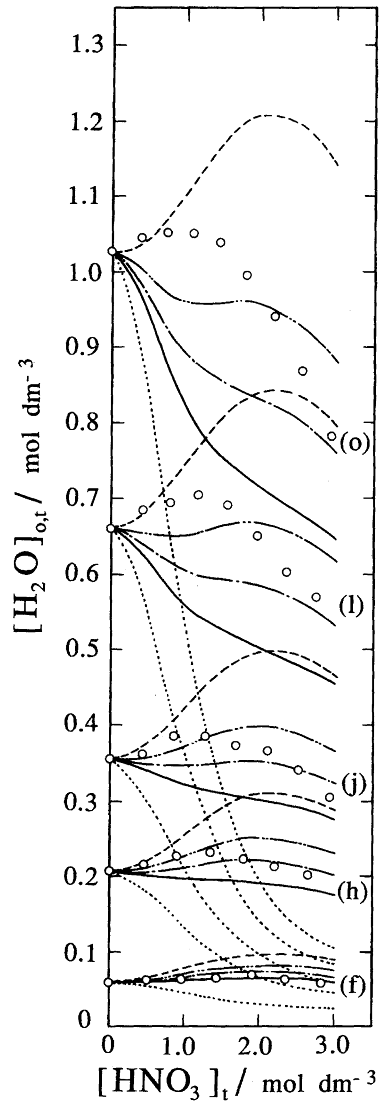

Fig. 5. Calculated values at $[TBP]_{o,t}$=(f) 0.3, (h) 0.7, (j) 1.0, (l) 1.5, and (o) 2.0 mol dm^{-3} by assuming only 2 : 1 complexes introducing the following values:
····: $h(2)=0$, $K_{21,0}=0.703$,
—: $h(2)=1$, $K_{21,1}=0.703$,
- - -: $h(2)=2$, $K_{21,2}=0.703$,
–·–: $h(2)=1$ and 2, $K_{21,1}=0.527$, $K_{21,2}=0.176$ ($K_{21,1}+K_{21,2}=0.703$),
–··–: $h(2)=1$ and 2, $K_{21,1}=0.352$, $K_{21,2}=0.351$ ($K_{21,1}+K_{21,2}=0.703$), into Eqs. 8 and 10.

$$\frac{\sum\limits_{m=2}\sum\limits_{h=0}[\mathrm{TBP}\cdot(\mathrm{HNO_3})_m\cdot(\mathrm{H_2O})_h]_\mathrm{o}}{\sum\limits_{h(1)=0}[\mathrm{TBP}\cdot\mathrm{HNO_3}\cdot(\mathrm{H_2O})_{h(1)}]_\mathrm{o}} = \frac{\sum\limits_{m=2}\sum\limits_{h=0}K_{1m,h}(\{\mathrm{H^+}\}\{\mathrm{NO_3}^-\})^{m-1}{a_\mathrm{w}}^h}{\sum\limits_{h(1)=0}K_{11,h(1)}{a_\mathrm{w}}^{h(1)}}, \tag{III}$$

where

$$K_{1m,h} = \frac{[\mathrm{TBP}\cdot(\mathrm{HNO_3})_m\cdot(\mathrm{H_2O})_h]_\mathrm{o}}{[\mathrm{TBP(ah)}]_\mathrm{o}(\{\mathrm{H^+}\}\{\mathrm{NO_3}^-\})^m\,{a_\mathrm{w}}^h} \quad (h=0,\ 1,\ 2,\ \cdots). \tag{IV}$$

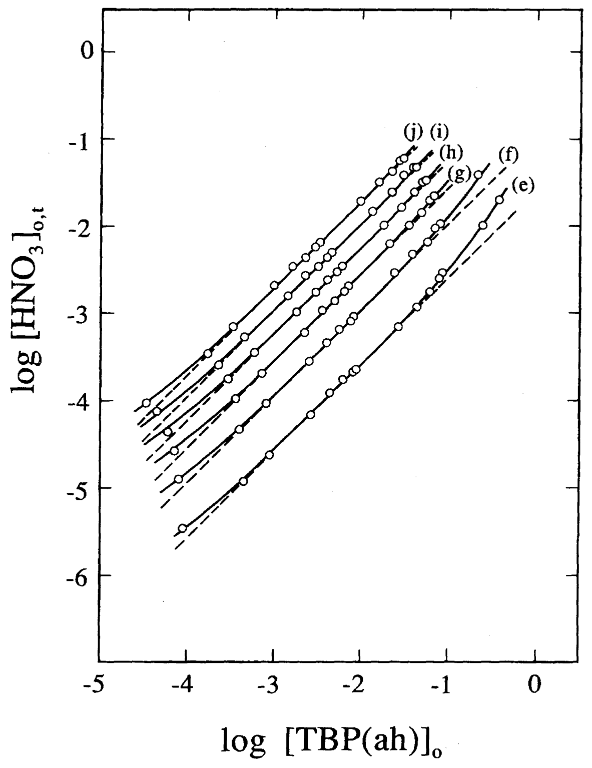

Fig. 6. $[HNO_3]_{o,t}$ as a function of $[TBP(ah)]_o$ at various $[HNO_3]_t$ on a logarithmic scale; $[HNO_3]_t$=(e) 0.5, (f) 1.0, (g) 1.5, (h) 2.0, (i) 2.5, and (j) 3.0 mol dm^{-3}.
—: calculated values by taking account of TBP hydrates, HNO_3(free), $TBP\cdot HNO_3$, $TBP\cdot HNO_3\cdot H_2O$, $(TBP)_2\cdot HNO_3\cdot H_2O$, and $(TBP)_3\cdot HNO_3\cdot (H_2O)_4$.
- - -: calculated values by taking account of TBP hydrates and only $TBP\cdot HNO_3$ and $TBP\cdot HNO_3\cdot H_2O$.

Thus, in this case, the shape of $\log[HNO_3]_{o,t}$ vs. $\log\{H^+\}\{NO_3^-\}$ (or $[HNO_3]_t$) plots should also be independent of $[TBP]_{o,t}$, when $[HNO_3]_t \geq 7$ mol dm^{-3} and $[TBP]_{o,t} \leq 2$ mol dm^{-3}. However, the experimental results reported previously by many investigators[1,15,20] did not show the case; obviously, a higher $[TBP]_{o,t}$ implies a higher $TBP\cdot(HNO_3)_m$ ratio. In fact, at a low TBP concentration, e.g., 0.01 mol dm^{-3}, no $TBP\cdot(HNO_3)_m$ was found in the organic phase, at least up to $[HNO_3]_t$=10 mol dm^{-3}, as can be seen in Fig. 8. Thus, the $TBP\cdot(HNO_3)_m$ complexes should be rather described as $(TBP)_i\cdot(HNO_3)_j\cdot(H_2O)_k$ ($j>i\geq 2$); from our preexperimental results, since such a species was found to be a highly hydrated complex, this may be a kind of micelle-like species.

TBP–HNO_3–H_2O Stoichiometry. At a fixed TBP concentration, the organic phase can be regarded as being the sole medium of a TBP–dodecane mixture. In such a uniform medium, the equilibria for the TBP–HNO_3 complex-formations can be treated stoichiometrically, and the equilibrium constants peculiar to the medium can be apparently obtained. The change in these constants due to a change in the TBP concentration was checked by analyses of the water and nitric acid distribution data at various TBP concentrations, introducing the equilibrium constants ($K_{11,0}$, $K_{11,1}$,

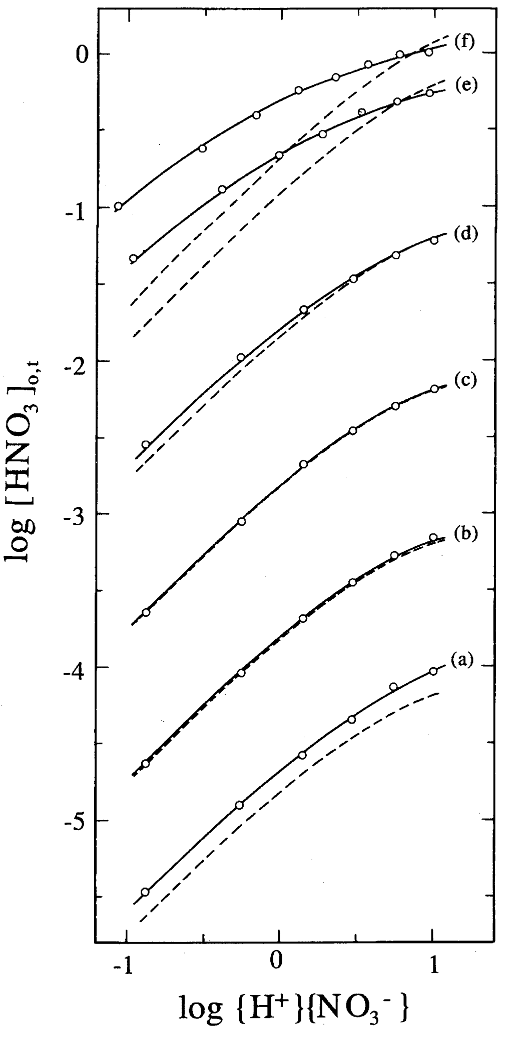

Fig. 7. $[HNO_3]_{o,t}$ as a function of $\{H^+\}\{NO_3^-\}$ at various $[TBP]_{o,t}$ on a logarithmic scale; $[TBP]_{o,t}$=(a) 0.0001, (b) 0.001, (c) 0.01, (d) 0.1, (e) 1.0, and (f) 2.0 mol dm^{-3}.
—: calculated values by taking account of TBP hydrates, HNO_3(free), TBP·HNO_3, TBP·HNO_3·H_2O, $(TBP)_2$·HNO_3·H_2O, and $(TBP)_3$·HNO_3·$(H_2O)_4$.
- - -: calculated values by taking account of TBP hydrates and only TBP·HNO_3 and TBP·HNO_3·H_2O.

$K_{21,1}$, and $K_{31,4}$), as unknown values, and the hydration numbers ($h(1)$, $h(2)$, and $h(3)$), as already-known values. These complexation constants, as well as the TBP hydration constants, were independent of TBP concentration, as can be seen from Table 4. Thus, the TBP–HNO_3–H_2O stoichiometry in the organic phase was applied quite completely without any activity correction.

Influence of the Medium Properties on the Equilibrium Constants. According to the change in the TBP concentration in dodecane, the physical properties of the organic phase, such as the dielectric constant (ε), also change. Since an equilibrium constant has generally been believed to be a value that is naturally changeable by such a change in the medium properties, the TBP–HNO_3–H_2O complexation constants, dependent on TBP concentration, were proposed in many previous studies.[10,13,20] However, on the contrary,

Table 4. Equilibrium Constants at Various TBP Concentrations with 3σ Errors

$[TBP]_{o,t}$	Species and constant							
	H_2O (free)	TBP·H_2O	$(TBP)_2$·$(H_2O)_2$	$(TBP)_3$·$(H_2O)_6$	TBP·HNO_3	TBP·HNO_3·H_2O	$(TBP)_2$·HNO_3·H_2O	$(TBP)_3$·HNO_3·$(H_2O)_4$
mol dm^{-3}	K_{fw} [a]	$K_{m,1}$ [a]	$K_{d,2}$ [a]	$K_{t,6}$ [a]	$K_{11,0}$	$K_{11,1}$	$K_{21,1}$	$K_{31,4}$
0.005	0.0027 (± 0.0002)	0.11 (± 0.009)	—	—	0.181 (± 0.008)	0.0180 (± 0.0009)	—	—
0.010	0.0027 (± 0.0003)	0.12 (± 0.009)	—	—	0.180 (± 0.008)	0.0185 (± 0.0009)	—	—
0.030	0.0028 (± 0.0003)	0.10 (± 0.012)	0.18 (± 0.18)	—	0.179 (± 0.008)	0.0180 (± 0.0009)	—	—
0.050	0.0033 (± 0.0004)	0.11 (± 0.012)	0.23 (± 0.14)	—	0.188 (± 0.009)	0.0182 (± 0.0010)	0.480 (± 0.18)	—
0.070	0.0024 (± 0.0006)	0.10 (± 0.012)	0.23 (± 0.09)	—	0.188 (± 0.009)	0.0177 (± 0.0010)	0.502 (± 0.070)	—
0.090	0.0029 (± 0.0007)	0.10 (± 0.012)	0.21 (± 0.08)	—	0.189 (± 0.009)	0.0177 (± 0.0010)	0.495 (± 0.032)	—
0.10	0.0032 (± 0.0007)	0.10 (± 0.009)	0.20 (± 0.07)	—	0.185 (± 0.010)	0.0172 (± 0.0009)	0.484 (± 0.021)	—
0.30	0.0042 (± 0.0022)	0.12 (± 0.012)	0.22 (± 0.02)	—	0.173 (± 0.009)	0.0188 (± 0.0012)	0.477 (± 0.022)	0.350 (± 0.12)
0.50	—	0.11 (± 0.012)	0.22 (± 0.03)	0.047 (± 0.025)	0.177 (± 0.008)	0.0179 (± 0.0015)	0.489 (± 0.024)	0.350 (± 0.036)
0.70	—	0.11 (± 0.011)	0.23 (± 0.03)	0.037 (± 0.018)	0.180 (± 0.009)	0.0179 (± 0.0033)	0.466 (± 0.021)	0.360 (± 0.022)
0.90	—	0.10 (± 0.009)	0.21 (± 0.02)	0.040 (± 0.011)	0.180 (± 0.009)	0.0175 (± 0.0043)	0.480 (± 0.021)	0.365 (± 0.013)
1.00	—	0.10 (± 0.009)	0.22 (± 0.02)	0.035 (± 0.009)	0.180 (± 0.009)	0.0186 (± 0.0052)	0.484 (± 0.021)	0.330 (± 0.011)
1.30	—	0.11 (± 0.011)	0.22 (± 0.02)	0.032 (± 0.007)	0.181 (± 0.009)	0.0188 (± 0.0055)	0.478 (± 0.023)	0.355 (± 0.012)
1.50	—	0.11 (± 0.010)	0.22 (± 0.02)	0.038 (± 0.006)	0.173 (± 0.008)	0.0180 (± 0.0065)	0.485 (± 0.020)	0.310 (± 0.013)
1.70	—	0.11 (± 0.009)	0.22 (± 0.02)	0.037 (± 0.006)	0.184 (± 0.010)	0.0187 (± 0.0072)	0.484 (± 0.022)	0.315 (± 0.012)
1.90	—	0.11 (± 0.011)	0.22 (± 0.02)	0.037 (± 0.006)	0.181 (± 0.011)	0.0190 (± 0.0096)	0.492 (± 0.021)	0.330 (± 0.012)
2.00	—	0.11 (± 0.009)	0.22 (± 0.02)	0.037 (± 0.005)	0.178 (± 0.009)	0.0192 (± 0.012)	0.495 (± 0.021)	0.334 (± 0.013)

a) Up to $[TBP]_{o,t}$ = 1.5 mol dm^{-3}, these values were cited from Ref. 23. The TBP–water stoichiometry, extended up to $[TBP]_{o,t}$ = 2 mol dm^{-3}, was confirmed in the present study.

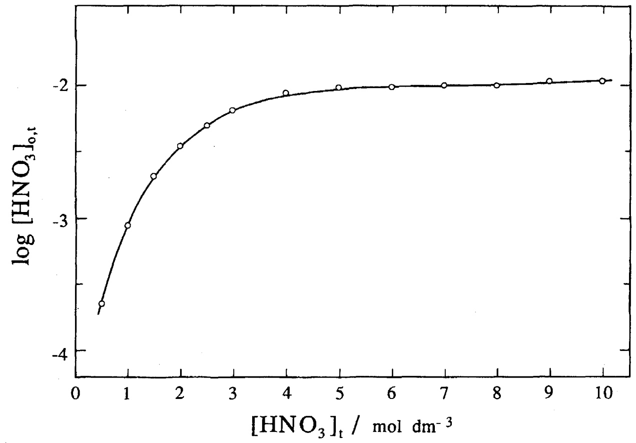

Fig. 8. log $[HNO_3]_{o,t}$ as a function of $[HNO_3]_t$ at $[TBP]_{o,t}$= 0.01 mol dm^{-3}.
—: calculated values by taking account of TBP hydrates, HNO_3 (free), TBP•HNO_3, and TBP•HNO_3•H_2O.

the equilibrium constants obtained in the present study were independent of the TBP concentration, consistently, from 0.005 mol dm^{-3} (0.137 vol%) to 2 mol dm^{-3} (54.6 vol%) TBP in dodecane, as can be seen from Table 4. Thus, the effect of such a medium property change on the equilibrium constants seems to be insignificant. We insist that the change in the physical properties of the organic phase does not alter the TBP–HNO_3–H_2O stoichiometry. Such a dependence on the TBP concentration can appear when the chemical interactions, actually working in the organic phase, are not thoroughly and correctly taken into account. Similarly, the hydration constants of *N,N*-bis(2-ethylhexyl)-hexanamide were consistent from 0.03 mol dm^{-3} (1.1 vol%) to 2.5 mol dm^{-3} (90 vol%) amide in dodecane without any activity correction; nevertheless, there was a wide change in ε of the medium from 2 to 8.[26] The hydration constants of TBP also remained unchanged by such a medium property change.[22,23] As another example, which is well-known, benzene and 1,2-dichloroethane, whose dielectric constant (ε), dipole moment, density, viscosity, etc, are quite different, make a perfectly ideal mixture solution; thus, such physical property changes due to a change in the mixing ratio do not seem to affect on the activities of the components.

Activity Coefficients in the Organic Phase. The experimental activity coefficients for TBP, previously obtained in the TBP–water binary system,[19,27] were nearly constant as unity up to water saturation (about 3.57 mol dm^{-3} water) in TBP at 25 °C; nevertheless, the physical properties were changed, e.g., $\varepsilon = 8.1$ in dry TBP, and $\varepsilon = 10.6$ in water saturated TBP.[27] Thus, TBP acts

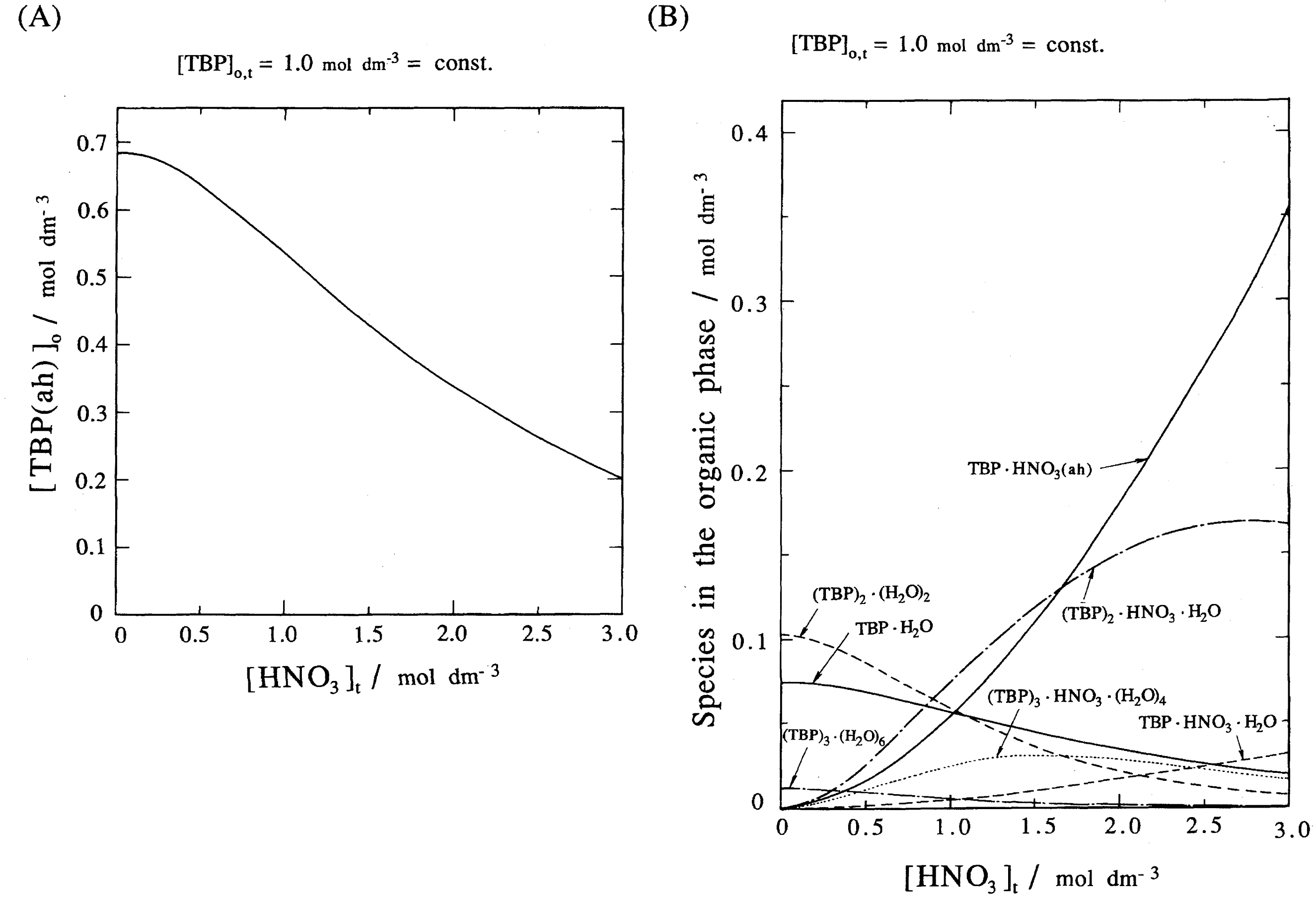

Fig. 9. Concentrations of the species present in the organic phase as a function of $[HNO_3]_t$ at $[TBP]_{o,t}$=1 mol dm^{-3}; (A) $[TBP\text{-}(ah)]_o$, (B) $[TBP{\cdot}H_2O]_o$, $[(TBP)_2{\cdot}(H_2O)_2]_o$, $[(TBP)_3{\cdot}(H_2O)_6]_o$, $[TBP{\cdot}HNO_3]_o$, $[TBP{\cdot}HNO_3{\cdot}H_2O]_o$, $[(TBP)_2{\cdot}HNO_3{\cdot}H_2O]_o$, and $[(TBP)_3{\cdot}HNO_3{\cdot}(H_2O)_4]_o$. The concentration of free HNO_3 was only a trace at this TBP concentration.

nearly ideally on water in the TBP–water binary system to the water saturation. Furthermore, the TBP hydration constants ($=[(\mathrm{TBP})_x\cdot(\mathrm{H_2O})_y]_\mathrm{o}/[\mathrm{TBP(ah)}]_\mathrm{o}{}^x a_\mathrm{w}{}^y$; $x=1, 2, 3$, $y=1, 2, 6$) in the TBP–dodecane–water system and the TBP–HNO_3 complexation and hydration constants ($=[(\mathrm{TBP})_n\cdot\mathrm{HNO_3}\cdot(\mathrm{H_2O})_h]_\mathrm{o}/[\mathrm{TBP(ah)}]_\mathrm{o}{}^n\{\mathrm{H^+}\}\{\mathrm{NO_3}^-\}a_\mathrm{w}{}^h$; $n=1, 2, 3$, $h=0, 1, 4$) in the TBP–dodecane–$HNO_{3(aq)}$ system were found to be consistent without any activity correction up to 2 mol dm^{-3} TBP in dodecane. From these, the activity coefficients for anhydrous TBP, TBP hydrates, and TBP–HNO_3 complexes in the organic phase seem to be unity, consistently, up to 2 mol dm^{-3} TBP in dodecane. This may be explained as follows:

1. In a nonpolar solvent, such as dodecane, the solvation interaction is quite negligible against TBP–HNO_3 and TBP–water interactions; in contrast, the hydration effect is very important in aqueous solutions.[24)]
2. In a low dielectric medium, an ionic species does not dissociate to a single ion, but exists as an ion-pair. Since an ion-pair is electrically neutral, there is no effect of the ionic atmosphere by the Coulomb force among ion-pairs. Furthermore, the change in activity due to a change from a single ion to an ion-pair does not have to be considered in such a medium.
3. The TBP–TBP interaction is much weaker than TBP–HNO_3 and TBP–water interactions; in fact, no anhydrous TBP dimer was found in the organic phase.[17,23,28,29)]

Therefore, the treatment of the change in activity coefficients seems to be essentially simple in a nonpolar solvent rather than in an aqueous solution. However, in fact, the treatment of the activity coefficients in a nonpolar solvent, in which very weak interactions, such as hydrogen bonding, dipole–dipole interactions, are also working stoichiometrically among the solute molecules, is usually complicated due to the formation of numerous complexes. However, in other words, if all of the stoichiometric interactions working in a nonpolar solvent are taken into account, no special correction in the activities for the solutes should be necessary, even in a highly concentrated solution.

Limit of Stoichiometry. The limit of TBP and nitric acid concentrations to the TBP–HNO_3–H_2O stoichiometry was also examined in the present study, and the available range, that $[\mathrm{TBP}]_\mathrm{o,t}\leq 2$ mol dm^{-3} and $[\mathrm{HNO_3}]_\mathrm{t}<5$ mol dm^{-3}, was derived; the stoichiometry applied completely up to $[\mathrm{HNO_3}]_\mathrm{t}=3$ mol dm^{-3}, but at $[\mathrm{HNO_3}]_\mathrm{t}=5$ mol dm^{-3}, the experimental data deviated slightly from the calculated values. Dannus[30)] and Mokili[20)] suggested nonstoichiometric hydration, which occurs with a nonordered interaction between TBP (or TBP–HNO_3 complexes) and water in organic phase, e.g., water pool enclosed with cyclic structures like reverse micelles.[31)] It is easily imaged that the formation of another distinctive physical phase, i.e., the inside of micelles, should break the stoichiometry in organic phase. When $[\mathrm{TBP}]_\mathrm{o,t}>2$ mol dm^{-3} and $[\mathrm{HNO_3}]_\mathrm{t}\geq 5$ mol dm^{-3}, such reverse micelles may be formed. Moreover, in such a condition, ion-pair species in the organic phase may dissociate to their single ions to some extent due to an increase in the dielectric constant.

Structure of $(TBP)_3\cdot HNO_3\cdot(H_2O)_4$. If the complex is ionic, four water molecules may hydrate with H^+ to form $H_3O^+(H_2O)_3$ ion: such a hydrated oxonium ion was found in an aqueous hydrochloric acid solution by X-ray diffraction.[32)] The $H_3O^+(H_2O)_3$ ion was also found in 4-methyl-2-pentanone, and this may be stabilized by the outer-sphere effect of the ketone molecules.[33)] Similarly, $H_3O^+(H_2O)_3$ ion may also be stabilized by TBP, which is a stronger base than the ketone; three TBP molecules may contact with a $H_3O^+(H_2O)_3$ ion through hydrogen-bonds from the outer-sphere of the primary hydration shell.

Survey of TBP–Dodecane–$HNO_{3(aq)}$ System. Finally, after all observations, when $[\mathrm{TBP}]_\mathrm{o,t}\leq 2$ mol dm^{-3} and $[\mathrm{HNO_3}]_\mathrm{t}\leq 3$ mol dm^{-3}, the following stoichiometric species were found to be present in the organic phase: TBP(ah), $TBP\cdot H_2O$, $(TBP)_2\cdot(H_2O)_2$, $(TBP)_3\cdot(H_2O)_6$, $HNO_3\cdot H_2O$, $H^+NO_3^-\cdot(H_2O)_{10}$, $TBP\cdot HNO_3$, $TBP\cdot HNO_3\cdot H_2O$, $(TBP)_2\cdot HNO_3\cdot H_2O$, and $(TBP)_3\cdot HNO_3\cdot(H_2O)_4$. Figure 9A shows the decrease in free TBP concentration ($[\mathrm{TBP(ah)}]_\mathrm{o}$) due to an increase in $[\mathrm{HNO_3}]_\mathrm{t}$ at $[\mathrm{TBP}]_\mathrm{o,t}=1$ mol dm^{-3}. The concentrations of the other species in the organic phase as a function of $[\mathrm{HNO_3}]_\mathrm{t}$ at $[\mathrm{TBP}]_\mathrm{o,t}=1$ mol dm^{-3} are also shown in Fig. 9B.

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