Bull. Chem. Soc. Jpn., **69**, 2869—2875 (1996)

Hydration of *N*, *N*-Bis(2-ethylhexyl)hexanamide in Dodecane

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(Received April 26, 1996)

The hydration and dimerization of *N*, *N*-bis(2-ethylhexyl) hexanamide (BEHHA) in dodecane were studied on the basis of the water distribution between aqueous solutions and dodecane. The data obtained at 298 K were analyzed as functions of the amide concentration in the organic phase and the water activity in the aqueous phase. When the amide was monomeric in the organic phase, only a monohydrate was formed. At high amide concentrations in the organic phase, dimerization of the monohydrate occurred and $(BEHHA)_2(H_2O)_2$ was formed. No other dimer hydrates were found in the organic phase. The results were compared with those of tributyl phosphate (TBP). The stoichiometry between BEHHA and water was investigated from low to very high amide concentrations in dodecane. The change in the activity coefficient for an amide contained in an inert solvent at high concentrations was also examined.

The monoamide is one of the most hopeful new alternative extractants to tributyl phosphate (TBP) for the separation process of actinides in the nuclear fuel cycle. However, the available information concerning the chemical properties of such an extractant is only very little;[1—3] especially, no hydration study has been made. In the present study, the hydration and dimerization of a monoamide, *N*, *N*-bis(2-ethylhexyl)-hexanamide (BEHHA), in dodecane were examined on the basis of the water distribution between aqueous solutions and the dodecane containing the monoamide. The water-distribution data were analyzed as functions of the BEHHA concentration in the organic phase and water activity in the aqueous phase (a_w). The BEHHA–water stoichiometry was investigated from low to very high amide concentrations, i. e., from 0.03 to 2.5 $\mathrm{mol\,dm^{-3}}$ (90 vol% BEHHA); in a practical reprocessing process of nuclear fuel, a highly concentrated solution with an extractant is necessary. By the addition of BEHHA at high concentration to dodecane, a problem involving a change in the activity coefficient occurs, which could be due to a medium property change. From this point of view, the effect of the BEHHA concentration in the organic phase on the equilibrium constants for the hydration was appraised. When the concentration of BEHHA in dodecane is constant, the organic phase having a fixed composition can be regarded as being a sole medium of the BEHHA–dodecane mixture on the condition that the water concentration in the organic phase is sufficiently low. In such a uniform medium, the hydration equilibria are stoichiometric and the apparent equilibrium constants can be obtained. Therefore, the hydration constants at various BEHHA concentrations were determined by analyzing the water-distribution data as a function of a_w, and the change in these constants due to a change in the BEHHA concentration was checked.

In previous studies in our laboratory,[4,5] the hydration of tributyl phosphate (TBP) was also investigated in a similar manner. This extractant was found to form three hydrates ($TBP\cdot H_2O$, $(TBP)_2(H_2O)_2$, and $(TBP)_3(H_2O)_6$) in dodecane; monomer monohydrate and dimer dihydrate were also proposed in other reports.[6,7] The hydration of BEHHA was compared with that of TBP.

Experimental

All of the reagents were of reagent grade. The monoamide, *N*, *N*-bis(2-ethylhexyl)hexanamide (BEHHA), was originally synthesized by Daihachi Chemical Industry Co., Ltd., Japan. The purity was checked by gas chromatography to be 99.6%. Lithium chloride (purity $> 99.0\%$) and dodecane (purity 99.3%) were used without further purification.

The water-distribution experiments were carried out at 298 K. A certain volume of water or an aqueous lithium chloride solution and the same volume of the monoamide–dodecane solution were shaken vigorously for 15 min in a stoppered glass tube and then centrifuged. The concentration of water extracted into the organic phase was measured by Karl–Fischer titration (MKA-210 type, Kyoto Electronics Manufacturing Co., Ltd., Japan).

The concentration of lithium chloride extracted by the monoamide into the organic phase was also checked in the present study. A portion of the organic phase was transferred into another tube, and a certain volume of water added. The two phases were shaken for 15 min and lithium chloride in the organic phase was completely back-extracted into water. The concentration of chloride in the aqueous solution was measured by an anion chromatography using a $2.5\times10^{-3}\ \mathrm{mol\,dm^{-3}}$ aqueous potassium hydrogen phthalate solution as an eluent. The detailed components of the chromatographic system were described in a previous study.[8]

Theoretical

The hydration of *N*,*N*-bis(2-ethylhexyl)hexanamide (BEHHA) can be written by the following two equilibria, monomer and dimer hydration:

$$\mathrm{BEHHA(ah)_{(o)}} + x\mathrm{H_2O} \rightleftharpoons \mathrm{BEHHA(H_2O)}_{x(\mathrm{o})}$$

$$K_{\mathrm{m},x} = \frac{[\mathrm{BEHHA(H_2O)}_x]_\mathrm{o}}{[\mathrm{BEHHA(ah)}]_\mathrm{o}{a_\mathrm{w}}^x} \qquad (x \geq 1), \tag{1}$$

$$2\ \mathrm{BEHHA(ah)}_{(o)} + y\mathrm{H_2O} \rightleftharpoons \mathrm{(BEHHA)_2(H_2O)}_{y(o)}$$

$$K_{\mathrm{d},y} = \frac{[\mathrm{(BEHHA)_2(H_2O)}_y]_\mathrm{o}}{[\mathrm{BEHHA(ah)}]_\mathrm{o}^2 a_\mathrm{w}^y} \qquad (y \geq 1), \tag{2}$$

where subscript "o" denotes the species in the organic phase, while the lack of a subscript denotes those in the aqueous phase. BEHHA(ah) is the anhydrous amide monomer and a_w is the water activity in the aqueous phase; $a_\mathrm{w}=1$ for pure water.

The total concentration of monoamide in the organic phase can be written as:

$$\begin{aligned}[\mathrm{BEHHA}]_{\mathrm{o,t}} &= [\mathrm{BEHHA(ah)}]_\mathrm{o} + \sum_{x=1} [\mathrm{BEHHA(H_2O)}_x]_\mathrm{o} \\ &\quad +2\sum_{y=1} [\mathrm{(BEHHA)_2(H_2O)}_y]_\mathrm{o} \\ &= (1+\sum_{x=1} K_{\mathrm{m},x} a_\mathrm{w}^x)[\mathrm{BEHHA(ah)}]_\mathrm{o} \\ &\quad +2\sum_{y=1} K_{\mathrm{d},y} a_\mathrm{w}^y [\mathrm{BEHHA(ah)}]_\mathrm{o}^2. \end{aligned} \tag{3}$$

The number of hydrates which must be taken into account is not defined in this equation; any number is possible in principle.

The total water concentration in the organic phase can be written as:

$$\begin{aligned}[\mathrm{H_2O}]_{\mathrm{o,t}} &= [\mathrm{H_2O(free)}]_\mathrm{o} + [\mathrm{H_2O}]_{\mathrm{o,E}} \\ &= [\mathrm{H_2O(free)}]_\mathrm{o} + \sum_{x=1}(x[\mathrm{BEHHA(H_2O)}_x]_\mathrm{o}) \\ &\quad + \sum_{y=1}(y[\mathrm{(BEHHA)_2(H_2O)}_y]_\mathrm{o}) \\ &= K_\mathrm{fw} a_\mathrm{w} + \sum_{x=1}(x K_{\mathrm{m},x} a_\mathrm{w}^x)[\mathrm{BEHHA(ah)}]_\mathrm{o} \\ &\quad + \sum_{y=1}(y K_{\mathrm{d},y} a_\mathrm{w}^y)[\mathrm{BEHHA(ah)}]_\mathrm{o}^2, \end{aligned} \tag{4}$$

where$[\mathrm{H_2O(free)}]_\mathrm{o}$ and $[\mathrm{H_2O}]_{\mathrm{o,E}}$ are the concentration of water free from the extractant and that extracted by the extractant, respectively. K_fw is the distribution constant of free water between the two phases,

$$K_\mathrm{fw} = \frac{[\mathrm{H_2O(free)}]_\mathrm{o}}{a_\mathrm{w}} = 0.0027.\text{[4,5]} \tag{5}$$

The value of K_fw corresponds to the water solubility in dodecane in the molarity unit at $a_\mathrm{w}=1$.

The hydration numbers (x, ⋯ and y, ⋯) and equilibrium constants ($K_{\mathrm{m},x}$, ⋯ and $K_{\mathrm{d},y}$, ⋯) are treated as unknown values in the calculations by a successive-approximation method using a least-squares computer program.

Results and Discussion

Hydration and Dimerization of BEHHA. The concentration of water extracted by *N*,*N*-bis(2-ethylhexyl)hexanamide (BEHHA) into dodecane is shown in Fig. 1 as a function of the monoamide concentration in the organic phase at various water activities (a_w). The water activities were varied by adding lithium chloride, whose distribution ratio to the organic phase was a mere trace; e.g., the concentration of LiCl extracted from a 13 mol dm^{-3} aqueous LiCl solution into a 2.5 mol dm^{-3} BEHHA/dodecane solution (90 vol% BEHHA) was only 1.2×10^{-4} mol dm^{-3}, which is negligible against $[\mathrm{H_2O}]_{\mathrm{o,t}}$ (=0.020 mol dm^{-3}). Thus, the concentration of the water co-extracted with LiCl–Amide complexes can also be negligible for $[\mathrm{H_2O}]_{\mathrm{o,t}}$. The values of $a_\mathrm{w}$were determined by water-distribution technique using benzene as a solvent in a similar manner to a method given in the literature;[9,10] the concentration of water extracted from various aqueous LiCl solutions into benzene was measured by Karl–Fischer titration, and the a_w values were obtained on the basis of the following equation:

$$a_\mathrm{w} = \frac{[\mathrm{H_2O(free)}]_{\mathrm{o(benz)}}}{0.032} \approx \frac{[\mathrm{H_2O}]_{\mathrm{o,t(benz)}}}{0.032}. \tag{6}$$

Here, 0.032[8] is the water solubility in benzene at 298 K in molarity unit at $a_\mathrm{w}=1$. The a_w values obtained by the water-distribution method agreed very well with those obtained by using vapor-pressure data above aqueous LiCl solutions from the literature.[11]

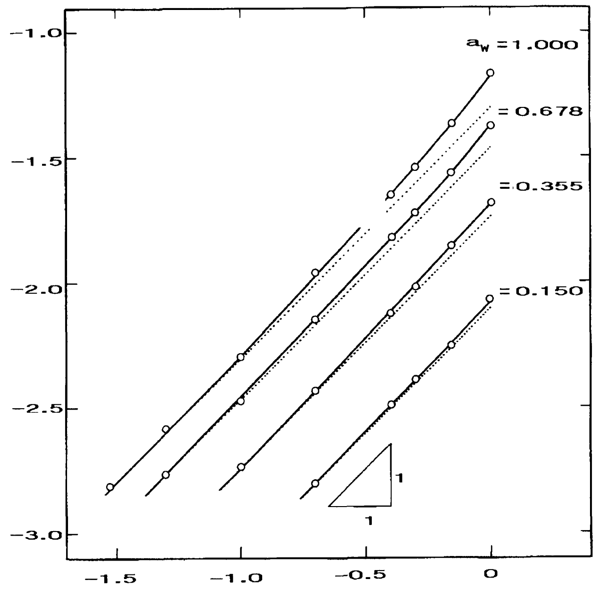

Fig. 1. The concentration of water extracted by BEHHA at a_w=0.150, 0.355, 0.678, and 1.000 as a function of total BEHHA concentration in the organic phase; the solid and dotted line were calculated by taking account of both BEHHA·H$_2$O and (BEHHA)$_2$(H$_2$O)$_2$ and by assuming only BEHHA·H$_2$O, respectively.

From the results shown in Fig. 1, since in all cases $[\mathrm{H_2O}]_{\mathrm{o,E}} \ll [\mathrm{BEHHA}]_{\mathrm{o,t}}$, roughly $[\mathrm{BEHHA}]_{\mathrm{o,t}} \approx [\mathrm{BEHHA\ (ah)}]_\mathrm{o}$; for a precise calculation, of course, such a rough approximation was not made. Accordingly, an approximate equation can be written from Eqs. 3 and 4, as follows:

$$[\mathrm{H_2O}]_{\mathrm{o,E}} \approx \sum_{x=1}(x K_{\mathrm{m},x} a_\mathrm{w}^x)[\mathrm{BEHHA}]_{\mathrm{o,t}} + \sum_{y=1}(y K_{\mathrm{d},y} a_\mathrm{w}^y)[\mathrm{BEHHA}]_{\mathrm{o,t}}^2. \tag{7}$$

If there is no BEHHA dimer in dodecane, the second term in this equation should be lacking. When the BEHHA concentration in the organic phase is low, i. e., ≤ 0.1 mol dm^{-3}, the slope of lines in Fig. 1 is almost one at every a_w. This implies that most BEHHA in the organic phase is monomeric in the low BEHHA concentration range; beware that $[H_2O]_{o,E}$ is in proportion to $[BEHHA]_{o,t}$, even when some differently hydrated BEHHA monomers exist at the same time. The hydration number of the BEHHA monomer can be determined by analyzing the distribution data of water as a function of a_w at low BEHHA concentrations. In the range of $[BEHHA]_{o,t}$ lower than 0.1 mol dm^{-3}, the slope of $\log [H_2O]_{o,E}$ vs. $\log a_w$ plots was almost one. From this, the hydration number of the BEHHA monomer (x) equals one; the values of x and $K_{m,x}$ obtained by the data analysis are shown in Table 1 with their 3σ errors.

When $[BEHHA]_{o,t}$ is higher than 0.1 mol dm^{-3}, the slope of the lines in Fig. 1 increases according to the increase in $[BEHHA]_{o,t}$; the dotted lines in this figure were calculated by assuming only $BEHHA\cdot H_2O$. The deviation of the experimental values from the dotted lines at low a_w is much smaller than that at high a_w. At $a_w=0.150$, for example, the dotted line approximately fits the experimental values; therefore, the value of $K_{m,1}$ ($=K_{m,x}$) remains constant, at least up to $[BEHHA]_{o,t}=1$ mol dm^{-3}. From this, the formation of $BEHHA\cdot H_2O$ occurs stoichiometrically, at least up to this high BEHHA concentration for a low a_w. If the stoichiometry also applies to the case of a_w higher than 0.150, the discrepancies between the experimental and calculated values should be due to the formation of hydrates other than $BEHHA\cdot H_2O$. Perhaps, this is true because, even at $a_w=1$, the amount of water extracted into 1 mol dm^{-3} BEHHA/dodecane is only a little, i. e., $[H_2O]_{o,E}=0.066$ mol dm^{-3} (about 0.15 wt%). Since such a small amount of water hardly affects the physical properties of the medium of the organic phase, the hydration equilibria are not disturbed, and no clusters of free water molecules form in the organic phase consistently, even at the higher water activities; this problem is discussed again later more precisely.

The formation of other monomer hydrates is not suitable for explaining the discrepancies, because the ratio of $BEHHA(H_2O)_{x'}$ ($x' \geq 2$) to $BEHHA\cdot H_2O$ is independent of the BEHHA concentration, as can be seen from the following equation:

$$\frac{[BEHHA(H_2O)_{x'}]_o}{[BEHHA\cdot H_2O]_o} = \frac{K_{m,x'}}{K_{m,1}} a_w^{x'-1}. \tag{8}$$

Thus, only the BEHHA association, such as dimerization, can explain the experimental data in Fig. 1. A BEHHA dimer hydrate, $(BEHHA)_2(H_2O)_y$ ($y \geq 1$), was first taken into account in the data analysis. The distribution data of water at $a_w=0.150$, 0.355, 0.678, and 1.000 as a function of $[BEHHA]_{o,t}$ were analyzed at the same time on the basis of Eqs. 3 and 4. The value of y was obtained as an integer, two, as is shown in Table 1. The calculated lines by introducing the values of y and $K_{d,y}$ in this table agreed very well with the experimental data. From these, only a dimer hydrate, $(BEHHA)_2(H_2O)_2$, was found in the organic phase.

BEHHA–Water Stoichiometry. The water-distribution was also measured as a function of the water activity in the aqueous phase (a_w) at certain BEHHA concentrations, and the equilibrium constants were determined for the respective BEHHA concentrations. The experimental results, where the BEHHA concentration is increased up to 2.5 mol dm^{-3} (90 vol% BEHHA in dodecane), are shown in Fig. 2. When the BEHHA concentration in dodecane is constant and the extracted water concentration is sufficiently low, the organic phase can be regarded as being the sole medium of a BEHHA–dodecane mixture. In such a uniform medium, stoichiometric equilibrium constants for BEHHA hydrates can be determined. Therefore, the constants apparently obtained for individual BEHHA concentrations can be compared with each other. The result was that they were independent of the BEHHA concentration, as can be seen in Table 2.

Anhydrous BEHHA Dimer. The formation of an anhydrous BEHHA dimer can also be estimated on the basis of the water-distribution data. However, if the anhydrous dimer is formed in only a small amount, the formation constant cannot be accurately determined, because the water-distribution data does not sensitively reflect the anhydrous-dimer formation; the term of an anhydrous dimer is not included in the water mass-balance equation, but is included only in the extractant mass-balance equation.

The mass-balance equations, which take into account the anhydrous dimer, can be written as:

$$\begin{aligned}[BEHHA]_{o,t} &= [BEHHA(ah)]_o + [BEHHA\cdot H_2O]_o + 2[(BEHHA)_2]_o \\ &\quad +2[(BEHHA)_2(H_2O)_2]_o \\ &= (1 + K_{m,1}a_w)[BEHHA(ah)]_o \\ &\quad +2(K_{d,0} + K_{d,2}a_w{}^2)[BEHHA(ah)]_o{}^2,\end{aligned} \tag{9}$$

Table 1. Hydration and Association Constants of BEHHA in Dodecane with 3σ Errors Obtained by a Simultaneous Analysis of the Data in Fig. 1 in Comparion with Those of TBP

Extractant	Hydration number	Complex	Equilibrium constant
BEHHA	x=1.02 (±0.04)	$BEHHA\cdot H_2O$	$K_{m,1}$=0.052 (±0.005)
	y=2.01 (±0.12)	$(BEHHA)_2(H_2O)_2$	$K_{d,2}$=0.010 (±0.001)
TBP[a]	x=1.02 (±0.06)	$TBP\cdot H_2O$	$K_{m,1}$=0.11 (±0.01)
	y=2.04 (±0.16)	$(TBP)_2(H_2O)_2$	$K_{d,2}$=0.22 (±0.03)
	z=6.02 (±0.88)	$(TBP)_3(H_2O)_6$	$K_{t,6}$=0.037 (±0.007)

a) Refs. 4 and 5.

Table 2. Dependence of Equilibrium Constants on BEHHA Concentration

$[\mathrm{BEHHA}]_{\mathrm{o,t}}/\mathrm{mol\ dm^{-3}}$	K_{fw}	$K_{\mathrm{m,1}}$	$K_{\mathrm{d,2}}$
0.03	0.0027 (±0.0001)	0.051 (±0.005)	—
0.05	0.0027 (±0.0001)	0.052 (±0.004)	—
0.07	0.0027 (±0.0002)	0.052 (±0.004)	—
0.1	0.0027 (±0.0002)	0.052 (±0.004)	—
0.2	0.0027 (±0.0004)	0.050 (±0.004)	—
0.5	0.0028 (±0.0009)	0.051 (±0.005)	0.010 (±0.004)
0.7	0.0029 (±0.0011)	0.053 (±0.005)	0.011 (±0.003)
1.0	0.0028 (±0.0019)	0.050 (±0.005)	0.010 (±0.001)
1.5	—	0.051 (±0.005)	0.010 (±0.001)
2.0	—	0.052 (±0.004)	0.009 (±0.001)
2.5	—	0.052 (±0.005)	0.011 (±0.001)

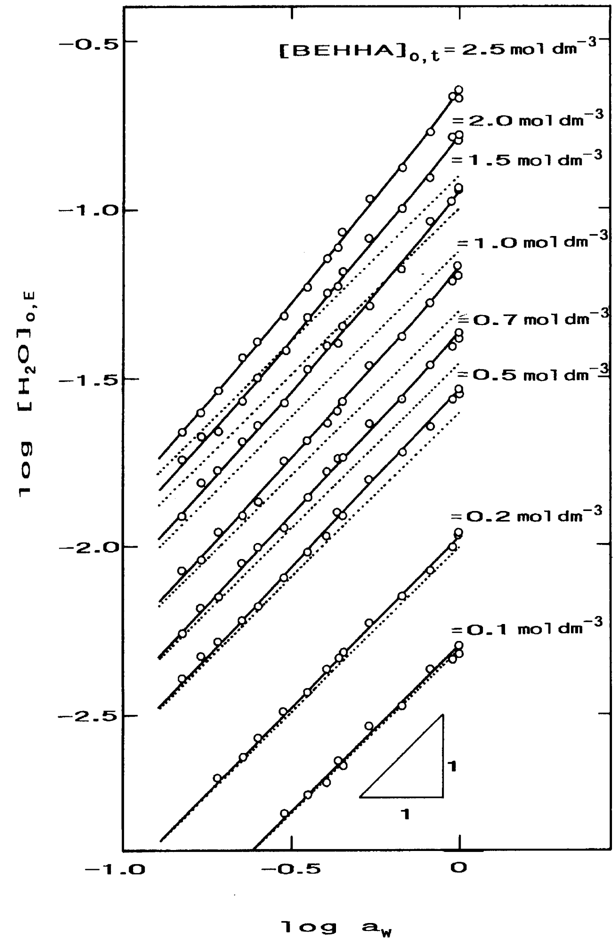

Fig. 2. The concentration of water extracted by BEHHA at $[\mathrm{BEHHA}]_{\mathrm{o,t}}=0.1$, 0.2, 0.5, 0.7, 1.0, 1.5, 2.0, and 2.5 mol dm^{-3} as a function of a_{w}; the solid and dotted line were calculated by taking account of both BEHHA·H_2O and $(\mathrm{BEHHA})_2(\mathrm{H_2O})_2$ and by assuming only BEHHA·H_2O, respectively.

$$[\mathrm{H_2O}]_{\mathrm{o,t}}=[\mathrm{H_2O(free)}]_{\mathrm{o}}+[\mathrm{BEHHA{\cdot}H_2O}]_{\mathrm{o}}+2[(\mathrm{BEHHA})_2(\mathrm{H_2O})_2]_{\mathrm{o}}$$
$$=K_{\mathrm{fw}}a_{\mathrm{w}}+K_{\mathrm{m,1}}a_{\mathrm{w}}[\mathrm{BEHHA(ah)}]_{\mathrm{o}}+2K_{\mathrm{d,2}}a_{\mathrm{w}}^2[\mathrm{BEHHA(ah)}]_{\mathrm{o}}^2. \tag{10}$$

By a data analysis on the basis of these equations, the value of $K_{\mathrm{d,0}}$ was not obtained accurately, while the values of $K_{\mathrm{m,1}}$ and $K_{\mathrm{d,2}}$ were obtained to be nearly equal to those obtained in the analysis without assuming an anhydrous dimer; after all, $K_{\mathrm{d,0}}<0.005$ was found. Thus, the ratio of the anhydrous dimer to the anhydrous monomer concentration was, at most, only 3%, even when the BEHHA concentration was 2.5 mol dm^{-3} (90 vol%) in dodecane.

Free Water in Organic Phase. The distribution constant of free water (K_{fw}) was found to be constant, at least up to 1 mol dm^{-3} (36 vol%) BEHHA in dodecane, as can be seen from Table 2; in a BEHHA concentration range higher than 1 mol dm^{-3}, the free water was concealed in the water extracted as the BEHHA hydrates. The concentration of free water is generally believed to be changeable along with a change in the physical properties of the medium. However, this was not the case in the present study, in which the value of K_{fw} was kept constant up to 1 mol dm^{-3} BEHHA. In fact, the dielectric constant, which could be the most influential physical property on water solubility, should change very much by the addition of BEHHA to dodecane; however, this is not a definitive factor for water solubility. For instance, 1,4-dioxane, whose dielectric constant is 2.2 at 25 °C, makes any mixtures with water unlimitedly, while nitrobenzene, whose dielectric constant is 34.8 at 25 °C, is immiscible with water. Thus, although the water solubility seems to be rather independent of the physical properties of the solvent, it is dependent on the water–solvent interaction. The solubility of water in alkanes, in which only the van der Waals force works between water and the solvent, is not very much changed by a change in the carbon number; e.g., 0.0041 mol dm^{-3} (Ref. 12) in hexane and 0.0027 mol dm^{-3} (Refs. 4 and 5) in dodecane. The free water, regarded as being practically independent of BEHHA, has no interactions with BEHHA, except for the van der Waals force. Thus, the amount of such free water in BEHHA as a solvent may roughly correspond to the water solubility in an alkane, which equals BEHHA in molecular weight; this is not very much different from the water solubility in dodecane. The results of K_{fw} (shown in Table 2) can be explained by the above.

Reliability for Hydration Number of BEHHA Dimer. The reliability of the hydration number of the BEHHA dimer and the equilibrium constant was thoroughly examined in the present study. Calculation curves with the variation in the hydration number at $[\mathrm{BEHHA}]_{\mathrm{o,t}}=2.5$ mol dm^{-3} are shown in Fig. 3a. The experimental points are also given together with the calculated lines in this figure. The dotted, solid, and chain line in Fig. 3a were calculated by using y=1.5, 2.0, and 2.5 (varied) and $K_{d,y}$=0.01 (fixed). In Fig. 3b, the calculated lines by using y=2 (fixed) and $K_{d,y}$=0.005, 0.010, and 0.015 (varied) are given. From these figures, it is concluded that no set of values other than that shown in Table 1 can explain the data; thus, the hydration number of the BEHHA dimer and its

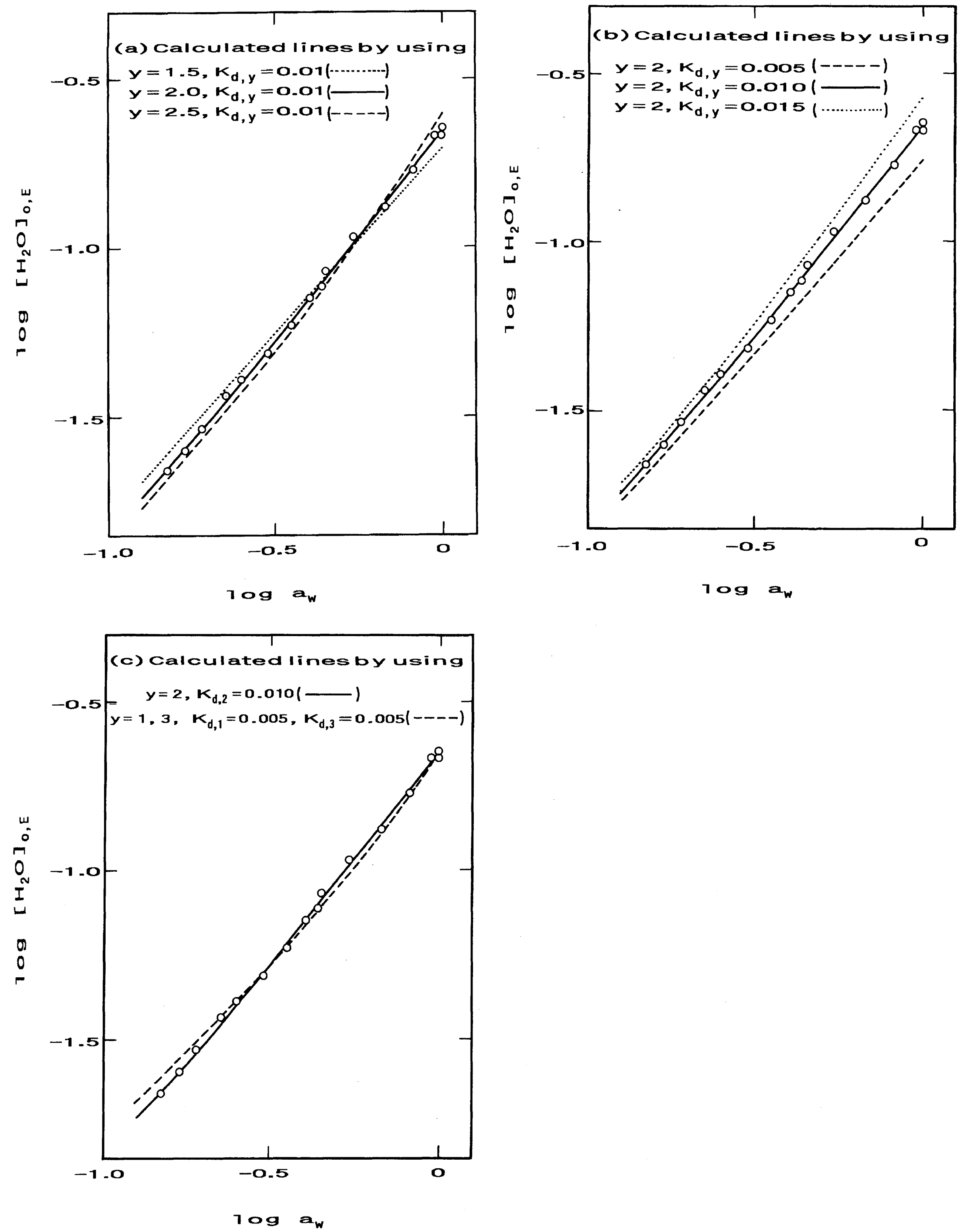

Fig. 3. Calculated values of $[H_2O]_{o,E}$ at $[BEHHA]_{o,t}=2.5$ mol dm^{-3} as a function of a_w: (a) variation of hydration number for BEHHA dimer (=y) at a fixed $K_{d,y}$, (b) variation of $K_{d,y}$ at a fixed y, (c) comparison between mono- and tri-hydrate mixture and a sole dihydrate. $K_{m,1}$ (=0.052) was introduced as an already-known value in these calculations.

formation constant can be precisely determined by the analysis. However, there is another possible explanation for the hydration number. If the BEHHA dimer is a mixture of some hydrates, the hydration number (two) is only apparent. For example, mono- and tri-hydrate mixtures could apparently give good fittings to the experimental curve. This possibility was checked, and denied, by the calculations shown in Fig. 3c. The best calculation curve, assuming mono- and tri-hydrate (chain line), gives a worse fitting than that assuming only a di-hydrate (solid line), as shown in Fig. 3c. The circle key in these figures indicates the experimental points and their average errors; this is a 5% (± 2.5%) error-circle, which corresponds to the experimental errors of the Karl–Fischer titration derived from its reproducibility.

Equilibria in Organic Phase. The hydration of BEHHA to form its monohydrate can be also written as the equilibrium in the organic phase:

$$K^{\mathrm{org}}_{\mathrm{m},x} = \frac{[\mathrm{BEHHA{\cdot}H_2O}]_\mathrm{o}}{[\mathrm{BEHHA(ah)}]_\mathrm{o}[\mathrm{H_2O(free)}]_\mathrm{o}} = \frac{K_{\mathrm{m},1}}{K_{\mathrm{fw}}} = 19.3. \qquad (11)$$

The formation of $(\mathrm{BEHHA})_2(\mathrm{H_2O})_2$ can be regarded as being a dimerization of the BEHHA monohydrate in the organic phase:

$$K^{\mathrm{org}}_{\mathrm{dim}} = \frac{[(\mathrm{BEHHA})_2(\mathrm{H_2O})_2]_\mathrm{o}}{[\mathrm{BEHHA{\cdot}H_2O}]^2_\mathrm{o}} = \frac{K_{\mathrm{d},2}}{K^2_{\mathrm{m},1}} = 3.70. \qquad (12)$$

The dimerization of anhydrous BEHHA is also an equilibrium in the organic phase:

$$K^{\mathrm{org}}_{\mathrm{d},0}(= K_{\mathrm{d},0}) = \frac{[(\mathrm{BEHHA})_2]_\mathrm{o}}{[\mathrm{BEHHA(ah)}]^2_\mathrm{o}} < 0.005. \qquad (13)$$

If solute–solvent interactions are negligible against solute–solute interactions, the values of $K^{\mathrm{org}}_{\mathrm{m},x}$, $K^{\mathrm{org}}_{\mathrm{d},0}$, and $K^{\mathrm{org}}_{\mathrm{dim}}$ reflect extractant–water, extractant–extractant, and monohydrate–monohydrate interactions, respectively; in fact, since dodecane is one of the most inert solvents, the solute–solvent interactions should be quite negligible. Since the value of $K^{\mathrm{org}}_{\mathrm{d},0}$ (<0.005) is much smaller than $K^{\mathrm{org}}_{\mathrm{m},x}$ (=19.3) and $K^{\mathrm{org}}_{\mathrm{dim}}$ (=3.70), the extractant–extractant interaction is much weaker than the extractant–water and monohydrate–monohydrate interactions.

Activity Coefficient of Extractant. The activity coefficient of the extractant in the organic phase is known to change from unity at a high concentration range. However, without any consideration for the correction in the activity, a set of hydration and dimerization constants (Table 1) can interpret all of the experimental data very well, consistently, up to $[\mathrm{BEHHA}]_{\mathrm{o,t}}=2.5$ mol dm^{-3} (90 vol% BEHHA in dodecane). It thus appears that the change in the physical properties of the organic phase, such as the dielectric constant, viscosity, etc, by adding BEHHA to dodecane, does not alter the stoichiometry of BEHHA hydration. Similarly, in the TBP–dodecane–water system previously studied in our laboratory,[4,5] the equilibrium constants for TBP hydration did not depend on the extractant concentration in the organic phase either, at least up to 1.5 mol dm^{-3} (40 vol% TBP).

In general, a solvent extraction system for practical use in nuclear fuel reprocessing is always highly concentrated with the extractant; thus, a stoichiometric approach has been believed to be unavailable to such a highly concentrated system because of the lack of a theory for correcting the activities in the organic phase. These studies in our laboratory give an important direction for the treatment of the activity in organic solutions containing an extractant at high concentrations. That is to say, the equilibrium constants for hydration and dimerization of the extractant can be applied, consistently, from low to very high concentrations of the extractant without any correction in activity so long as an inert organic solvent is used as the diluent. The change in the activity coefficient for an extractant in an inert solvent, as a deviation from ideality, should be due to the hydration and association of the extractant in the organic phase, and not due to the medium property nor a solution structure change; the activity of the extractant experimentally obtained includes in itself such chemical interactions as solvation and dimerization of extractant.[13] In an inert solvent, such as an alkane, the extractant–solvent interaction is quite negligible compared to the extractant–water interaction. Furthermore, for BEHHA and TBP systems, the extractant–extractant interaction

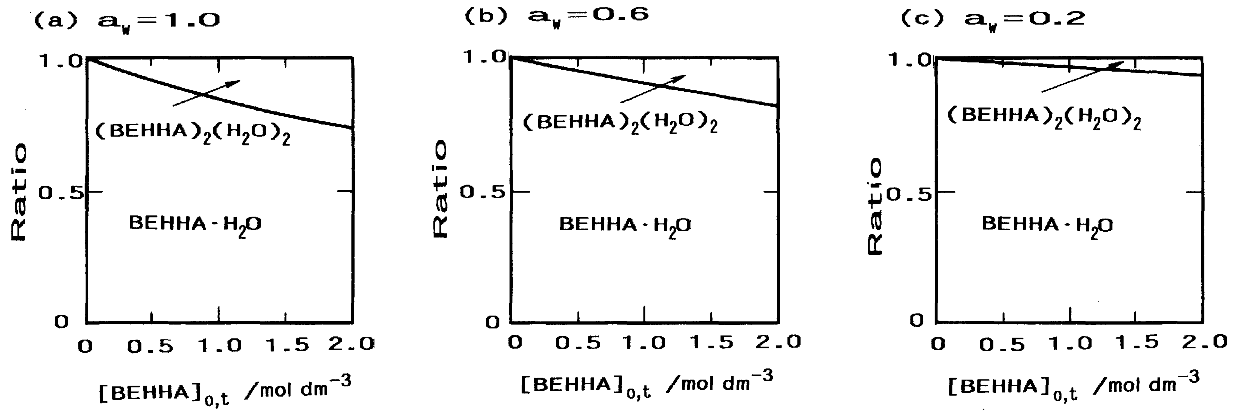

Fig. 4. Calculated ratios of BEHHA hydrates in dodecane at (a) a_w=1.0, (b) a_w=0.6, and (c) a_w=0.2 as a function of $[\mathrm{BEHHA}]_{\mathrm{o,t}}$.

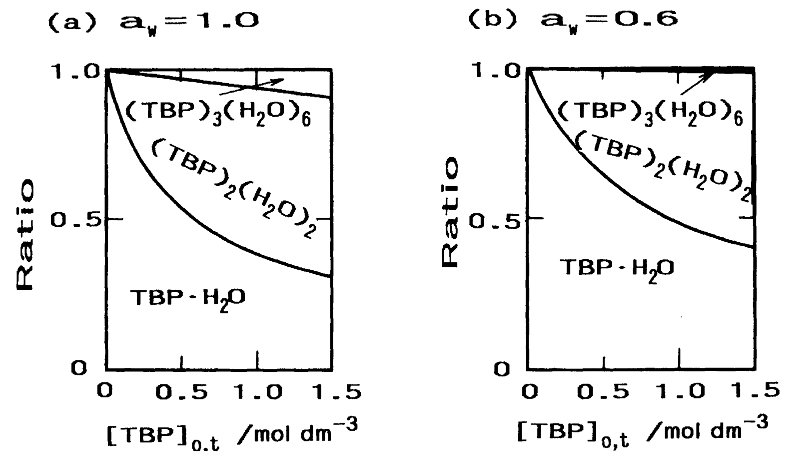

Fig. 5. Calculated ratios of TBP hydrates in dodecane at (a) $a_w = 1.0$ and (b) $a_w = 0.6$ as a function of $[TBP]_{o,t}$.

Table 3. Comparison of Dimerization Constant of $E\cdot H_2O$ between BEHHA and TBP

Extractant (E)	Dimerization constant(K_{dim}^{org})
BEHHA	3.70
TBP	18.2

is also quite negligible against the extractant–water interaction; in fact, no anhydrous dimer of BEHHA and of TBP[5] were found practically in the organic phase. These are the reasons why such a stoichiometric treatment can be extended to organic solutions highly concentrated with an extractant.

Comparison with TBP. *N*, *N*-Bis(2-ethylhexyl)hexanamide (BEHHA) as well as TBP forms a monomer monohydrate and a dimer dihydrate. From this, the hydration mechanism of BEHHA seems to be the same as that of TBP, i.e., the monomer monohydrate is first formed, and then dimerizes to form a dimer dihydrate:

$$E_{(o)} + H_2O \rightleftharpoons E\cdot H_2O_{(o)},$$
$$2E\cdot H_2O_{(o)} \rightleftharpoons (E\cdot H_2O)_{2(o)},$$

where E is an extractant. As can be seen from Table 1, the hydration constants of BEHHA are smaller than those of TBP; thus, BEHHA is concluded to be hydrated less than TBP. A remarkable difference between BEHHA and TBP is a successive hydration forming a highly hydrated trimer, such as $(TBP)_3(H_2O)_6$; BEHHA did not form higher associates than a dimer. This may have been because the dimerization constant (K_{dim}^{org}) for BEHHA is too small to cause such a successive hydration; a highly hydrated trimer is formed through the dimer.[5] The values of K_{dim}^{org} for BEHHA and TBP are compared in Table 3. Figure 4 gives the ratios of BEHHA hydrates in dodecane as a function of $[BEHHA]_{o,t}$ at $a_w = 1.0$, 0.6, and 0.2, which were calculated using the equilibrium constants listed in Table 1. Figure 5 also gives the calculated ratios of the TBP hydrates at $a_w = 1.0$ and 0.6 using the values in Table 1. These figures clearly indicate the difference between BEHHA and TBP; that is, since the ratio of the dimer to the monomer for BEHHA is always much smaller than that for TBP, there is no trimer for BEHHA. Possibly, the long alkyl chains of BEHHA may sterically hinder the monomeric monohydrate from forming its dimer and trimer.

The authors wish to thank Professor Tatsuya Sekine from Science University of Tokyo for his helpful contribution.

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