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Phase Behavior of Tetrabutylammonium Salt in Aromatic Hydrocarbons or Aqueous Solutions

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The solubility of tetrabutylammonium salt (TBAX; X = Cl, Br, or I) in benzene was examined as a function of temperature. The solubility curve had specific features, which were characterized by critical values corresponding to the Krafft point and the critical micelle concentration of ionic surfactants in water. Above the critical concentration, TBAX was assumed to aggregate in benzene, based on NMR analyses. A slight difference of the oil structure exerted a significant effect on the solubility behavior. In the presence of sodium halides, TBACl or TBABr with water exhibited a specific temperature that was similar to the cloud point. Above that temperature, TBAX was liberated as a liquid to form a liquid–liquid two-phase. The solubility of TBAI in water was poor. It gave a liquid–solid two-phase at low temperatures or a liquid–liquid two-phase above 69 °C, unless the TBAI concentration was too low. The solubility of TBAX in aqueous solution was also dependent on the metal cation of the inorganic salts.

Since the introduction of phase-transfer catalysis (PTC) for organic synthesis by Makosza, Brandstrom, and Starks in the 1960's, numerous papers have been published.[1—5] Tetrabutylammonium salt (TBAX; X = Cl, Br, or I) is one of the most popular catalysts used for various PTC reactions under liquid–liquid two-phase conditions. Earlier studies on the PTC mechanism adopted Starks's ion-pair extraction model[6—8] in which the reacting species is supposed to be a molecularly-isolated ion pair that is extracted into the organic layer under liquid–liquid two phase conditions. However, many recent studies have pointed out the necessity of modifying the reaction model. Some effective catalysts reside only in the organic layer and do not distribute into the aqueous layer.[9] Some reaction systems form a so-called "third liquid phase", depending on the solvent and the salt concentration.[10—15] Similar catalytic reactions also proceed smoothly in normal micelle and O/W microemulsion uniphase systems.[16—21] Surface-active single- or double-chained onium salts effectively catalyze simple nucleophilic substitutions without emulsification when water-insoluble alcohols are used as organic solvents.[22]

At an early stage of our studies on the mechanism of polymer-supported phase-transfer catalysis, one of the authors suggested the aggregation of quaternary salts forming inverted micelles in a polymer matrix. This is based on a quantitative analysis of an organic solvent and water that are imbibed by the catalyst polymer under the reaction conditions.[23,24] We have recently extended this inverted micelle model and have given a new interpretation, which lays stress on the intra-resin microstructure in the presence of oil and an aqueous solution. This model supposes that the reaction takes place at micro-interfaces within the catalyst polymer particles.[25]

All of these experimental results imply that one particular equilibrium state should not be premised when a given quaternary salt is mixed with an aqueous solution and a water-immiscible organic solvent. The type of macroscopic phase separation and the microscopic state of quaternary salts in each phase may depend on the combination of components, their compositions, and other factors, such as temperature. Before elucidating the rate process of a phase-transfer catalysis on the molecular basis, it is necessary to clarify the macroscopic phase behavior of the system and the microstructure formed by the catalysts residing in each layer.

The system of a phase-transfer catalytic substitution reaction usually consists of as many as seven components: organic substrate, inorganic reagent, quaternary salt as a catalyst, oil as a solvent, water, and the corresponding two products from the organic substrate and the inorganic reagent. Among them, quaternary salt, oil, water, and inorganic salt are the main components that determine the phase equilibrium. It is very surprising that there have been only a few reports about the phase behavior of TBAX,[26—28] while there have been a number of studies on PTC reactions using TBAX. In this work, we examined the phase behavior of TBAX in aromatic oils or TBAX/water/NaX (X = Cl, Br, or I) systems before elucidating the phase behavior of TBAX/benzene/water/NaX four-component systems.

We will show that specific features of the phase behavior are observable in these systems, and that the solubility behavior resembles those of surfactant systems.

Experimental

Materials and Equipments. Decyl methanesulfonate was prepared by the reaction of methanesulfonyl chloride with 1-decanol in pyridine.[29] Tetrabutylammonium chloride (TBACl), tetrabutylammonium bromide (TBABr), and tetrabutylammonium iodide (TBAI) were purchased from Tokyo-kasei and were used without further purification. Benzene and other aromatic hydrocarbons were purified by distillation from sodium diphenylketyl under nitrogen. Deionized water was used throughout the experiments. ^{1}H NMR spectra were recorded on a Varian Mercury 300 spectrometer. GLC analyses were performed using a Hitachi 163 FID instrument with a 1 m column of SE-30 or PEG-20M.

Phase-Equilibrium. The solubility of TBAX in oil was measured in the following way. Given amounts of a quaternary salt (TBAX) and an aromatic oil were added to a 10 mL Teflon®-coated screw-capped test tube with an inside diameter of 10.5 mm. After the tube was transferred to a temperature-variable water bath, the mixture was stirred with magnetic stirring. The temperature was raised at a rate of 1 °C min^{-1}. The temperature was read when all of the TBAX crystalline solid or TBAX-rich liquid disappeared. The solubility of TBAX in an aqueous NaX solution was measured in the following way. Prescribed amounts of a quaternary salt and an aqueous solution of a given concentration of NaX were added to a 10 mL Teflon®-coated screw-capped test tube. The cloud point of quaternary salts in the aqueous NaX solution was defined as the temperature that the solution became turbid when the temperature was raised at a rate of 1 °C min^{-1}. If a system contained a solid phase, a mixture with a pertinent composition was prepared separately. The precipitated solid was separated by filtration and analyzed by ^{1}H NMR. Another solubility measurement for the TBAX/water/NaX system was carried out. 0.25 mmol of TBAX was dissolved in 1.0 mL of water. To this solution, a given amount of NaX was added. The cloud point as well as the temperature at which a solid phase disappeared was measured in a similar manner as mentioned above.

Results and Discussion

Solubility and Microstructure of TBAX in Benzene. The solubility of TBAX in benzene is shown in Fig. 1 as a function of the temperature. Among TBACl, TBABr, and TBAI, TBABr is the most soluble in benzene; TBAI is the lowest. The order is not always coincident with that of their extractability from water into an oil that has often been quoted: TBAI > TBABr > TBACl.[3] At low temperatures, solid quaternary salt (Q) coexists with the benzene-rich oil phase (O). The concentration of TBAX in the O phase is very low. The weight fraction of TBABr in an O phase is as low as 0.003—0.004. An increase in the solubility is very gradual, even if the temperature is elevated. Within a very limited range of temperatures, however, the amount of the solid quaternary salt is sharply decreased as if the quaternary salt melts at the temperatures. The solubility suddenly increased and TBAX was soluble freely in benzene up to a considerably high concentration above the temperature. We define the resulting uniphase as an Om phase. When the weight fraction of TBACl or TBABr was beyond 0.2, the solubility temperature again gradually increased.

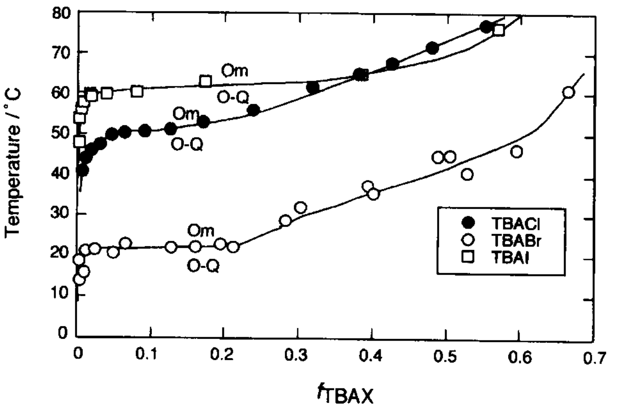

Fig. 1. Solubility of TBAX in benzene. Weight fraction of TBAX is represented as f_{TBAX}.

This type of solubility curve resembles those observed for a number of ionic surfactants in water.[30] In the same way, it seems possible to define a critical solubility temperature (T_c) and a critical solubility concentration (*csc*), which may correspond to the Krafft point and cmc, respectively. It is said that surfactants are able to dissolve as an aggregate above the Krafft point, and that their solubility increases sharply at a temperature a few degrees higher than the Krafft point. At temperatures higher than the Krafft point, surfactants form a micelle if the concentration is higher than cmc, but are present as a molecular solution below cmc. For TBAX/benzene systems, therefore, an O phase and solid quaternary salt (Q) may coexist below T_c if the content of TBAX is larger than its *csc*. The critical concentration should correspond to the maximum weight fraction of TBAX in the O phase. We estimate the T_c and *csc* of TBABr in benzene to be around 20.5 °C and 0.003 (in weight fraction), respectively. A liquid phase of Om appears when the temperature and TBAX concentration are both higher than T_c and *csc*. Above T_c, the solid quaternary salt may coexist with the Om phase only if the TBAX content is extremely high. The Om phase may be distinguishable from the liquid phase (O) because the quaternary salt forms some aggregates in the Om phase. The aggregate may be something like a reverse type instead of a normal micelle formed by surfactants in water above the cmc. It seems reasonable to consider TBABr being aggregated, since tetrabutylammonium salts are, though weak, surface-active.[31] However, a gradual increase in the solubility temperature above *csc* suggests a progressive increase in the aggregation number with the TBAX concentration. Because it is said that the Krafft point represents a melting point of a hydrated surfactant,[30] it may be assumed that the T_c of TBAX in benzene is the melting point of TBAX solvated by benzene. Therefore, the dissolution of TBAX into benzene may be assumed to be a liquid–liquid mutual mixing rather than a solid–liquid mixing.

The change in the nature of TBABr in the vicinity of the critical concentration was distinctly observable in the ^{1}H NMR spectra. As shown in Fig. 2, the chemical-shift difference ($\Delta\delta$) between two peaks corresponding to methyl protons and α-methylene protons of TBABr in benzene-d_6 tended to sharply increase above a certain weight fraction of TBABr at a given temperature. This clearly shows the existing state of TBABr changes depending on its concentration. It was possible to obtain a *csc* from plots of $\Delta\delta$ vs the reciprocal of TBABr concentration (c), supposing that the following equation stands:[32]

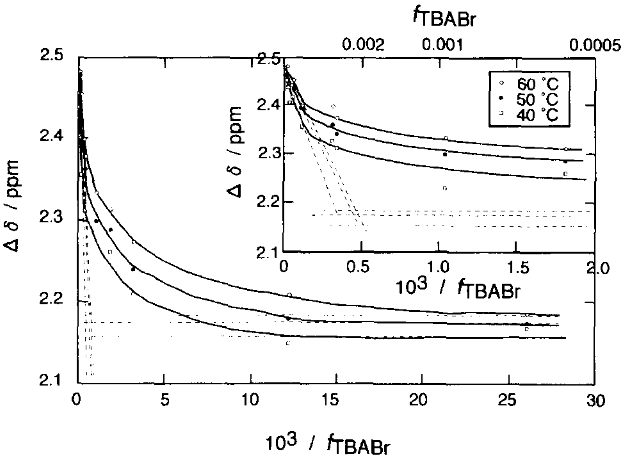

Fig. 2. Influence of TBABr concentration on the chemical shift difference between methyl and α-methylene peaks of TBABr in benzene-d_6. Weight fraction of TBABr is represented as f_{TBABr}. Dashed lines indicate the set of two straight lines that the equation in the text predicts if the aggregation number is constant. The part of the Figure at high TBABr concentrations was magnified and shown at the right-top corner.

$$\Delta\delta = \{(c - csc)/c\}\Delta\delta_{\mathrm{M}} + (csc/c)\Delta\delta_1, \qquad (1)$$

where $\Delta\delta_{\mathrm{M}}$ and $\Delta\delta_1$ represent the chemical-shift differences of an aggregate and a monomer, respectively. The equation presumes a definite number of aggregation. A rather curved line instead of two straight lines indicates that there is a distribution in the aggregation number and/or a dependence of the aggregation number on the TBABr concentration.[32,33] However, the *csc* that was obtained by intersecting two approximated straight lines was around 0.003 in weight fraction. If the *csc* is plotted against temperature, it merged near to the bending point of the solubility curve of TBABr in benzene (Fig. 1).

In Fig. 3, the solubility of TBAX in toluene is shown. Although toluene is often used as a substitute for benzene, owing to the resemblance of their properties as a solvent, the solubility of TBAX is greatly different. A similar solubility curve was observed only for TBACl. TBACl melted at around 63 °C in toluene and gave a homogeneous Om phase, irrespective of TBACl concentration. TBABr and TBAI melted at 54 °C and 83.5 °C, respectively. The melt was miscible with toluene to form an O phase when the concentration of TBABr or TBAI was very low. However, the melt was not miscible unlimitedly with toluene at that temperature. A liquid–liquid two-phase system (O–Om) was formed if the TBAX concentration was within a certain range. Both endpoints of the horizontal tie lines should represent the compositions of the two phases. In fact, the volume of the Om phase was much larger than the volume of added TBAX, indicating that the Om phase contains a large volume of toluene. The system may become an uniphase at considerably high temperatures. If the weight fraction of TBABr was larger than 0.23, a homogeneous Om phase was formed, because the TBABr melt absorbed the whole amount of toluene. This is concrete evidence that the dissolution of TBAX into oil is a liquid–liquid mutual mixing. The fact that TBACl is most soluble in toluene suggests that small counter ions make it easy to form a reverse-type aggregate.

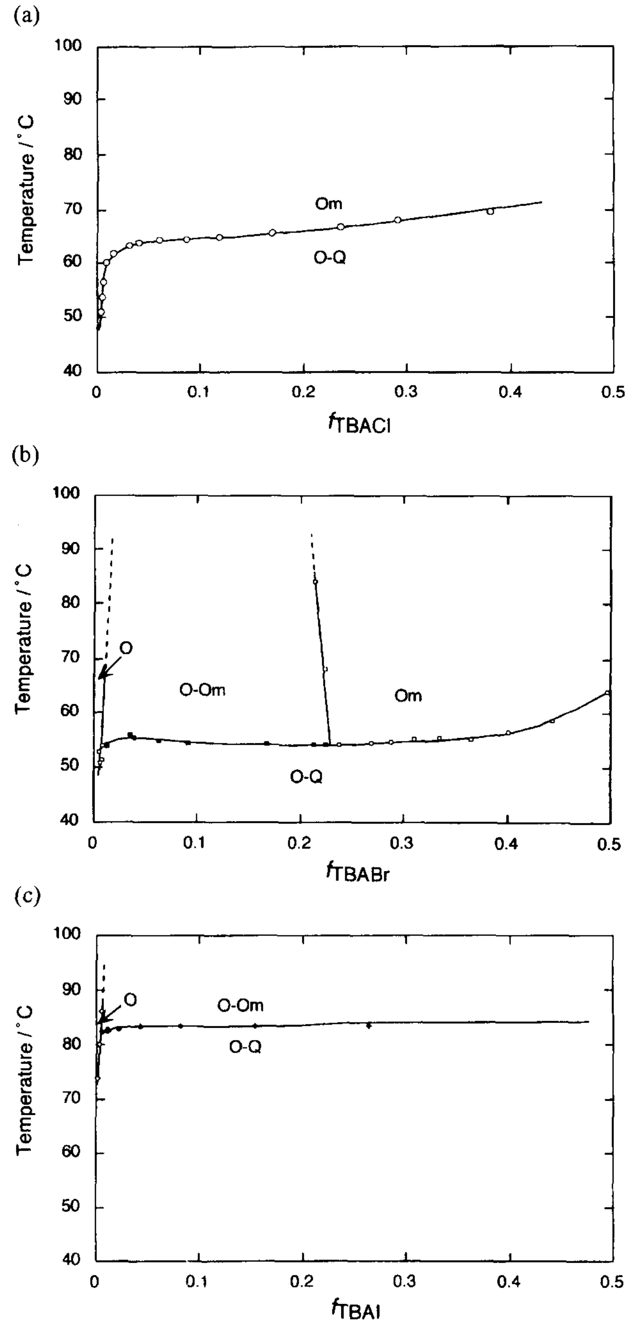

Fig. 3. Solubility of TBAX in toluene. Open keys represent the transition from a liquid–solid two-phase (O–Q) to a liquid phase (Om or O) and closed keys, from O–Q to a liquid–liquid two-phase (O–Om).

In ethylbenzene and *p*-xylene, the solubility behavior of TBABr happened to be very similar and an O–Om two-phase was formed above the melting point of ca. 70 °C. The weight fractions of TBABr in the Om phases were higher than 0.5, as was the case in the TBAI/toluene system. These results together with those in Figs. 1 and 3 indicate that

TBAX is more soluble in oil with a smaller molar volume, and suggest that such a small oil feasibly penetrates into the butyl moiety of TBAX, leading to the formation of a more compact reverse-type aggregate.

As shown in Fig. 4, the presence of a minimal amount of water drastically influenced the solubility behavior of TBABr in benzene. The addition of water may lower the melting point of a quaternary salt. Thus, the transition temperature from O–Q to Om was first lowered by the addition of water. This means that an elevated solubility on water addition is not due to an increase in the saturated concentration of molecularly dispersed quaternary salts in benzene. This is due to a lowering of the critical solubility temperature (or the melting point of TBAX), followed by an enhanced readiness for TBAX to dissolve as aggregated forms in benzene, that is, the formation of water-containing reverse-type aggregates (Om). If the water content is beyond the mutual solubility between benzene and water, we represent the Om phase as a microemulsion (M phase). Along with an increase in the molar ratio of water to quaternary salt (R_w), however, the miscibility of the hydrated melt with benzene decreases, resulting in the appearance of a liquid–liquid two-phase region (O-M). This situation is very similar to the solubility behavior of TBABr/toluene, TBAI/toluene, or TBABr/ethylbenzene (*p*-xylene). It is probable that water more strongly hydrates ionic portions of TBAX. By the analogy that the Krafft point of ionic surfactants is an index of the melting point of the surfactant tails in water, the critical solubility temperatures in our systems may reflect the melting point of the hydrated ionic portions of TBAX.

Solubility and Microstructure of TBAX in NaX Aqueous Solution. TBACl and TBABr were very soluble in water. A homogeneous aqueous solution was obtained irrespective of the TBAX concentration and the temperature. The Krafft point that ionic surfactants often afforded was not observed.

It has been assumed in a number of studies on PTC that the addition of inorganic salts to the aqueous layer induces a preferable partition of quaternary salts into oil. This phenomenon has been referred to as a salting-out effect.[1–4] As shown in Fig. 5, the solubility of TBABr in water was indeed lowered by increasing the NaBr concentration. However, TBABr did not precipitate as a solid crystal, but was liberated as a liquid phase. Contrary to the expectation, the solubility rather decreased at high temperature. This means that TBABr has a cloud point at a given NaBr concentration. When the temperature was raised above its cloud point, the aqueous solution became turbid and another aqueous phase was liberated as a bottom layer, which contained few parts of TBABr. Most of the TBABr remained in the upper layer and formed a more TBABr-rich transparent liquid phase. Further elevation of the temperature led to a decrease in the volume of the upper layer and an increase in the volume of the bottom layer. NaBr preferred to be present in the bottom layer. We represent the upper phase as Wm and the bottom phase as W. The homogeneous aqueous solution just below the cloud point may also be represented as the Wm phase, as long as the liberated W phase has a smaller volume than the Wm phase after phase separation. The Wm phase is different in its microstructure from the W phase because they are immiscible. TBABr is assumed to be present as a certain form of aggregates in the Wm phase. Cloud points are commonly observed for nonionic surfactants in water.[34] It is believed that they also form aggregates at temperatures below their cloud points. A few papers have also showed that the presence of salt lowered the cloud points of ionic surfactants in aqueous solutions.[35]

As shown in Fig. 6, the solubility of TBACl in a NaCl aqueous solution was similar to that of TBABr if the NaCl concentration was lower than 20 wt%. At temperatures lower than 40 °C, however, the addition of TBACl to an 25 wt% NaCl aqueous solution leads to the precipitation of solid NaCl (S phase), rather than the liberation of TBACl, indicating that TBACl is more soluble in water than NaCl at low temperatures. As shown in Fig. 7, the cloud points were lowered with an increasing NaX concentration. From this Fig. 7, it is also clear that NaCl precipitates in preference to the liberation of TBACl at low temperatures. For the TBABr / NaBr aqueous solution system, on the other hand, a Wm-W phase separation always took place upon the incremental addition of NaBr, irrespective of the temperature. We

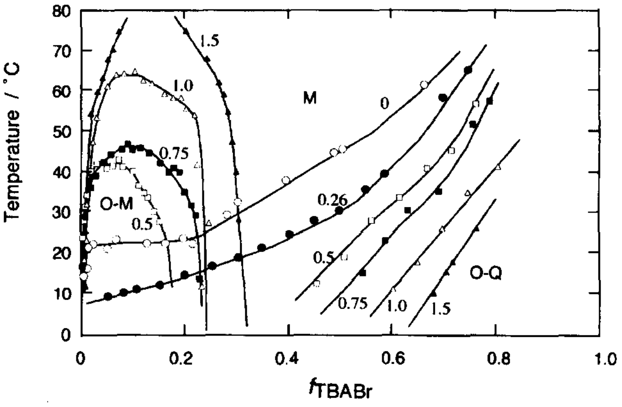

Fig. 4. Effect of water on the solubility of TBABr in benzene. The numbers in the Figure represent the R_w values. The state in equilibrium at R_w of 1.0 was shown in the Figure.

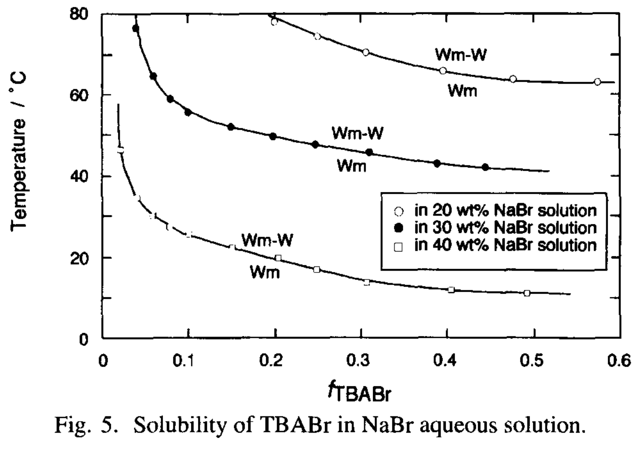

Fig. 5. Solubility of TBABr in NaBr aqueous solution.

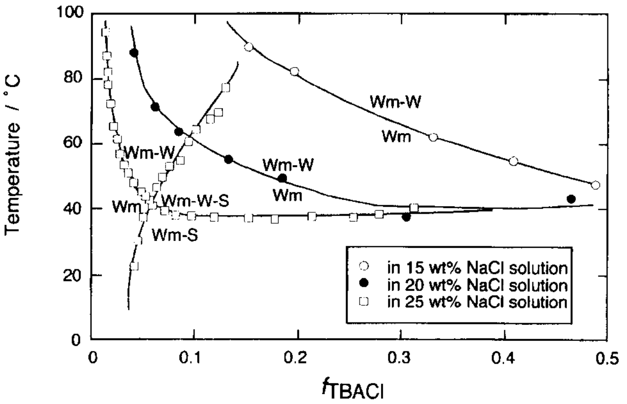

Fig. 6. Solubility of TBACl in NaCl aqueous solution.

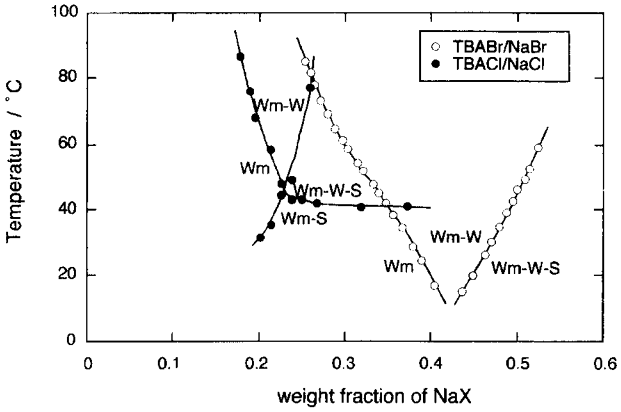

Fig. 7. Effect of added NaX in water on the phase behavior of TBAX/water/NaX systems. NaX was added to the solution of 0.25 mmol of TBAX in 1.0 mL of water.

could not find a liquid–solid Wm–S region, although there was some possibility that the region was present at very low temperatures.

Although the addition of TBABr to a NaBr aqueous solution never induced the precipitation of solid NaBr, irrespective of the NaBr concentration, the use of KBr instead of NaBr led to another solubility behavior. As shown in Fig. 8, the behavior rather resembles that of TBACl in a NaCl solution. When TBABr was added to a 40 wt% KBr aqueous solution at a temperature lower than 33.5 °C, KBr precipitated as a solid (S) before TBABr was liberated. An elevation of temperature to over 33.5 °C induced the separation of the liquid Wm phase into a TBABr-rich liquid phase (Wm) and a TBABr-poor aqueous phase (W). The system was transformed from Wm–S to Wm–W–S at this temperature.

On the other hand, the addition of TBABr to a concentrated LiBr aqueous solution led to the precipitation of TBABr as a solid (Q phase). In other words, LiBr has a real "salting-out" effect to precipitate TBABr from an aqueous solution. As shown in Fig. 9, the solubility behavior of TBABr is normal if the concentration of aqueous LiBr is lower than 40 wt%. The cloud point was observed at temperatures higher than 80 °C. When the LiBr concentration was 45 wt%, however, the maximum solubility of TBABr was ca. 1.0 wt% in the solution, and excess TBABr was present as a solid at 60 °C. If the weight fraction of TBABr was between 0.01 and 0.05, an elevation of the temperature made the system transform into a homogeneous Wm phase, and then a liquid–liquid two-phase (Wm–W). When the weight fraction of TBABr was higher than 0.05, the Q–W solid–liquid state at low temperatures never changed to a liquid uniphase, but directly to a Wm-W two-phase at a constant temperature of 73 °C. The boundary curve, ab, may correspond to the solubility curves of such ionic surfactants that have Krafft points. A further increase in the concentration of aqueous LiBr induced to move the melting point of TBABr, that is, the bc line, upward (to higher temperature) and the ab curve left (to lower weight fraction of TBABr).

In the absence of an inorganic salt, the solubility behavior of TBAI somewhat resembles that of TBABr in a 45 wt% LiBr solution. As shown in Fig. 10, the solubility of TBAI in water is limited, and the excess TBAI is present as a solid precipitate: the mixture of TBAI and water afforded a homogeneous aqueous solution (W) or a liquid–solid two-phase (W–Q) according to the content of TBAI. When the weight fraction of TBAI is below 0.1 or beyond 0.8, a homogeneous solution (W or Wm) is obtained at high temperatures. When the fraction was between 0.1 and 0.8, the temperature of 69 °C was the boundary at which point the system gave a solid–liquid two-phase (Q–W) or a liquid–liquid two-phase (Wm–W). For the latter liquid–liquid state, both endpoints

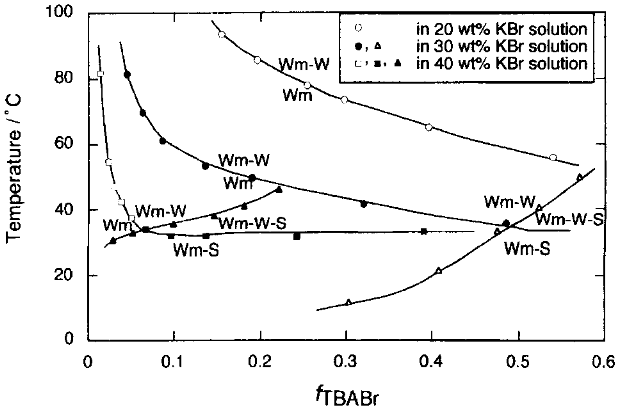

Fig. 8. Solubility of TBABr in KBr aqueous solution.

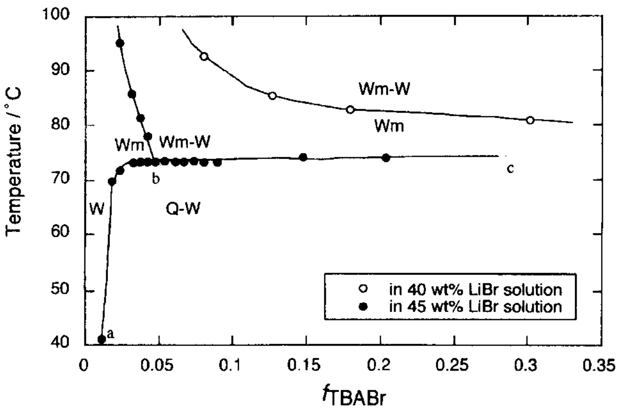

Fig. 9. Solubility of TBABr in LiBr aqueous solution.

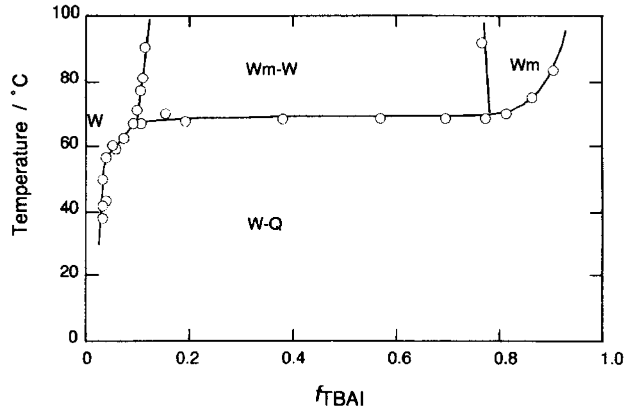

Fig. 10. Phase diagram of TBAI/water system.

of the horizontal tie lines represent the compositions of the two phases. The diagram suggests that TBAI melts at 69 °C under hydrated conditions, and that the dissolution of TBAI into water is also a liquid–liquid mutual mixing rather than a solid–liquid mixing at high temperatures. It is noted that the solubility of TBAI in water rather resembles that of TBABr in toluene in spite of the different type of aggregates to be assumed.

We have suggested the existence of two types of aggregates that are formed by TBAX: Om and Wm. The phase Om (or Wm) is formed when the TBAX concentration is beyond a certain critical value (*csc*), and when water (or benzene) is absent, or only in a minimal quantity in the system. The addition of water to an Om phase or the addition of benzene to a Wm phase always leads to the formation of the M phase, which contains benzene and water beyond the amounts of their mutual miscibility. As TBAX aggregates in the Om and Wm phases, it is reasonably assumed that TBAX also aggregates in the M phase. There are two other homogeneous phases, an O phase and a W phase, in which TBAX is assumed to be present with more or less non-aggregated form. In these phases, TBAX is probably present almost as an isolated ion-pair in the O phase and as a dissociated form in the W phase.

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