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Phase Behavior of Benzyltributylphosphonium Salts in Aromatic Hydrocarbons or Aqueous Solutions

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The solubility of benzyltributylphosphonium salt (BTBPX: X = Cl, Br, or I) in aromatic hydrocarbons was examined as a function of the temperature. The solubility curve had specific features, which were characterized by critical values corresponding to the Krafft point and critical micelle concentration. A slight difference in the oil structure exerted a significant effect on the solubility behavior. The Krafft boundary as well as a liquid–liquid immiscibility gap, on the other hand, featured the solubility behavior of BTBPX in an aqueous solution. The shape of the gap was assumed to be a closed loop and the region of the gap was sharply dependent on the concentration of the added metal halide (MX). The phase behavior of the three- or four-component systems, composed of BTBPX, benzene, water, and MX, has been examined in detail. According to their constituent, composition, and temperature, the system afforded a single- to four-phase state form. There were at least three kinds of liquid phases: a BTBPX-rich phase (M), an aqueous solution phase (W), and an oil solution phase (O). When these three liquid phases coexist, the system affords an O–M–W three-liquid-phase equilibrium state. The three-liquid phase may be converted to O–M or M–W two-liquid-phase, depending on the temperature and MX concentration in the W phase. In the presence of excess MX (S), BTBPCl gave an O–M–W–S four-phase state, while BTBPBr or BTBPI never formed a four-phase state. The phase behavior of the four-component systems is discussed based on phase diagrams of fewer component systems.

Quaternary phosphonium salts have been used as catalysts of phase-transfer catalysis (PTC)[1] or as catalytic moieties of the corresponding polymer-supported phase-transfer catalysis.[2] Benzyltributylphosphonium salts are quaternary salts that have been most often used for being attached to an insoluble polymer matrix in order to prepare immobilized phase-transfer catalysts.[3] The solution behavior and reactivity of the corresponding linear polymers containing the phosphonium salts (cationic ionomers) have shown that the quaternary salts aggregate in nonpolar oils.[4]

Recently, we reported on the phase behavior of tetrabutylammonium salts (TBAX) in oils or in aqueous electrolyte solutions.[5] They afford Krafft boundaries in oils, which are closely dependent on the oil molecular volume and on their counter-ions. The behavior was rather similar to the solubility of common ionic surfactants in water. The quaternary salts afford a lower consolute behavior in aqueous solutions. The behavior was very similar to those of micelle-forming quaternary ammonium surfactants.[6] We also disclosed that, under adequate conditions, TBAX/benzene/water/NaBr four-component systems form microemulsions, with which an oil phase and aqueous phase may coexist, depending on the temperature and constituent composition.[7] This suggests that the conventional PTC mechanism of Stark's ion-pair extraction model is rather applied to limited systems, and that a wider survey of the phase behavior of quaternary salts is necessary to understand the PTC systems. It is also important to clarify whether the findings about TBAX systems can be generally applied to other quaternary onium salt systems.

The recent development of studies on both theoretical and experimental aspects of microemulsions has provided a better understanding of their formation, properties, and phase behavior. However, the understanding has not yet progressed to the point of being able to predict all details of the phase behavior of PTC reaction systems, because the systems not only contain so many components, but also involve relatively symmetric quaternary onium salts. It is important to know the phase behavior of quaternary salts in multi-component systems for elucidating the kinetics and mechanism of PTC as well as the microstructure formed in each layer of PTC systems.

In this article, we examine the phase behavior of benzyltributylphosphonium salts (BTBPX: X = Cl, Br, and I) as a function of the temperature or composition. We show how the parameters, such as temperature, counter-anion, or electrolyte concentration, influence the formation of aggregates or microemulsions. The conditions where the phase containing these aggregates coexists with other phases under the BTBPX/benzene/water/KX four-component systems are given to correlate to the corresponding PTC systems that involve these quaternary salts. The similarity and difference between this system and TBAX system are also described.

Experimental

Materials and Equipments. Decyl methanesulfonate was prepared by the reaction of methanesulfonyl chloride with 1-decanol in pyridine.[8] Benzyltributylphosphonium chloride (BTBPCl) or benzyltributylphosphonium bromide (BTBPBr) was prepared by the reaction of benzyl chloride or benzyl bromide with tributylphosphine in toluene for 72 h at 90 °C under nitrogen. They were recrystallized twice from benzene. Benzyltributylphosphonium iodide (BTBPI) was prepared by the reaction of BTBPCl with iodomethane for 48 h at 40 °C in benzene. The degree of counter-ion substitution was determined by a GLC analysis of 1-iodododecane, which was formed through the reaction of BTBPI with an excess amount of decyl methanesulfonate. 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.

Phase-Equilibrium.[5] The solubility of BTBPX in oil was measured in the following way. Given amounts of a quaternary salt (BTBPX) and an aromatic oil were added to a 10 mL Teflon-coated screw-capped test tube with an inside diameter of 10.5 mm. The tube was transferred to a temperature-variable water bath, and 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 BTBPX crystalline solid or BTBPX-rich liquid disappeared. The cloud points of quaternary salts in aqueous NaX solution were measured in such a way that the temperature was raised at a rate of 1 °C min^{-1} and the temperature of the phase transition was read when the solution became turbid.

Phase Composition.[7] The amounts of BTBPX, benzene, and water in a phase were analyzed by ^{1}H NMR. An aliquot of a BTBPX-rich phase or benzene-rich phase was added to a prescribed amount of methanol-d_4, and the composition of the phase was determined based on the residual proton in the methanol-d_4. The uncertainty of the composition was within ±0.02 in weight fraction.

Results and Discussion

Solubility and Microstructure of BTBPX in Oils. The solubility of BTBPX in oils is shown in Figs. 1a–c as a function of the temperature. The solubility behavior was classified into two types (I or II), depending on BTBPX and oil. The first one (I) is like that of a number of ionic surfactants in water.[9] It was characterized by a critical solubility temperature (Tc) and a critical solubility concentration (csc), which correspond to the Krafft point and the cmc of ionic surfactants, respectively. A typical example is BTBPCl in benzene. At low temperatures, solid quaternary salt (Q) coexists with a quaternary salt-poor oil phase (O). Within a very limited range of temperature, however, the amount of the solid quaternary salt was sharply decreased as if the quaternary salt melts at the temperatures. The solubility suddenly increased and BTBPX was soluble freely in the oil up to a considerably high concentration above the temperature. The system becomes a homogeneous solution (Om) where BTBPX is assumed to form a certain aggregate, although, in an O phase, BTBPX may be present as a monomer or a very small aggregate or a very small aggregate.[5] The second type (II) was the occurrence of liquid–liquid two-phase separation at high temperatures. The example is BTBPBr in ethylbenzene or BTBPI in toluene. BTBPX melts at a certain temperature. In this case, however, the melt was not unlimitedly miscible with oil at the temperature. A liquid–liquid two-phase system (O–Om) was formed unless the BTBPX concentration was extremely high or low. The volume of the Om phase was much larger than that of added BTBPX, indicating that the Om phase contained a large volume of oil. It is noted that the solubility behavior was significantly different among aromatic oils, though they are often used as a substitute for benzene, owing to the resemblance of their properties as a solvent. A similar trend has been observed for TBAX.[5] BTBPX tends to be more soluble in an oil with a smaller molar volume, which suggests that such a small oil feasibly penetrates into the alkyl moiety of BTBPX.

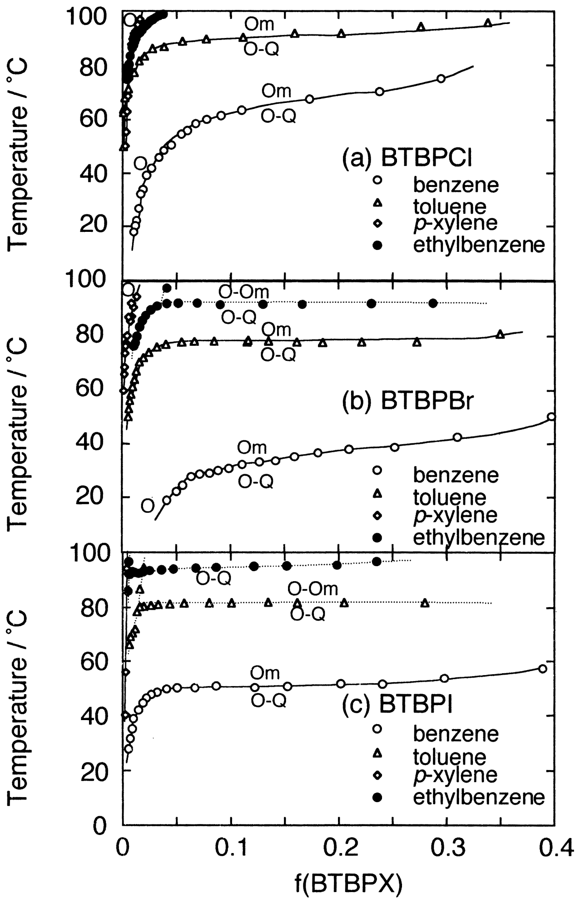


Fig. 1. Solubility behavior of BTBPX in oils. (a) BTBPCl, (b) BTBPBr, and (c) BTBPI. The weight fraction of a component X in a system is represented as f(X) in this study. The full lines show the boundaries between uniphase and liquid–solid two-phase for the systems of Type I. The dotted lines show the phase boundaries for the systems of Type II. The symbol O represents an oil phase that contains few amounts of BTBPX and coexists with other phase(s), the symbol Q, the solid of BTBPX, and the symbol Om, a homogeneous solution of BTBPX in oil.

Solubility of BTBPX in Aqueous Solution. The solubility of BTBPX in water was greatly dependent on its counterion. BTBPCl was very soluble in water. A homogeneous aqueous solution was obtained irrespective of the BTBPCl concentration and temperature. The addition of an electrolyte lowered the solubility of BTBPCl, as shown in Figs. 2a–d. The solubility rather decreased at a high temperature. BTBPCl did not precipitate as a solid crystalline, but was liberated as a liquid phase, except for one case using a 20 wt% LiCl solution. This means that BTBPCl has a cloud point. When the temper-

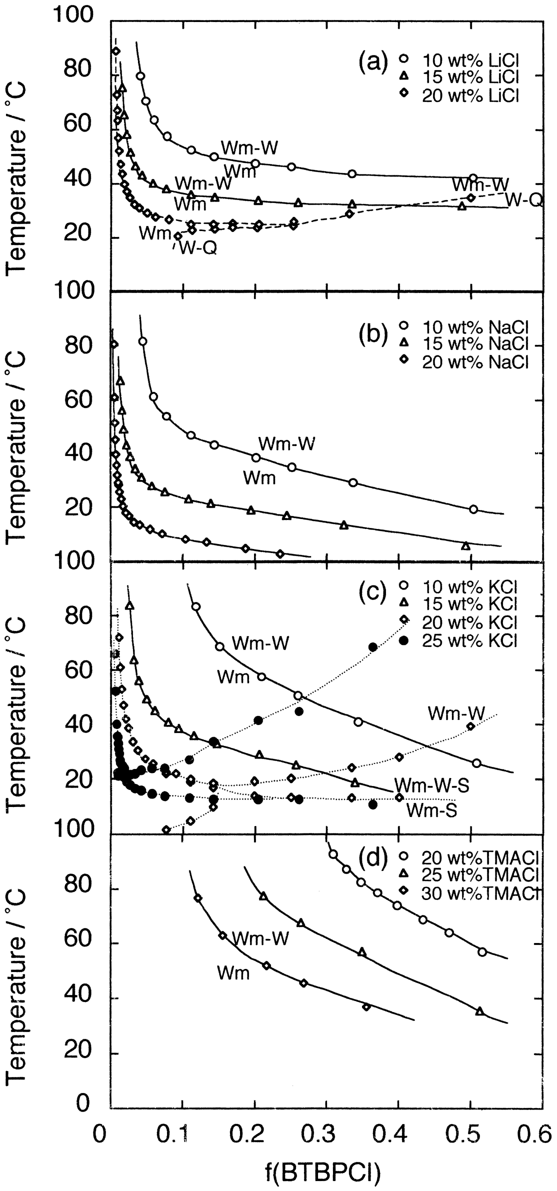


Fig. 2. Solubility behavior BTBPCl in aqueous solutions containing electrolytes. (a) LiCl, (b) NaCl, (c) KCl, and (d) TMACl. The full lines show the boundaries between uniphase (Wm) and liquid–liquid two-phase (Wm–W). The phase boundaries of the system that affords a W–Q liquid–solid three-phase are given by dashed lines. The phase boundaries of the systems that afford liquid–liquid–solid three-phase (Wm–W–S) are given by dotted lines. The symbol W represents an aqueous solution that contains few amounts of BTBPCl and coexists with other phase(s), the symbol Wm, a homogeneous aqueous solution of BTBPCl, the symbol Q, the solid of BTBPX, and the symbol S, the solid of electrolytes.

ature was raised to its cloud point, the aqueous solution suddenly became turbid, and most of the BTBPCl eventually formed a BTBPCl-rich transparent liquid phase (Wm). The lower consolute boundary was lowered with an increasing electrolyte concentration. It is noted that BTBPCl is more soluble in water than KCl. KCl was preferentially precipitated as a solid from the aqueous solution to form a Wm–W–S three-phase.

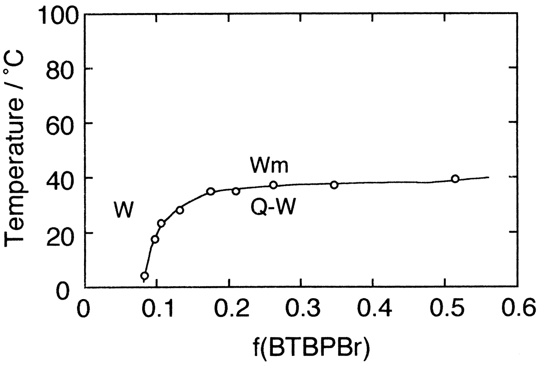


Fig. 3. Solubility behavior of BTBPBr in water. The symbol W represents an aqueous solution that contains few amounts of BTBPBr and coexists with other phase(s), the symbol Wm, a homogeneous aqueous solution of BTBPBr, and the symbol Q, the hydrated solid of BTBPBr.

Like BTBPCl, the solubility behavior of BTBPBr was greatly different from that of TBABr.[5] As shown in Fig. 3, the solubility of BTBPBr in water is limited at low temperatures, and that excess BTBPBr is present as a solid precipitate. Above 40 °C, however, a homogeneous aqueous solution was obtained irrespective of the concentration of BTBPBr. Although the critical solubility concentration was rather high (ca. 0.35 mol dm^{-3}) compared with that of ionic surfactants in water, this solubility behavior was also characterized by the Krafft boundary. Therefore, BTBPBr may be assumed to form an aggregate above the csc.

The addition of a minimal amount of NaBr to this system induced a significant influence on the solubility behavior of BTBPBr (Fig. 4). In addition to the Krafft boundary, one could observe an immisibility gap, that is, a region of liquid–liquid phase separation (Wm–W). The region was enlarged with an increasing weight fraction of NaBr in water. Thus, the homogeneous aqueous solution (W) was restricted only to a very low BTBPBr concentration region when the weight fraction of NaBr was high. We also found that the immiscibility gap is a closed loop and that the gap intersects with the Krafft boundary when the NaBr concentration is higher than 0.5 wt%. It has been reported that TBABr gives a similar looped immiscibility gap when a very high pressure is applied.[10] This suggests that the addition of an electrolyte to a symmetric quaternary salt system exerts an effect on the phase behavior, somewhat similar to an elevation of the pressure.

The solubility behavior of BTBPI is shown in Fig. 5. The melting point of BTBPI in water was 85 °C and the crystalline solid BTBPI (Q) coexists with a BTBPI-poor aqueous solution (W) below the temperature. Because the melt of BTBPI was not miscible with water, a liquid–liquid two-phase (Wm–W) was formed above 85 °C. The addition of NaI to the system slightly enlarged the Wm–W region, as shown in Figs. 5b and 5c.

The influence of NaX over a wide concentration range is shown in Figs. 6a–c. The Krafft boundary (the boundary line between W–Q and Wm) was not observed for BTBPCl. The solid NaCl crystalline was precipitated rather than the BTBPCl

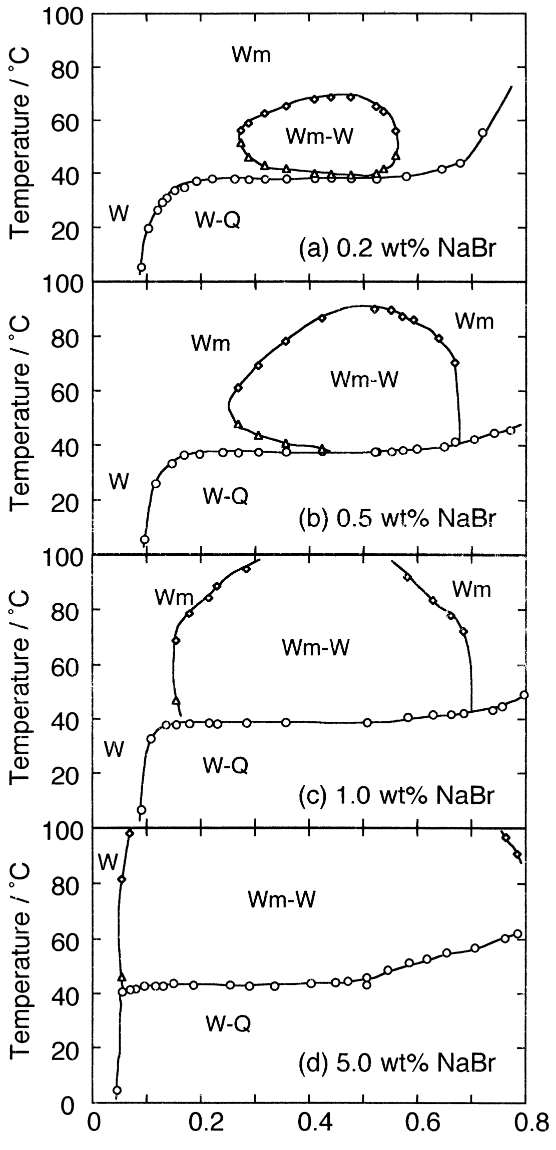


Fig. 4. Solubility behavior of BTBPBr in NaBr aqueous solutions. (a) in 0.2 wt% NaBr aqueous solution, (b) in 0.5 wt% NaBr aqueous solution, (c) in 1.0 wt% NaBr aqueous solution, and (d) in 5.0 wt% NaBr aqueous solution. The symbols used in the Figures are the same phases represented in Fig. 3.

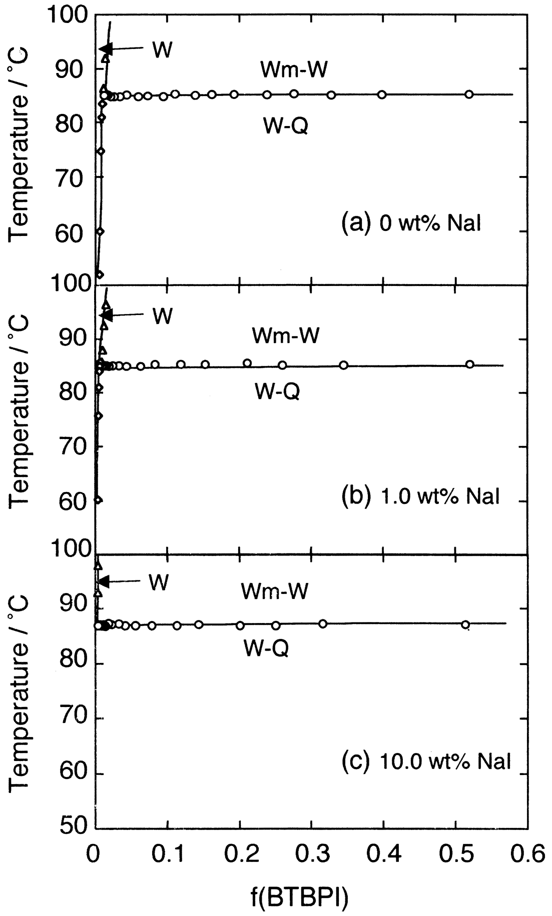


Fig. 5. Solubility behavior of BTBPI in NaI aqueous solutions. (a) in water, (b) in 1.0 wt% NaI aqueous solution, and (c) in 10.0 wt% NaI aqueous solution. The symbols used in the Figures are the similar phases represented in Fig. 3.

precipitation. The boundary line between W–Q and Wm–W of BTBPBr or BTBPI, which corresponds to the Krafft boundary, gradually increased with the concentration of NaX until the excess NaX precipitated as a solid phase (S). The phase equilibrium of Wm–W–S was not observed for the BTBPI system.

The presence of the Krafft boundary of BTBPX strongly suggests that BTBPX forms a certain aggregate in the homogeneous Wm phase. The formation of a spherical micelle may be difficult due to the closely symmetrical structure of the phosphonium ions. The candidate may be a rod-like oligomer, which can at least solubilize some amount of oil. The steric bulky structure of the phosphonium ions inevitably exposes some alkyl groups (or the part of the alkyl groups) to water, leading to the formation of hydrophobic hydration around the groups. An elevation of temperature weakens the hydrophobic hydration to promote the hydrophobic interaction among phosphonio groups. The size of the aggregate gradually increases with temperature. When the short-range attractive hydrophobic interaction overwhelms the repulsive electrostatic interaction between the phosphonium-ion aggregate, phase separation (Wm–W) takes place. An electrolyte may also deprive of some water from the hydrophobic hydration around the alkyl groups. The aggregate in the Wm of the Wm–W two-phase state is probably much larger than that of the homogeneous Wm phase below the cloud point. As shown later in this paper, the Wm phase coexisting with the aqueous W phase beyond the cloud point is able to absorb a considerable amount of benzene, indicating that the microstructure of the aggregate is likely to be bicontinuous, rather than of an o/w type. The specific binding of soft counter-anions (such as Br or I) to phosphonium ions and the increase in the electrolyte concentration both reduce the electrostatic repulsion among the phosphonium aggregates. Thus, the cloud point of BTBPX was lowered with adding the electrolyte, particularly for BTBPBr or BTBPI. The difference in the onium ion structure influences the aggregate structure, which in turn effects the hydrophobic hydration around the aggregates, to which the variation of lower conso-

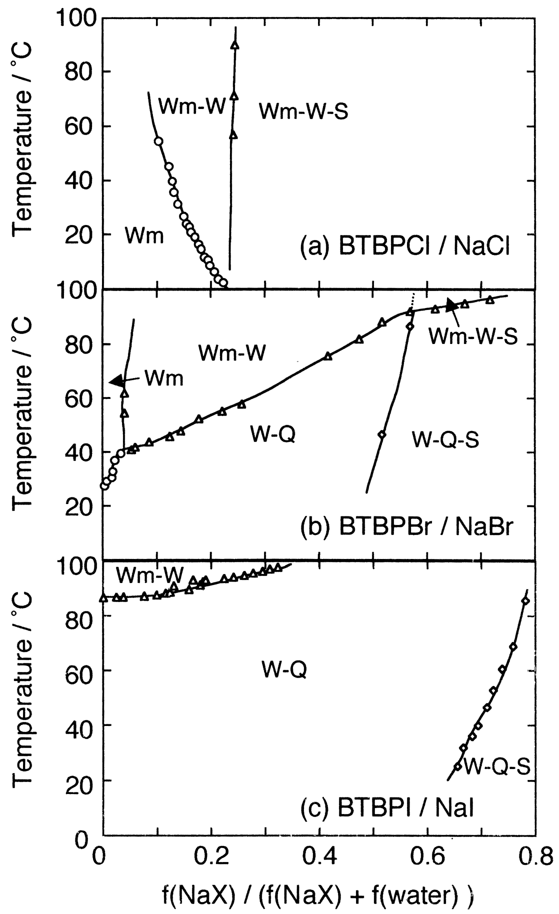


Fig. 6. Effect of NaX concentration on phase behavior of BTBPX. (a) BTBPCl, (b) BTBPBr, and (c) BTBPI. To a mixture of 0.25 mmol of BTBPX and 1.0 mL of water, a given amount of NaX was added.

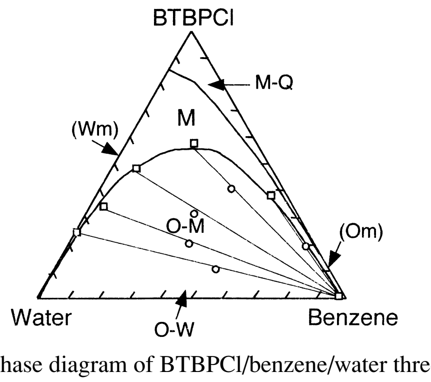


Fig. 7. Phase diagram of BTBPCl/benzene/water three-component system at 60 °C. Coordinates are in weight fractions of the components. The symbol M represents a microemulsion phase that contains benzene and water beyond their mutual miscibility. Tie lines are shown with the total compositions (round keys) and the observed compositions of the two phases (square keys).

lute behavior may be attributable.

On the other hand, the microstructure in the W phase is either a non-aggregate form (dissociated monomer) or a very small aggregate. The csc of each BTBPX should be strictly determined in order to distinguish between them.

BTBPX/Benzene/Water Three-Component Systems. We have suggested the existence of two types of aggregates that are formed by BTBPX: Om and Wm. The phase Om (or Wm) is formed when the BTBPX 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 an M phase, which contains benzene and water beyond the amounts of their mutual miscibility. Because BTBPX possibly aggregates in the Om and Wm phases, it is reasonable to assume that BTBPX also aggregates in the M phase. There are two other homogeneous phases, an O phase and a W phase, in which BTBPX is assumed to be present with a more or less non-aggregated form. In these phases, BTBPX is probably present almost as an isolated ion-pair in the O phase and as a dissociated form in the W phase.

The three-component system of BTBPCl/benzene/water at 60 °C gave a phase diagram that was very similar to that of TBACl/benzene/water.[7] As shown in Fig. 7, there was an M-phase region, under which a broad liquid–liquid two-phase region (O–M) was observed. The M phase region was attached to the Wm region of the zero oil line. The region was also attached to the Om region of the zero water line at the part of small BTBPCl fractions. There was a liquid–solid M–Q region attached to the zero water line at the higher BTBPCl fractions. The tie lines in the O–M two-phase region indicate that the M phase is able to coexist with a benzene-rich phase (O phase), but not with a water-rich phase (W phase). This suggests that the microstructure in the M phase is water-continuous.

The phase diagram of BTBPBr (or BTBPI)/benzene/water at 60 °C is greatly different from that of BTBPCl. The diagram rather resembles that of TBAI/benzene/water system.[7] As shown in Figs. 8 and 9, there is a broad region of a three-liquid-phase region of O–M–W, above which there are a two-liquid-phase region (M–W) on the left, and another two-liquid-phase region (O–M) on the right. The O–M regions of BTBPBr and BTBPI are very narrow. There is a distinct O–W region below the O–M–W region. In addition, we find a narrow M

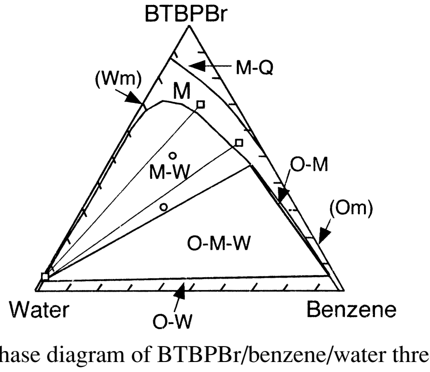


Fig. 8. Phase diagram of BTBPBr/benzene/water three-component system at 60 °C. Coordinates are in weight fractions of the components. Tie lines are shown with the total compositions (round keys) and the observed compositions of the two phases (square keys).

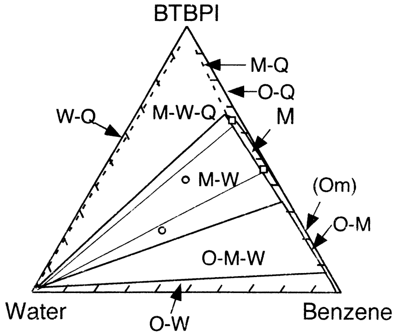


Fig. 9. Phase diagram of BTBPI/benzene/water three-component system at 60 °C. Coordinaters are in weight fractions of the components. Tie lines are shown with the total compositions (round keys) and the observed compositions of the two phases (square keys). Ambiguous phase-boundaries are shown in dashed lines.

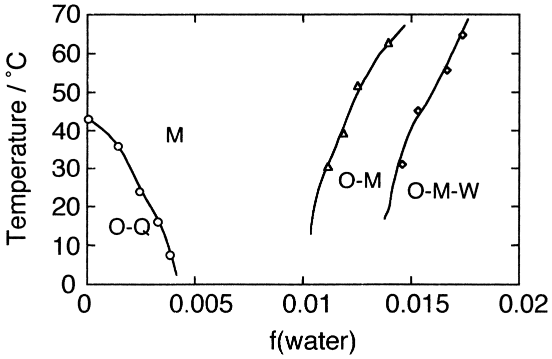
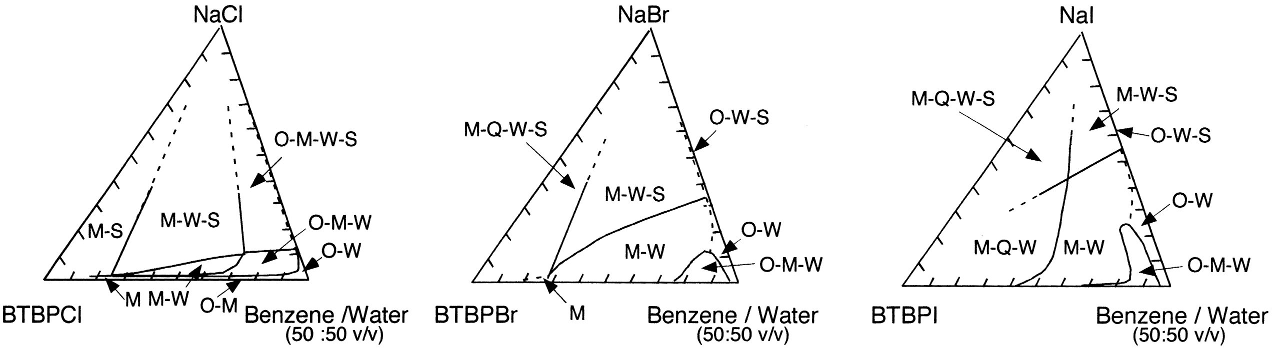


Fig. 10. Temperature dependence of phase behavior of BTBPBr/benzene/water three-component system. Water was added to a mixture of BTBPBr (0.6 mmol) and benzene (1.0 mL).

phase region that is extended to the benzene corner. The occurrence of an O–M–W phase-separation clearly shows that the presence of inorganic salt is not always a prerequisite for the formation of a so-called “third liquid phase,” often cited in PTC systems.[11] Thermodynamically, each phase of an O–M–W three-phase equilibrium of a three-component system should have constant compositions at a given temperature and pressure. The composition of each phase (BTBPBr, benzene, water) by weight fraction was obtained by an NMR analysis: O(0.06, 0.93, 0.01), M(0.43, 0.47, 0.10), and W(0.04, 0.01, 0.95) at 60 °C. The composition for the BTBPI system was O(0.07, 0.92, 0.01), M(0.35, 0.64, 0.01), and W(0.006, 0.004, 0.99). The M phase compositions at least reject an o/w microstructure being formed in the M phase of the BTBPBr or BTBPI system under the O–M–W three-phase equilibrium conditions. The microstructure may be bicontinuous or of a w/o type, possibly for BTBPI system.

The temperature dependence of the BTBPBr system is shown in Fig. 10, where a small amount of water is added to a BTBPBr/benzene two-component system. The results show that the M phase tends to absorb more oil upon warming. Because no electrolyte except BTBPBr is present, more water is also absorbed by the M phase upon warming. Thus, an O–M two-liquid state is transformed to a homogeneous M phase at higher temperatures. An O–M–W three-liquid state was transformed to an O–M two-liquid state before the whole amount of benzene was absorbed by the M phase, because the volume of the W phase was very small compared with that of the O phase under these conditions.

BTBPX/benzene/water/NaX Four-Component Systems. The phase diagrams of BTBPX/benzene/water/NaX system at 60 °C are shown in Figs. 11a–c. The benzene/water volume ratio was fixed at 50:50. Although the phase diagram of tetrabutylammonium salts (TBAX) was similar each other irrespective of the counter-ions,[7] the counter-ion exerted a significant influence on the phase equilibrium of BTBPX. Under the BTBPCl/benzene/water three-component conditions, the BTBPCl system did not afford a three-liquid-state, O–M–W, at 60 °C. When a slight amount of NaCl was added to an O–M two-phase, however, the three-liquid-state was formed if the BTBPCl content was low. It is noted that the O–M–W three-liquid-phase was converted into a liquid–liquid–liquid–solid four-phase equilibrium state (O–M–W–S) with a further addition of



(a) BTBPCl / Benzene / Water NaCl (b) BTBPBr / Benzene / Water / NaBr (c) BTBPI / Benzene / Water / NaI

Fig. 11. Phase diagrams of BTBPX/benzene/water/NaX four-component systems at 60 °C. (a) BTBPCl, (b) BTBPBr, and (c) BTBPI. One corner of the pseudo-ternary phase diagrams is an equi-volume mixture of benzene and water. Coordinates are in weight fractions of the components. Ambiguous phase-boundaries are shown in dashed lines.

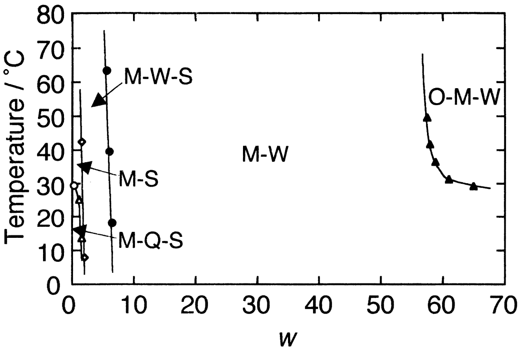


Fig. 12. Temperature dependence of phase behavior of BTBPBr under four-component conditions. To a mixture of 0.125 mmol of BTBPBr, 1.0 mL of benzene, and 0.01 g of NaBr, water was added. The content of water is shown as a molar ratio of water to BTBPBr (*w*).

NaCl. This phase transition was the same as those of TBAX.[7] Although a liquid–liquid–liquid–solid four-phase equilibrium state (O–M–W–S) was always observed for the TBAX systems, irrespective of the counter-ions, only the BTBPCl system gave four-phase equilibrium in this study. Therefore, if we add BTBPCl to a mixture of benzene and a NaCl aqueous solution, of which the NaCl concentration is higher than 0.05 by weight fraction, the O–W two-liquid state is always transformed into an O–M–W three-liquid state.

On the other hand, we could not find any region of the O–M–W–S phase separation for the BTBPBr or BTBPI system at 60 °C. Instead, the addition of NaX to an O–M–W system afforded an M–W two-liquid phase. If a further amount of the electrolyte was added to the M–W, an M–W–S liquid–liquid–solid three-phase was formed. These phase transformations took place even at very low contents of BTBPX. Figures 10b and 10c also show that the concentration of NaX in the aqueous phase determines what kind of phase transformation is induced upon adding BTBPX to a two-liquid mixture of benzene and an aqueous solution. At low concentrations of NaX, the system was transformed from O–W, through O–M–W, to M–W. At high concentrations of NaX, the system was transformed from O–W to M–W without any visual indication of a phase-transition. Hypothetical boundaries between O–W and M–W were drawn in the Figures, assuming that the BTBPX concentration in the W phase at a given NaX concentration was equal to the value at the cloud point.

The phase transition of O–M–W to M–W may be qualitatively explained as follows. The addition of NaX to an O–M–W system decreases the water content and increases the benzene content in the M phase. The microstructure of the M phase changes its state from an o/w or bicontinuous type to a w/o one. Eventually, the miscibility between M with O becomes as high as they are completely miscible with each other at a given temperature, leading to the formation of an M–W system. On the other hand, the M phase formed by BTBPCl cannot reduce its water content on the addition of NaCl to such a level that the microstructure becomes a w/o type to make complete miscibility with the O phase. Thus, in this case, an O–M–W–S equilibrium is attained.

The occurrence of an O–M–W–S phase separation is easily judged by whether an O–M–S area is present or not. The presence of an O–M–S equilibrium state was easily found for the BTBPCl system through adding water to a BTBPCl/benzene/NaCl mixture (Om–S state). Before a NaCl aqueous solution (W) was formed, a BTBPCl-rich liquid (M) was liberated from the benzene-solution of BTBPCl (Om). The O–M–S area was never seen in the BTBPBr system, as shown in Fig. 12. In this case, the addition of water to a BTBPX/benzene/NaX mixture led to the phase-separation of an M–W–S. The yielding W phase was an almost saturated aqueous solution of NaX. A further increase in water transformed the system to an M–W, and then to an O–M–W when the NaBr concentration in the W phase was sufficiently diluted. This may correspond to a change in the microstructure of the M phase from a w/o type to a bicontinuous one.

Table 1 shows what kind of phase-transition occurs for BTBPBr/oil/NaBr systems upon adding water. As shown in Fig. 1b, BTBPBr was hardly soluble in oils, except benzene at 60 °C. Thus, most of the BTBPBr was present as a solid Q in the absence of water; the system was a liquid–solid–solid three-phase (O–Q–S). When toluene was used as oil, the system became an O–M–S state via O–M–Q–S four-phase. This means that the melting point of BTBPBr in toluene was lowered by the addition of water. The O–M–S three-phase was transformed to an O–M–W–S four-phase upon adding a further amount of water, as was the case for the BTBPCl/benzene/water/NaCl sysyem. It is noted that the BTBPBr/toluene/water/NaBr system affords an O–M–W–S because the corresponding system with benzene never gives the four-phase. The solubility of BTBPBr in p-xylene or ethylbenzene was very low due to the high Krafft point. The water added to the BTBPBr/oil/NaBr rather dissolved NaBr to form an O–Q–W three-phase. The Krafft point of BTBPBr in aqueous solution was much higher than 60 °C in the presence of saturated NaBr (Fig. 6b). Therefore, the formation of the O–Q–W three-phase indicates that the melting point of BTBPBr in these oils was not lowered down to 60 °C, even in the presence of a saturated NaBr aque-

Table 1. Phase Transition of BTBPBr/Oil/Water/NaBr Systems at 60 °C Depending on Water Content[a)]

Oil	*w* (type of phase transition)		
Benzene	3.0 (Om–S/M–W–S)		
Toluene	0.35 (O–Q–S/O–M–S)	4.4 (O–M–S/O–M–W–S)	
p-Xylene	0.93 (O–Q–S/O–Q–W–S)	28 (O–Q–M–S/O–Q–W)	51 (O–Q–W/O–M–W)
Ethylbenzene	0.93 (O–Q–S/O–Q–W–S)	28 (O–Q–M–S/O–Q–W)	38 (O–Q–W/O–M–W)

a) Water was added to a mixture of BTBPBr (0.25 mmol), oil (1.0 mL), and NaBr (0.15 g) at 60 °C. Molar ratio of water to BTBPBr is shown as *w*.

ous solution. BTBPBr did not melt at 60 °C until the aqueous solution (W) was diluted with a further addition of water. The data in Fig. 6b suggest that it may be possible to form an O–M–W–S four-phase with these oils at temperatures higher than 90 °C.

Conclusions

Counter-ions and oils exerted significant influences on the phase behavior of the BTBPX/oil/water NaX four-component systems. Simple partition of BTBPX between the oil and aqueous phase could not explain the phase behavior of these systems. The specific feature was the formation of a microemulsion phase, M. The M phase coexists with other phases to give several equilibrium states. The change in the microstructure of the M phase may cause the phase transition of four-component system. The difference of the phase behavior primarily depended on the BTBPX solubility in oil and in NaX aqueous solution. The solubility in oils was characterized by the Krafft boundary. The solubility in aqueous solutions was characterized not only by the Krafft boundary, but also by the immiscibility gap that defines the region of liquid–liquid two-phase coexistence. The shape of the gap was assumed to be a closed loop, as embodied for the BTBPBr/water/NaBr system.

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