

# Phase-behavior and solid–liquid phase-transfer catalytic activity of tetrabutylammonium bromide

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## Abstract

The addition of water to tetrabutylammonium bromide (TBABr)/benzene/sodium bromide ternary component systems induced the separation of TBABr-rich liquid phase (L phase) prior to the appearance of an aqueous phase (W phase). The L phase was assumed to be a bicontinuous phase similar to a microemulsion based on the phase composition. TBABr catalyzed the “solid–liquid” phase-transfer reaction of decyl methanesulfonate with sodium bromide either when the L phase was fully hydrated or after a distinct W phase was formed. The phase-transfer catalytic activity was correlated to the phase behavior of TBABr/benzene/water/NaBr four-component system. The difference and similarity between TBABr and tetrabutylphosphonium bromide (TBPBr) were discussed based on the microstructure of the phases formed by TBABr and TBPBr under the phase-transfer catalytic reaction conditions.

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**Keywords:** Tetrabutylammonium bromide; Tetrabutylphosphonium bromide; Benzene- $d_6$ ; PTC

## 1. Introduction

The technique of phase-transfer catalysis (PTC) using quaternary salts as catalysts has been established as one of the most useful methods for the acceleration of heterogeneous reactions [1–5]. The recent trend toward “green and sustainable chemistry” has again attracted a strong attention to its significance for organic syntheses. Water sometimes interferes with the desired reaction through suppression or diversion. Thus, PTC was often carried out with solid reagent salts in the absence of water (solid–liquid PTC). In many solid–liquid systems, however, small quantities of water play an important role in the catalytic processes [6–9]. The catalytic reactions hardly proceeded under anhydrous conditions. Though the role of water is still ambiguous, it has been often assumed that water hydrates the surface of the crystal lattice of inorganic reagents to facilitate the ion-exchange

process until an aqueous phase discretely appears in the system [10–12].

Our recent studies on the phase behavior of quaternary salts have shown that quaternary salts are able to form a liquid quaternary salt phase (L phase) [13–18]. The L phase is a homogeneous liquid phase similar to a microemulsion that can contain considerable amounts of both organic oil and water beyond their mutual solubility. The L phase sometimes coexists with other phases such as, a liquid oil-rich phase (O), a liquid aqueous phase (W), and a solid inorganic salt phase (S). Thus, O + L + W liquid–liquid–liquid triphase systems or O + L + W + S liquid–liquid–liquid–solid quaternary-phase systems are often observed.

Probably, tetrabutylammonium salts (TBAX: X = Cl, Br, and I) are the quaternary salts that have been most often used as PTC catalysts. We have found that TBAX is also able to form a microemulsion-like phase (L phase) on adding some amounts of benzene and an aqueous electrolyte solution [13,14]. The L phase coincides with the “third liquid phase” that has been often referred to in phase-transfer catalytic systems [19–23]. The L phase plays a key role in the

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interface-mediated catalysis that TBAX brings about under “liquid–liquid” PTC conditions [24]. It is suggested that the L phase and ionic liquid resemble each other in nature. We have also found that TBAX/benzene/water/NaX four-component systems afford an O + L + W + S quaternary phase equilibrium in the presence of an excess amount of NaX. The occurrence of the quaternary phase strongly suggests that an O + L + S three-phase state is directly involved in the TBABr-catalyzed “solid–liquid” PTC.

In this article, we show the phase behavior of TBABr/benzene/water/NaBr four-component system that is relevant to the “solid–liquid” PTC. The change in equilibrium states and compositions of coexisting phases were examined in detail as a function of water content or temperature. The phase behavior of tetrabutylphosphonium bromide (TBPBr), whose structure was quite similar to that of TBABr, was also examined. The model PTC reaction that we examined in this study was the nucleophilic substitution reaction of decyl methanesulfonate with sodium bromide because we do not need to consider its reverse reaction for the kinetics analysis. The phase behavior is correlated to the solid–liquid phase-transfer catalytic activity of TBABr or TBPBr. Based on the kinetics and microstructures of coexisting phases, the role of the L phase to solid–liquid PTC will be discussed.

## 2. Experimental

### 2.1. Materials and equipment

Tetrabutylammonium bromide (TBABr, >99%) and tetrabutylphosphonium bromide (TBPBr, 98%) were purchased from Tokyo-Kasei and from Aldrich, respectively, and were used without further purification. Decyl methanesulfonate was prepared by the reaction of methanesulfonyl chloride with 1-decanol in pyridine [25]. Benzene was purified by distillation from sodium benzophenone ketyl under nitrogen. Benzene- $d_6$  was used without further purification. Sodium bromide was thoroughly dried by sintering at 700 °C for 3 h and was pulverized. Deionized water was used throughout the experiments.  $^1\text{H}$  NMR spectra were recorded on a Varian Mercury 300 spectrometer. GLC analyses were done using a Hitachi 163 FID instrument with a 1 m column of SE-30 or PEG-20M.

### 2.2. Determination of phase-equilibrium and composition [13,14]

Prescribed amounts of TBABr, NaBr, water and benzene were added to a 10 mL Teflon-coated screw-capped test tube with an inside diameter of 10.5 mm. The mixture was vigorously stirred with a tube shaker, and the tube was transferred to a temperature-controlled bath maintained at  $60.0 \pm 0.1$  °C. After 10 min, the tube was shaken vigorously by a tube shaker again and allowed to stand still to wait for the phases to clearly separate at that temperature. The composition of the mixture

was then slightly varied by adding a small amount of water or NaBr. The boundary lines of any two phase-equilibrium states were obtained from at least four data points.

In order to determine the phase composition of a liquid layer, benzene- $d_6$  or a prescribed mixture of benzene- $d_6$  and benzene was used. The composition was determined by  $^1\text{H}$  NMR analysis, using the  $\alpha$ -methylene peak of TBABr, the residual proton of benzene- $d_6$  or the proton of benzene added, and the water peak. When the volume of TBABr-rich phase was small, an aliquot of the layer was added to a given amount of methanol- $d_4$  and the composition of the phase was analyzed by  $^1\text{H}$  NMR based on the residual proton of the methanol. The concentration of NaBr in the TBABr-rich phase was analyzed by the reaction method, in which the 1-bromodecane formed by the reaction with the excess amount of decyl methanesulfonate was quantitatively analyzed on GLC. The amount of 1-bromodecane was, however, nearly equal to that of TBABr measured by the NMR method within the experimental errors. Therefore, the weight fraction of NaBr in the TBABr-rich phase was neglected. The composition uncertainty was  $\pm 0.005$  in weight fraction. Similarly, the phase behavior and composition concerning TBPBr have been determined. The chemical shifts of  $^1\text{H}$  NMR peaks of TBABr (or TBPBr) and water in a quaternary salt-rich phase at 60 °C were measured using the residual proton of benzene- $d_6$  (7.20 ppm) as a standard.

### 2.3. Kinetics run of phase-transfer reaction

The general procedure is as follows unless otherwise noted. A 30 mL culture tube with a Teflon-lined screw cap was charged with prescribed amounts of TBABr (or TBPBr), NaBr plus prescribed amounts of water, and 2 mL of an organic solvent containing pentadecane as an internal standard. The tube was placed in an oil bath maintained at 60 °C and the mixture was stirred for 20 min with a Teflon-coated magnetic stirring bar, followed by injection of 0.2 mL of decyl methanesulfonate via a micropipette. Aliquots of the organic layer (0.1 mL) were withdrawn periodically with a pipette and were poured into 0.5 mL of diethyl ether. The top clear layers were quantitatively analyzed on GLC to determine the concentrations of the substrate and product. The semilogarithmic plot of the fraction of unreacted substrate against time gave a straight line with a slope, from which the pseudo-first-order rate constant was calculated.

## 3. Results and discussion

### 3.1. Phase behavior of TBABr/benzene/water/NaBr four-component systems

The most characteristic feature of TBABr/benzene/water/NaBr four-component systems is that these systems afford a liquid (O) + liquid (L) + liquid (W) + solid (S) quaternary phase equilibrium [14]. This means that the TBABr-rich L

Table 1  
Compositions of L and O phases under O + L + W + S four-phase conditions for TBABr/benzene/water/NaBr systems<sup>a</sup>

Temperature (°C)	L phase					O phase			
	TBABr	Benzene	Water	$\alpha_Q^b$	$w_Q^c$	TBABr	Benzene	Water	$w_Q^c$
60	0.41	0.55	0.04	5.6	1.6	0.0096	0.989	0.0014	2.3
40	0.47	0.47	0.06	4.1	2.2	0.0095	0.989	0.002	3.0
30	0.53	0.38	0.09	3.0	3.0	0.0104	0.985	0.004	6.9

<sup>a</sup> Compositions are represented by the weight fraction of a component against the sum of TBABr, benzene, and water but NaBr;  $f_X/(f_{\text{TBABr}} + f_{\text{benzene}} + f_{\text{water}})$ .  $f_X$  represents the weight fraction of component X in the phase.

<sup>b</sup> Molar ratio of benzene to TBABr.

<sup>c</sup> Molar ratio of water to TBABr.

phase and the benzene-rich O phase do not intermix each other even in the presence of a concentrated NaBr aqueous solution. This property of TBABr contrasts with that of benzyldodecyldimethylammonium halide. The latter easily intermixed with the benzene-rich phase if the sodium halide concentration of the coexisting W phase was beyond a certain value [16]. Tetrabutylphosphonium bromide (TBPBr), whose structure was quite similar to that of TBABr, never formed an O + L + W + S equilibrium state. As mentioned below, an L + W two-phase was formed when the NaBr concentration was higher than 40 wt.%.

If a four-component system affords phase equilibrium consisting of quaternary phases, according to the thermodynamic rule, the composition of each phase should be definitely given when temperature and pressure are constant. The compositions of the L phase of TBABr are shown in Table 1, together with the compositions of the corresponding coexisting O phases. All the L phases contain benzene more abundantly than water. The amounts of water were, however, considerably beyond the solubility of water in benzene. This suggests that the L phases are bicontinuous microemulsion-like phases. The composition of the L phase strongly depended on the temperature while the composition of the coexisting O phase was slightly varied. With increasing temperature, the L phase tended to be rich in benzene and poor in water. The concentration of TBABr in the O phase of O + L + W + S was generally low. This means that TBABr almost resides in the L phase.

TBABr forms a certain aggregate beyond the critical solubility concentration (csc) in a benzene solution ( $L_2$  or  $O_m$ ) [13]. The csc corresponds to the critical micelle concentration of surfactants. The solubility curve of TBABr in benzene bends at the critical temperature (Krafft point), at which the concentration of TBABr is defined as csc. TBABr is soluble freely in benzene up to a considerably high concentration above the Krafft point. The csc may be also determined by the change in <sup>1</sup>H NMR chemical shift of TBABr peaks [13]. The weight fraction of TBABr in the O phase of O + L + W + S (Table 1) was slightly higher than the csc that was found in our previous study on the solubility of TBABr in benzene (0.003 in weight fraction). Thus, we can assume that TBABr exists as a certain aggregate form ( $L_2$ ) in the benzene-rich phase (O). In this article, we represent an  $L_2$  phase as L unless there is any other phase that contains TBABr more

abundantly than the phase. If another TBABr-rich phase is present, we represent it as L and the benzene-rich phase as O even if the benzene phase consists of  $L_2$ . Therefore, the symbol, O, does not necessarily mean the state of TBABr but stands for a benzene-rich phase.

The W phase of an O + L + W + S state was almost a saturated NaBr solution that contained a negligibly small amount of TBABr. The weight fraction of TBABr in the W phase was as low as 0.0003 in weight fraction at 60 °C.

Fig. 1 schematically shows the regular tetrahedron phase diagram of the TBABr/benzene/water/NaBr four-component system at 60 °C. Using the data in Table 1, we can draw the O + L + W + S body, which is located in the center of the regular tetrahedron phase diagram. The O + L + W + S body should be tetrahedral and the presence of the O + L + W + S quaternary phase strongly suggests that there are four triphase equilibrium states (O + L + W, O + L + S, O + W + S, and L + W + S) and six biphasic equilibrium states (O + L, O + W, O + S, L + W, L + S, and W + S). The cross sections of the regular tetrahedron phase diagram may visualize some of these equilibrium states. The detailed pseudo-three-component diagram of the QDC section for the TBABr/benzene/water/NaBr system at 60 °C was already given by us [24].

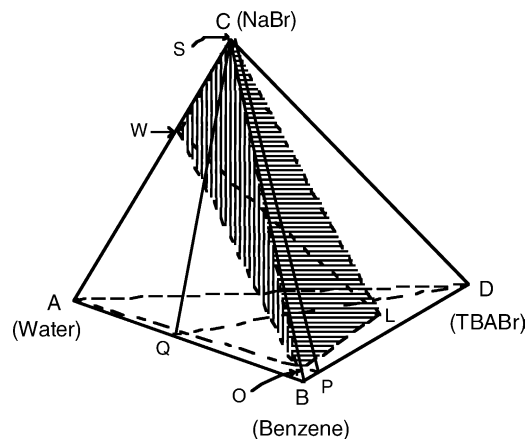


Fig. 1. Regular tetrahedron diagram of the TBABr/benzene/water/NaBr four-component system at 60 °C. The four-phase body of O + L + W + S is represented by a tetrahedron of broken lines. Point P represents a mixture of TBABr and benzene. Cross section PAC of the regular tetrahedron diagram that is closely relevant to solid–liquid PTC systems.

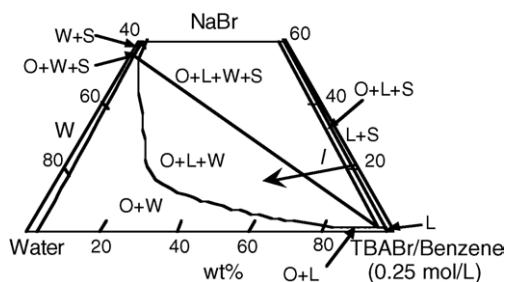


Fig. 2. Pseudo-three-component diagram of the PAC section for TBABr/benzene/water/NaBr system at 60 °C. O phase shows a benzene-rich phase that coexists with other phase(s) and contains very small amounts of TBABr. W phase is a water-rich phase that coexists with other phase(s) and contains few amounts of TBABr. L phase is a TBABr-rich liquid phase that is assumed as one type of microemulsions. S phase is a solid crystalline of NaBr. A phase equilibrium state is represented in the order of phases identified as layers from top to bottom.

We determined the boundaries between equilibrium states by adding water or NaBr to a benzene solution of TBABr (0.25 mol/L). In Fig. 2 (the plane section at PAC of Fig. 1), is shown the pseudo-ternary phase diagram of the TBABr/benzene/water/NaBr system at 60 °C. One can see three triphase regions (O+L+S, O+L+W, and O+W+S) and four biphasic regions (L+S, O+L, O+W, and W+S) as well as a quaternary phase region (O+L+W+S). The important states for solid–liquid PTC conditions are L+S, O+L+S, and O+L+W+S. The detection of the boundary between L+S and O+L+S states was easy. An L phase of L+S suddenly became turbid when water was added beyond a certain limit. The system soon became a clear O+L+S triphase state. It is noted that an aqueous phase W never appears without the occurrence of benzene-rich O phase: the transformation from L+S state is not to L+W+S but to O+L+S. After an O phase appeared, further addition of water to the O+L+S state made the volume of the O phase sharply increase accompanied by an abrupt decrease in the L phase volume. The L phase volume became very small. On the other hand, the detection of the boundary between O+L+S and O+L+W+S was slightly hard if there were large amounts of solid NaBr, because the NaBr powder soaked up the newly formed W phase. Therefore, we measured the boundary at relatively low contents of NaBr.

It was impossible to visually detect the boundary between O+L and O+W because the transformation occurred without any change in appearance, though TBABr was assumed to aggregate in L of the O+L state and to be of a monomeric form in W of the O+W state. This phase diagram is useful to explain the phase transitions relating to solid–liquid PTC.

The corresponding pseudo-ternary phase diagram of TBPBr is shown in Fig. 3. Although TBPBr resembles TBABr in structure, its phase diagram is greatly different. There was no region of O+L+W+S, despite a wide region of L+W+S. Thus, an addition of water to an L+S state of the TBPBr/benzene/NaBr system induces the formation of an L+W+S state. An L+W two-phase was formed when the NaBr concentration in the W phase was between 40 and 55 wt.%. Below the L+W region, there was a three-liquid O+L+W region. The region of O+L+W contacted the NaBr zero-line. This means that the three-component system, TBPBr/benzene/water, affords a three-liquid O+L+W state at a wide range of composition. This property of TBPBr is noted. TBPBr is freely soluble both in water and in benzene at 60 °C [26]. Nevertheless, TBPBr forms a third quaternary salt-rich phase.

### 3.2. Constituent composition and PTC activity

The phase behavior shown in Fig. 2 strongly suggests the participation of L phase in the PTC reactions. Along the line I of Fig. 2, an incremental addition of water to a TBABr/benzene/NaBr mixture induces a phase transition from liquid (L)+solid (S), through O+L+S (not an L+W+S), to O+L+W+S. Further addition of water eventually makes the system an O+L+W three-phase equilibrium.

The corresponding change in the phase composition of the most upper layer, L of the L+S and O of the O+L+S or O+L+W+S, is shown in Fig. 4. The amount of water added is represented by the molar ratio of water to TBABr ( $w_Q$ ). When the system was L+S, the TBABr was almost present in the L phase. The coincidence between  $w_Q$  and  $w$  shows that all the water added resides in the L phase. This indicates that the water serves to hydrate TBABr in preference to NaBr. The water present in the L phase gave a very high  $^1\text{H}$  NMR chemical shift (around 2.8 ppm) as compared with that of

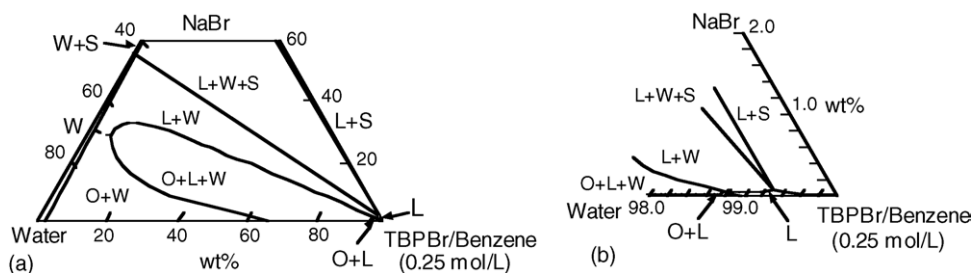


Fig. 3. Pseudo-three-component diagram of the PAC section for TBPBr/benzene/water/NaBr system at 60 °C. (b) is the figure that is enlarged at the TBPBr/benzene corner of (a). Description of phases is same as in Fig. 2.

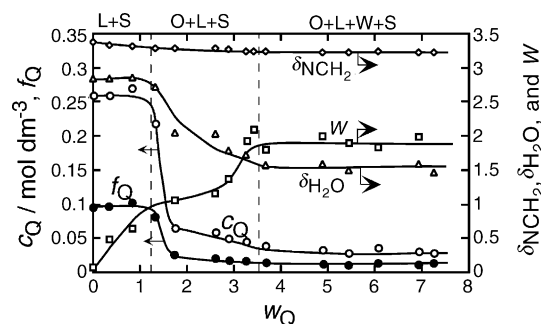


Fig. 4. Phase transitions of the TBABr/benzene/water/NaBr system and concentration of TBABr in the most upper layer as a function of the molar ratio of water to TBABr ( $w_Q$ ). Conditions: TBABr, 0.25 mmol; benzene- $d_6$ , 1.0 mL; NaBr, 4.0 mmol; 60 °C. An incremental amount of water was added along the line 1 of Fig. 2. Broken lines show the values of  $w_Q$  at which phase transitions occur. The concentration of TBABr in the layer is represented as molar concentration ( $c_Q$ ) or weight fraction ( $f_Q$ ). The  $^1\text{H}$  NMR chemical shifts of water and N-adjacent methylene protons of TBABr in the most upper layer are also shown in the figure, together with the water–TBABr ratio,  $w$ , in the layer.

free water dissolved in benzene (ca. 0.5 ppm). It is consistent with our previous results that water affords a large chemical shift if TBABr aggregates in the L phase beyond the csc in benzene [13].

Beyond the value of  $w_Q$  that the transition from L+S to O+L+S took place, the O phase sharply reduced the TBABr content (Fig. 4). The concentration of TBABr that was detected in the O phase ( $f_Q$  or  $c_Q$ ) became considerably small compared with the total amount of TBABr, although the volume of the O phase became large. This means that TBABr was concentrated into the L phase. Under O+L+S conditions, nevertheless, the TBABr concentration in the O phase ( $f_Q$ ) was kept higher than 0.009 in weight fraction, indicating that the O phase remained  $L_2$ . This corresponds to the shift of the  $^1\text{H}$  NMR water peak. The chemical shift remained higher than 1.5, though it gradually moved up-field. The volume of the L phase sharply decreased after the O phase appeared. The L phase eventually went out of sight under the NaBr powder (S phase). The system looks as if the system consisted of two phases. Thus, the evaluation of the L phase composition was difficult under the conditions.

If we increase the relative weight fraction of TBABr to benzene (1.0 mmol of TBABr in 1.0 mL of benzene) and decrease the amount of NaBr, the effect of water on the L phase composition can be evaluated (Fig. 5). The addition of water induced a similar change in equilibrium state as that shown in Fig. 4: the same transitions took place at the similar values of  $w_Q$ . The TBABr content in the L phase of O+L+S was in fact increased after an O phase appeared. Under O+L+S conditions, further addition of water reduced the benzene content of the L phase accompanied by the gradual increases in TBABr and water contents. The  $\delta$  value of water peak was around 3.2 for the L of L+S system. The value is comparable to that of bulk water (ca. 4.3 ppm). Furthermore, a very gradual down-field shift of

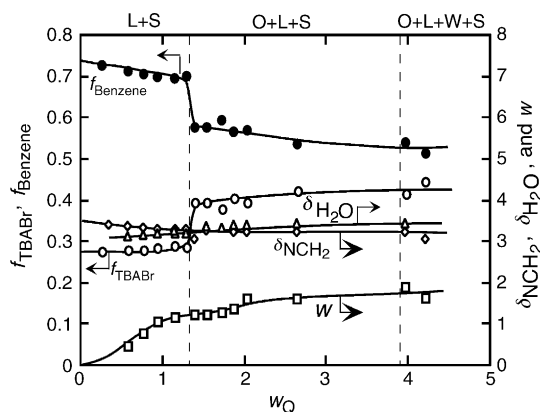


Fig. 5. Phase transitions and concentration of TBABr in the TBABr-rich L phase depending on water–TBABr molar ratio ( $w_Q$ ). Conditions: TBABr, 1.0 mmol; benzene- $d_6$ , 1.0 mL; NaBr, 0.1 g; 60 °C. The weight fraction of benzene is represented as  $f_{\text{benzene}}$ . Other symbols are the same as in Fig. 4.

water proton in the L of O+L+S was observed, suggesting that the nature of water in the L phase resembles that of bulk water. Thus, the microstructure of the L phase in an O+L+S three-phase is assumed to be of an oil–water bicontinuous structure while the O phase of O+L+S is assumed to be an  $L_2$  phase that contains w/o aggregates. The phase compositions of O and L phases approached those that were observed under O+L+W+S conditions (see Table 1). After an O+L+W+S state was formed, the composition of each phase was constant even with a further addition of water. When the S phase disappeared, an O+L+W three-liquid state was formed.

In Fig. 6, is shown the PTC catalytic activity of TBABr for the reaction between decyl methanesulfonate and NaBr. When  $w_Q$  was lower than 1.0 (L+S two-phase), the catalytic action of TBABr was not observed. The catalytic reaction was very slow, although the stoichiometric reaction of the substrate with the TBABr in the L phase took place smoothly at the initial stage of the reaction. The phase separation of

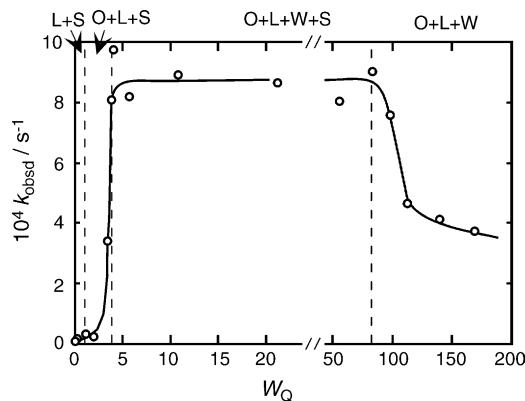


Fig. 6. Influence of water on the pseudo-first-order rate constant of the reaction between decyl methanesulfonate and sodium bromide under “solid–liquid” PTC conditions. Reaction conditions: TBABr, 0.5 mmol; benzene, 2.0 mL; NaBr, 8.0 mmol; decyl methanesulfonate, 0.3 mL; temperature, 60 °C.

the upper liquid phase into O and L two-phase has not a direct relation to an increase in the catalytic activity. The rate began to increase at the point that the O + L + S system was hydrated beyond  $w_Q > 3$ . As the hydration numbers,  $w$ , of O and L phases are both lower than 2 at this point, it is suggested that the adsorption of some water on the NaBr solid also takes place. Although we visually detected the appearance of W phase at  $w_Q = 4$ , the data of phase composition and NMR chemical shifts suggest that the phase transition from O + L + S to O + L + W + S takes place around  $w_Q = 3.5$  (Fig. 4). The increase of the rate constant was very sharp beyond the  $w_Q$  of 3.5 but ceased after an O + L + W + S was formed in the presence of an excess amount of water. The rate constant remained unchanged under O + L + W + S conditions. When water was added enough to dissolve the NaBr solid, the catalytic rate began to decrease with the dilution of NaBr concentration of the W phase under O + L + W conditions. This NaBr concentration effect is consistent with our previous results [24]. Therefore, it is clear that the presence of W phase and/or the full hydration of L phase are essential for the rate enhancement of this catalytic reaction. It is also clear that the reaction takes place in the L phase. The L phase of an O + L + S state somewhat resembles Liotta's omega phase [27] of crown ether-catalyzed solid-liquid PTC systems though it is reported that the crown ether-catalyzed PTC reaction smoothly proceeds under liquid-liquid-solid conditions. On the basis of the phase diagram data, the fundamental nature of the L phase observed in this study is the same as that of "third phase" reported for many PTC systems where a catalytic amount of quaternary 'onium salt' is mixed with a large amount of water as well as oil [19–24].

Tetrabutylphosphonium bromide (TBPBr) forms neither O + L + S nor O + L + W + S states at 60 °C under the TBPBr/benzene/water/NaBr four-component systems (Fig. 3). Thus, the addition of water to a TBPBr/benzene/NaBr mixture (an L + S state) led to the formation of L + W + S phase equilibrium. Even after a distinct W phase was formed, TBPBr kept residing in the L phase. The data in Fig. 7 concerning  $w$  value,  $\delta$  value of water, and chemical shift difference between methyl protons and P-adjacent methylene protons of TBPBr, all indicate that the phase transition from L + S to L + W + S takes place around 1.9 of  $w_Q$  value, though a distinct W phase was visually observed beyond the  $w$  value of 2.7. As shown in Fig. 7, however, the chemical shift of water that was present in the L phase was very high compared with that of water dissolved in pure benzene. The  $\delta$  value was 2.74–2.86. The water added was mostly present in the L phase of the L + S state when  $w_Q$  was below 0.6. According to similar NMR experiments of the literature [13], the change in chemical shifts of TBPBr versus its concentration in benzene suggests that the csc of TBPBr is as low as 0.002 in weight fraction (5 mmol/L) at 60 °C. These suggest that TBPBr is present as L<sub>2</sub> in the L phase. It may be also suggested that the water adsorbed on the NaBr was present at the value of  $w_Q$  between 0.6 and 1.9.

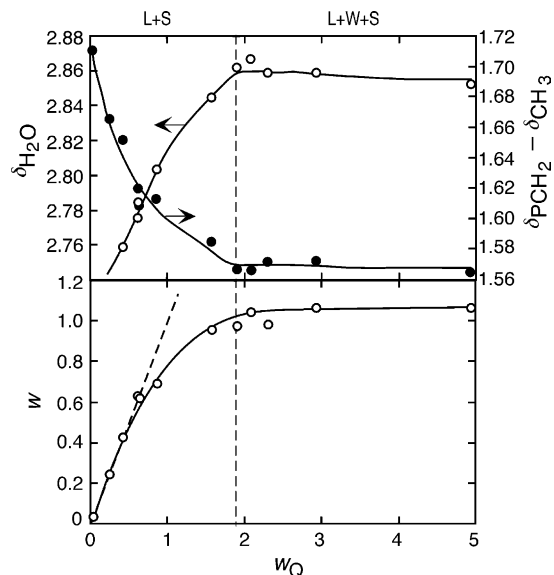


Fig. 7. Phase transition of the TBPBr/benzene/water/NaBr system and water concentration in the L phase as a function of the molar ratio of water to TBPBr ( $w_Q$ ). Conditions: TBPBr, 0.25 mmol; benzene- $d_6$ , 1.0 mL; NaBr, 4.0 mmol; 60 °C. A vertical broken line shows the probable value of  $w_Q$  at which the phase transition occurs. Another slant broken line shows 100% distribution of water to L phase. The  $^1\text{H}$  NMR chemical shift of water is standardized by the residual proton of benzene- $d_6$  (7.20 ppm). The chemical shift difference between methyl protons and P-adjacent methylene protons of TBPBr in the L phase is also shown in the figure.

Fig. 8 shows the effect of water addition on the catalytic activity of TBPBr. The variation apparently resembled that of TBABr. The catalytic activity sharply increased beyond  $w_Q$  value of 3.7 and ceased to increase around  $w_Q$  value of 5. The sharp rate enhancement occurred at the  $w_Q$  value much higher than the  $w_Q$  value (1.9) that the phase transition from L + S to L + W + S took place. This is probably because the L phases of L + S and L + W + S consist of L<sub>2</sub> and because

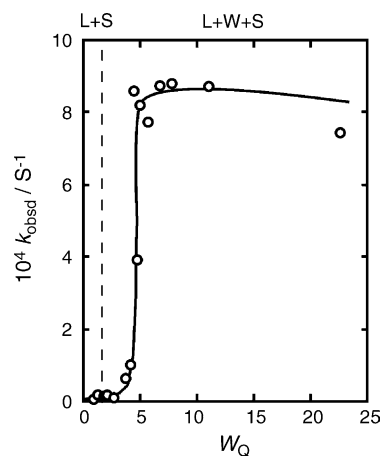


Fig. 8. Influence of water on the pseudo-first-order rate constant of the reaction between decyl methanesulfonate and sodium bromide under "solid-liquid" PTC conditions. Reaction conditions: TBPBr, 0.5 mmol; benzene, 2.0 mL; NaBr, 8.0 mmol; decyl methanesulfonate, 0.3 mL; temperature, 60 °C.

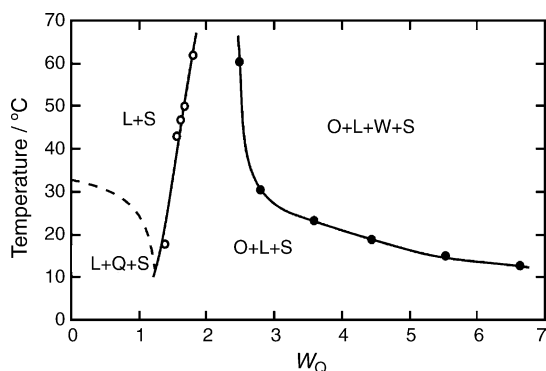


Fig. 9. Effect of temperature on phase behavior of the TBABr/benzene/water/NaBr four-component system with low contents of water. Conditions: TBABr, 1.0 mmol; benzene, 1.0 mL; NaBr, 0.10 g.

it may be necessary to provide a large surface area between L and W at which the anion-exchange of quaternary salts smoothly proceeds.

### 3.3. Microstructures of liquid phases and PTC activity

The aggregates of  $L_2$  exert an attractive interaction with each other in the medium while the entropy of dilution prevents the association. The increase in the water content in an  $L_2$  phase would strengthen the attractive interaction among the w/o-type aggregates, leading to the two-phase separation: one is an L phase with a bicontinuous structure and the other an  $L_2$  phase (O) with a w/o structure [16]. This is the reason why an L+S two-phase is transformed to an O+L+S three-phase on an addition of water to the TBABr system. An elevation of temperature exerts a reverse effect on the association of w/o aggregates. As shown in Fig. 9, it is found that an L phase ( $L_2$ ) of L+S can keep larger amounts of water with increasing temperature. An elevation of temperature makes the entropy of dilution surpass the attractive interaction between  $L_2$  aggregates. Thus, an O+L+S phase transformed into an L+S two-phase at a certain temperature. On the other hand, an L phase of O+L+S phase absorbs more water at low temperatures. When the water content was high, therefore, an L phase tended to liberate an aqueous solution on heating, leading to the formation of an O+L+W+S phase before an intermixing of L and O phases takes place. This effect of temperature was identical to the observation for the change in the L phase composition of the O+L+W+S four-phase (Table 1). It may be concluded that one cannot realize an L+W+S equilibrium state under the TBABr/benzene/water/NaBr four-component system except when TBABr content is extremely high. We could not detect the catalytic activity of w/o aggregates of TBABr ( $L_2$ ) under solid–liquid PTC conditions. This is merely due to the unfeasible ion-exchange between  $L_2$  and NaBr solid. In fact, tetrabutylammonium chloride (TBACl) ion-exchanged its counter-ions into bromide form as low as 8% even after 6 h under the L+S conditions with  $w_Q$  of 1.0 where the com-

position of other constituents was kept identical to those in Fig. 6. Water prefers to hydrate TBABr, rather than to loose the crystal lattice through the hydration of solid NaBr surface. An L phase of the O+L+S state does not furnish the phase-transfer catalytic action, either, unless the L phase is considerably hydrated. This may be due either to an increase in the bicontinuous nature of the L phase or to an occurrence of the hydration to solid surface.

If the affinity of quaternary salts to an oil is stronger than to water, on the other hand, the quaternary salts keep residing in the oil phase as  $L_2$  and consequently an addition of water liberates an aqueous solution as a W phase [16,28]. This is the case for TBPBr with concentrated NaBr aqueous solution. Therefore, TBPBr did not start to show its catalytic action until the reaction system became an L+W+S state that contained a large surface area of W. The enlarged surface area of W phase may be necessary for the smooth ion-exchange between  $L_2$ -forming quaternary salts and NaBr in the W phase.

It should be lastly mentioned that the phase behavior and catalytic activity subtly depend on the kind of oil and/or inorganic salt. If we use toluene instead of benzene, for example, the phase transformation of TBABr with adding water becomes completely different [13,15]. The phase behavior of the TBPBr/toluene/NaBr system with the addition of water will be from L+S through O+L+S, to O+L+W+S, which is similar to that of TBABr reported in this paper. The kind of counter-anion strongly affects the phase behavior [13,16]. If there is any solubility of inorganic reagent into the oil, the catalytic activity is drastically influenced because the ion-exchange process is altered. This has been already pointed out in our papers [25,29].

## 4. Conclusion

In benzene, TBABr forms w/o aggregates ( $L_2$ ), which convert to bicontinuous aggregates (L phase) with the liberation of a benzene-rich phase when water is added. The TBABr-catalyzed nucleophilic substitution of decyl methanesulfonate with solid NaBr proceeds only in the presence of water. The reaction takes place within a microemulsion-like L phase, which is a quaternary salt-rich liquid phase that can contain considerable amounts of oil and water. At the microinterface within the bicontinuous L phase, decyl methanesulfonate is assumed to react with the counter-ion nucleophile [24]. TBPBr also forms w/o aggregates ( $L_2$ ) but keeps residing even after water is added. In this case, the PTC reaction proceeds only when an aqueous W phase is present.

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