# Phase Behavior of Tetrabutylammonium Salt/Oil/Water/Inorganic Salt Four-Component Systems

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The phase behavior of four-component systems composed of tetrabutylammonium halide (TBAX; X = Cl, Br, or I), nonpolar benzene, water, and sodium halide (NaX) has been examined in detail. According to their constituents, compositions, and temperatures, the four-component systems afforded from single- to four-phase states. There were at least three kinds of liquid phases: a TBAX-rich phase (M), an aqueous solution phase (W), and an oil solution phase (O). In the M phase, TBAX was assumed to form aggregates, like microemulsions, while, in the latter two solution phases, TBAX was present without any aggregated form. When these three liquid phases coexisted, an O–M–W three-liquid-phase equilibrium state occurred. Depending on the temperature and NaX concentration in the W phase, the system changed its state from the O–M–W to the O–M or M–W two-liquid-phase. In some cases, a solid TBAX phase (Q) or solid NaX phase (S) coexisted with these liquid phases. In the presence of excess sodium halide, an O–M–W–S four-phase state was often observed due to the solid sodium halide being precipitated as a solid phase. These phase-separation phenomena were explained based on the amphiphilic nature of the quaternary salts, which bore some resemblance to the surfactant properties.

Tetrabutylammonium salt is one of the most popular catalysts used for various phase-transfer catalysis (PTC) under "liquid–liquid" two-phase conditions.[1—5] The recent development of PTC studies has implied 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.[6—15] Any kinetic study on PTC necessitates clarifying the macroscopic phase behavior of the system and the microstructure formed by the catalysts residing in each layer before elucidating the PTC mechanism on a molecular basis. In a preceding paper,[16] we revealed the existence of two types of aggregates that are formed by tetrabutylammonium salt (TBAX; X = Cl, Br, or I), that is, Om in benzene and Wm in aqueous solution. The Om (Wm) phase is formed above a certain concentration of TBAX when water (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 a microemulsion phase (M phase), which contains benzene and water beyond the amounts of their mutual miscibility.

The usual PTC system contains 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. Thus, in this article, we examine the phase behavior of four-component systems, TBAX/benzene/water/NaX (X = Cl, Br, or I). We used benzene as an oil because it was reported that active catalysts work better in nonpolar oils rather than in polar oils.[6]

We show that, depending on the experimental conditions, various type of phase separation occurs for these four-component systems and their phase behaviors are discussed using the parameters that control surfactant systems.

## Experimental

**Materials and Equipments.** Decyl methanesulfonate was prepared by the reaction of methanesulfonyl chloride with 1-decanol in pyridine.[17] Tetrabutylammonium chloride (TBACl, Tokyo-Kasei, > 98%), tetrabutylammonium bromide (TBABr, Tokyo-Kasei, > 99.0%), tetrabutylammonium iodide (TBAI, Nacalai, polarographic grade), tetrametylammonium chloride (TMACl, Tokyo-Kasei, > 98.0%), tetrametylammonium bromide (TMABr, Tokyo-Kasei, > 98%), and tetrametylammonium iodide (TMAI, Tokyo-Kasei, > 98%) were purchased and used without further purification. Benzene was purified by distillation from sodium diphenylketyl under nitrogen. Deionized water was used throughout the experiments. $^1$H NMR spectra were recorded on a JEOL EX-270 spectrometer or 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.** Prescribed amounts of a quaternary salt (TBAX), NaX, 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 by a tube shaker, and the tube was transferred to a temperature-controlled bath maintained at 60.0±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 tube containing a mixture, the composition of which was estimated to be very close to that of the phase-transition boundary, was transferred to a temperature-

Table 1. Typical Compositions in Weight Fraction at Which Phase Transition Took Place at 60 °C

TBABr / benzene / water system

| Transition type | TBABr | Benzene | Water | Note |
|---|---|---|---|---|
| O / O-W | 0 | 0.998 | 0.002 | Fig. 1 |
| M / O-M | 0.009 | 0.988 | 0.003 | Fig. 1 |
| M / O-M | 0.084 | 0.911 | 0.005 | Fig. 1 |
| M / O-M | 0.084 | 0.911 | 0.005 | Fig. 1 |
| M / O-M | 0.262 | 0.719 | 0.019 | Fig. 1 |
| M / O-M | 0.356 | 0.61 | 0.034 | Fig. 1 |
| M / O-M | 0.423 | 0.521 | 0.056 | Fig. 1 |
| M / O-M | 0.478 | 0.427 | 0.095 | Fig. 1 |
| M / O-M | 0.301 | 0.062 | 0.637 | Fig. 1 |
| M / O-M | 0.205 | 0.04 | 0.755 | Fig. 1 |
| W / O-W | 0 | 0.021 | 0.979 | Fig. 1 |
| M / O-M | 0.567 | 0.107 | 0.326 | Fig. 1 |
| M / O-M | 0.576 | 0.243 | 0.181 | Fig. 1 |
| M / O-M | 0.613 | 0.123 | 0.264 | Fig. 1 |
| M / O-M | 0.622 | 0.139 | 0.239 | Fig. 1 |
| M / O-M | 0.624 | 0.181 | 0.195 | Fig. 1 |
| M / O-M | 0.581 | 0.277 | 0.142 | Fig. 1 |
| M / O-M | 0.201 | 0.778 | 0.021 | Fig. 1 |
| M / O-M | 0.468 | 0.473 | 0.059 | Fig. 1 |
| M / O-M | 0.543 | 0.356 | 0.101 | Fig. 1 |
| M / O-M | 0.592 | 0.258 | 0.15 | Fig. 1 |

TBAI / benzene / water system

| Transition type | TBAI | Benzene | Water | Note |
|---|---|---|---|---|
| M-Q / M | 0.661 | 0.282 | 0.057 | Fig. 2 |
| M-Q / M | 0.251 | 0.748 | 0.001 | Fig. 2 |
| M-Q / M | 0.497 | 0.495 | 0.008 | Fig. 2 |
| M / O-M | 0.249 | 0.74 | 0.011 | Fig. 2 |
| M / O-M | 0.181 | 0.815 | 0.004 | Fig. 2 |
| O-M / O-M-W | 0.18 | 0.808 | 0.012 | Fig. 2 |
| O-M / O-M-W | 0.248 | 0.736 | 0.016 | Fig. 2 |
| M / M-W | 0.723 | 0.13 | 0.147 | Fig. 2 |
| M / M-W | 0.645 | 0.275 | 0.08 | Fig. 2 |
| M / M-W | 0.459 | 0.456 | 0.085 | Fig. 2 |
| M-W / O-M-W | 0.042 | 0.136 | 0.822 | Fig. 2 |
| M-W / O-M-W | 0.231 | 0.346 | 0.423 | Fig. 2 |
| M-W / O-M-W | 0.375 | 0.564 | 0.061 | Fig. 2 |
| O-W / O-M-W | 0.015 | 0.45 | 0.535 | Fig. 2 |
| W-Q / W | 0.047 | 0 | 0.953 | Fig. 2 |
| M-W / Q-M-W | 0.153 | 0.017 | 0.83 | Fig. 2 |
| M-W / Q-M-W | 0.048 | 0.01 | 0.942 | Fig. 2 |
| M-W / Q-M-W | 0.456 | 0.11 | 0.434 | Fig. 2 |
| O / O-W | 0 | 0.998 | 0.002 | Fig. 2 |
| W / O-W | 0 | 0.021 | 0.979 | Fig. 2 |
| O / O-Q | 0.038 | 0.962 | 0 | Fig. 2 |

TBACl / benzene / water system

| Transition type | TBACl | Benzene | Water |
|---|---|---|---|
| M / O-M | 0.484 | 0.23 | 0.286 |
| M / O-M | 0.08 | 0.914 | 0.006 |
| M / O-M | 0.21 | 0.066 | 0.724 |
| M / O-M | 0.289 | 0.119 | 0.592 |
| O / O-W | 0 | 0.998 | 0.002 |
| W / O-W | 0 | 0.021 | 0.979 |

TBABr / water / NaBr system

| Transition type | TBABr | Water | NaBr | Note |
|---|---|---|---|---|
| W / Wm-W | 0.016 | 0.489 | 0.495 | Fig. 3 |
| W / Wm-W | 0.023 | 0.609 | 0.368 | Fig. 3 |
| W / Wm-W | 0.048 | 0.634 | 0.318 | Fig. 3 |
| Wm / Wm-W | 0.661 | 0.233 | 0.106 | Fig. 3 |
| Wm / Wm-W | 0.559 | 0.334 | 0.107 | Fig. 3 |
| Wm / Wm-W | 0.444 | 0.428 | 0.128 | Fig. 3 |
| Wm / Wm-W | 0.385 | 0.465 | 0.15 | Fig. 3 |
| Wm / Wm-W | 0.323 | 0.51 | 0.167 | Fig. 3 |
| Wm / Wm-W | 0.279 | 0.541 | 0.18 | Fig. 3 |
| Wm / Wm-W | 0.243 | 0.561 | 0.196 | Fig. 3 |
| Wm / Wm-W | 0.203 | 0.591 | 0.206 | Fig. 3 |
| Wm / Wm-W | 0.118 | 0.623 | 0.256 | Fig. 3 |
| Wm / Wm-W | 0.093 | 0.619 | 0.288 | Fig. 3 |
| Wm-W / Wm-W-S | 0.432 | 0.279 | 0.289 | Fig. 3 |
| Wm-W / Wm-W-S | 0.337 | 0.319 | 0.344 | Fig. 3 |
| Wm-W / Wm-W-S | 0.256 | 0.348 | 0.396 | Fig. 3 |
| Wm-W / Wm-W-S | 0.162 | 0.384 | 0.454 | Fig. 3 |
| Wm-W / Wm-W-S | 0.068 | 0.422 | 0.51 | Fig. 3 |
| Wm-W / Wm-W-S | 0.675 | 0.197 | 0.128 | Fig. 3 |
| Wm-S / Wm-W-S | 0.528 | 0.118 | 0.354 | Fig. 3 |
| Wm-S / Wm-W-S | 0.695 | 0.174 | 0.131 | Fig. 3 |
| Wm / Wm-S | 0.731 | 0.169 | 0.099 | Fig. 3 |
| W / W-S | 0 | 0.448 | 0.552 | Fig. 3 |

TBACl / water / NaCl system

| Transition type | TBACl | Water | NaCl |
|---|---|---|---|
| Wm / Wm-W | 0.456 | 0.462 | 0.082 |
| W / Wm-W | 0.369 | 0.536 | 0.095 |
| W / Wm-W | 0.176 | 0.666 | 0.158 |
| W / Wm-W | 0.102 | 0.718 | 0.18 |
| W / Wm-W | 0.055 | 0.737 | 0.208 |
| W / Wm-W | 0.025 | 0.731 | 0.244 |
| Wm-W / Wm-W-S | 0.053 | 0.71 | 0.237 |
| W / W-S | 0 | 0.728 | 0.272 |

TBAI / water / NaI system at 70 °C

| Transition type | TBAI | Water | NaI |
|---|---|---|---|
| Q-Wm-W / Wm-W | 0.1013 | 0.8197 | 0.079 |
| Q-Wm-W / Wm-W | 0.0413 | 0.8549 | 0.1038 |
| W / Wm-W | 0.097 | 0.903 | 0 |
| Wm / Wm-W | 0.776 | 0.224 | 0 |

TBACl / benzene / water / NaCl system

| Transition type | TBACl | Benzene | Water | NaCl | Note |
|---|---|---|---|---|---|
| M / O-M | 0.503 | 0.222 | 0.275 | 0 | Fig. 6a |
| O-M / O-M-W | 0.44 | 0.248 | 0.301 | 0.011 | Fig. 6a |
| O-M(W) / O-M-W | 0.079 | 0.388 | 0.467 | 0.066 | Fig. 6a |
| O-M(W) / O-M-W | 0.047 | 0.396 | 0.479 | 0.078 | Fig. 6a |
| O-W / O-M-W | 0.025 | 0.399 | 0.475 | 0.101 | Fig. 6a |
| O-W / O-M-W | 0.022 | 0.402 | 0.476 | 0.1 | Fig. 6a |
| O-M / O-M-W | 0.379 | 0.281 | 0.326 | 0.014 | Fig. 6a |
| O-M / O-M-W | 0.346 | 0.295 | 0.341 | 0.018 | Fig. 6a |
| O-M / O-M-W | 0.279 | 0.324 | 0.374 | 0.023 | Fig. 6a |
| O-M / O-M-W | 0.198 | 0.358 | 0.409 | 0.035 | Fig. 6a |
| M-W / O-M-W | 0.446 | 0.242 | 0.289 | 0.023 | Fig. 6a |
| M-W / O-M-W | 0.438 | 0.244 | 0.29 | 0.028 | Fig. 6a |
| M-W / M-W-S | 0.504 | 0.213 | 0.257 | 0.026 | Fig. 6a |
| M-W / M-W-S | 0.433 | 0.241 | 0.287 | 0.039 | Fig. 6a |
| M / M-S | 0.707 | 0.12 | 0.155 | 0.018 | Fig. 6a |
| M-S / M-W-S | 0.547 | 0.192 | 0.233 | 0.028 | Fig. 6a |
| O-M-W / O-M-W-S | 0.336 | 0.268 | 0.333 | 0.063 | Fig. 6a |
| O-M-W / O-M-W-S | 0.291 | 0.286 | 0.348 | 0.075 | Fig. 6a |
| O-M-W / O-M-W-S | 0.212 | 0.31 | 0.377 | 0.101 | Fig. 6a |
| O-M-W / O-M-W-S | 0.149 | 0.329 | 0.403 | 0.119 | Fig. 6a |
| O-M-W / O-M-W-S | 0.075 | 0.364 | 0.438 | 0.123 | Fig. 6a |

Table 1. (Continued)

| | | | | | |
|---|---|---|---|---|---|
| O-M-W / O-M-W-S | 0.073 | 0.365 | 0.441 | 0.121 | Fig. 6a |
| O-M-W / O-M-W-S | 0.036 | 0.371 | 0.448 | 0.145 | Fig. 6a |
| M-W-S / O-M-W-S | 0.379 | 0.247 | 0.292 | 0.082 | Fig. 6a |
| M-W-S / O-M-W-S | 0.4 | 0.248 | 0.304 | 0.048 | Fig. 6a |

TBABr / benzene / water / NaBr system

| Transition type | TBABr | Benzene | Water | NaBr | Note |
|---|---|---|---|---|---|
| O-M / O-M-W | 0.038 | 0.409 | 0.465 | 0.088 | Fig. 6b |
| O-M / O-M-W | 0.076 | 0.414 | 0.47 | 0.04 | Fig. 6b |
| O-M / O-M-W | 0.35 | 0.292 | 0.346 | 0.012 | Fig. 6b |
| O-M / O-M-W | 0.032 | 0.397 | 0.473 | 0.098 | Fig. 6b |
| M / O-M | 0.54 | 0.211 | 0.249 | 0 | Fig. 6b |
| M / M-S | 0.767 | 0.09 | 0.117 | 0.026 | Fig. 6b |
| M / M-S | 0.711 | 0.108 | 0.138 | 0.043 | Fig. 6b |
| M-W / O-M-W | 0.502 | 0.225 | 0.266 | 0.007 | Fig. 6b |
| M-W / O-M-W | 0.454 | 0.232 | 0.276 | 0.038 | Fig. 6b |
| M-W / O-M-W | 0.412 | 0.239 | 0.293 | 0.056 | Fig. 6b |
| M-W / O-M-W | 0.387 | 0.249 | 0.307 | 0.057 | Fig. 6b |
| M-W / O-M-W | 0.253 | 0.259 | 0.326 | 0.162 | Fig. 6b |
| M-W / O-M-W | 0.229 | 0.25 | 0.312 | 0.209 | Fig. 6b |
| M-W / O-M-W | 0.168 | 0.252 | 0.315 | 0.265 | Fig. 6b |
| M-W / O-M-W | 0.148 | 0.251 | 0.314 | 0.287 | Fig. 6b |
| M-W / O-M-W | 0.298 | 0.256 | 0.299 | 0.147 | Fig. 6b |
| M-W / M-W-S | 0.63 | 0.134 | 0.171 | 0.065 | Fig. 6b |
| M-W / M-W-S | 0.433 | 0.161 | 0.208 | 0.198 | Fig. 6b |
| M-W / M-W-S | 0.37 | 0.175 | 0.226 | 0.229 | Fig. 6b |
| M-W / M-W-S | 0.36 | 0.18 | 0.23 | 0.23 | Fig. 6b |
| M-W / M-W-S | 0.204 | 0.222 | 0.277 | 0.297 | Fig. 6b |
| M-W / M-W-S | 0.194 | 0.222 | 0.278 | 0.306 | Fig. 6b |
| M-W / M-W-S | 0.139 | 0.236 | 0.294 | 0.331 | Fig. 6b |
| O-M-W / O-M-W-S | 0.05 | 0.271 | 0.308 | 0.371 | Fig. 6b |
| M-W-S / O-M-W-S | 0.116 | 0.238 | 0.294 | 0.352 | Fig. 6b |
| O-W / O-W-S | 0 | 0.273 | 0.334 | 0.393 | Fig. 6b |

TBAI / benzene / water / NaI system

| Transition type | TBAI | Benzene | Water | NaI | Note |
|---|---|---|---|---|---|
| O-W / O-M-W | 0.015 | 0.45 | 0.535 | 0 | Fig. 6c |
| O-W / O-M-W | 0.014 | 0.449 | 0.534 | 0.003 | Fig. 6c |
| M-W / O-M-W | 0.231 | 0.346 | 0.423 | 0 | Fig. 6c |
| M-W / O-M-W | 0.152 | 0.275 | 0.334 | 0.239 | Fig. 6c |
| M-W / O-M-W | 0.092 | 0.237 | 0.283 | 0.388 | Fig. 6c |
| M-W / M-W-S | 0.413 | 0.229 | 0.262 | 0.096 | Fig. 6c |
| M-W / M-W-S | 0.401 | 0.235 | 0.27 | 0.094 | Fig. 6c |
| M-W / M-W-S | 0.359 | 0.233 | 0.266 | 0.142 | Fig. 6c |
| M-W / M-W-S | 0.158 | 0.216 | 0.247 | 0.379 | Fig. 6c |
| M-W / M-W-S | 0.117 | 0.207 | 0.236 | 0.44 | Fig. 6c |
| M-W / M-W-S | 0.079 | 0.197 | 0.226 | 0.498 | Fig. 6c |
| M-W-S / O-M-W-S | 0.046 | 0.199 | 0.228 | 0.527 | Fig. 6c |
| O-M-W / O-M-W-S | 0.046 | 0.2 | 0.23 | 0.524 | Fig. 6c |
| M / M-Q | 0.799 | 0.098 | 0.103 | 0 | Fig. 6c |
| M / M-W | 0.723 | 0.13 | 0.147 | 0 | Fig. 6c |

TBABr / decane / water / NaBr system

| Transition type | TBABr | Decane | Water | NaBr | Note |
|---|---|---|---|---|---|
| M / M-Q | 0.906 | 0.038 | 0.056 | 0 | Fig. 7 |
| M / O-M | 0.753 | 0.102 | 0.145 | 0 | Fig. 7 |
| M / M-S | 0.839 | 0.038 | 0.052 | 0.071 | Fig. 7 |
| O-M / O-M-S | 0.72 | 0.098 | 0.138 | 0.044 | Fig. 7 |
| M-S / O-M-S | 0.68 | 0.08 | 0.114 | 0.126 | Fig. 7 |
| O-M / O-M-W | 0.333 | 0.238 | 0.335 | 0.094 | Fig. 7 |
| O-M / O-M-W | 0.287 | 0.251 | 0.356 | 0.106 | Fig. 7 |
| O-M / O-M-W | 0.094 | 0.307 | 0.433 | 0.166 | Fig. 7 |
| O-M / O-M-W | 0.081 | 0.31 | 0.437 | 0.172 | Fig. 7 |
| O-W / O-M-W | 0.013 | 0.301 | 0.422 | 0.264 | Fig. 7 |
| O-W / O-M-W | 0.006 | 0.293 | 0.404 | 0.297 | Fig. 7 |
| O-W / O-M-W | 0.003 | 0.277 | 0.385 | 0.335 | Fig. 7 |
| O-M-S / O-M-W-S | 0.628 | 0.113 | 0.159 | 0.1 | Fig. 7 |
| O-M-S / O-M-W-S | 0.613 | 0.115 | 0.159 | 0.113 | Fig. 7 |
| O-M-W / O-M-W-S | 0.589 | 0.132 | 0.185 | 0.094 | Fig. 7 |
| O-M-W / O-M-W-S | 0.534 | 0.131 | 0.184 | 0.151 | Fig. 7 |
| O-M-W / O-M-W-S | 0.221 | 0.194 | 0.274 | 0.311 | Fig. 7 |
| O-M-W / O-M-W-S | 0.181 | 0.207 | 0.292 | 0.32 | Fig. 7 |
| O-M-W / O-M-W-S | 0.585 | 0.129 | 0.178 | 0.108 | Fig. 7 |

variable oil or water bath. The temperature of the system was raised or lowered at a rate of 1 °C $min^{-1}$ in such a way that the number of phases of the system was increased. The temperature of the phase transition was read when either liquid phase became turbid. The composition of the mixture was then slightly varied by adding a small amount of one component or a homogeneous solution with a given concentration. When a phase transition took place at a temperature of 60.0±0.5 °C, the composition was used as that of the phase-transition boundary at 60 °C. The composition uncertainty was ±0.005 in weight fraction.

When a phase transition involved the appearance or disappearance of a solid phase, the temperature of the system was raised and the temperature was read when the solid totally disappeared. The composition was varied until the phase transition took place at a temperature of 60.0±0.5 °C.

Typical data of phase transitions for three- or four-component systems are given in Table 1.

**Phase Volume.** To measure the volume of each separated phase, a graduated tube with a ground joint, of which the maximum volume was either 5.0 mL or 10.0 mL, was used. After a heterogeneous mixture (total volume of 1 to 3 mL) was vigorously stirred with a tube shaker, it was allowed to stand in a temperature-controlled bath maintained at a given temperature. The volume of each phase was read after the phases clearly separated. The uncertainty of the volume measurement was ±0.02 mL. If it took more than an hour to equilibrate the system, a 10 mL screw-capped test tube was used. The tube was calibrated prior to use. After the volume of each layer was measured at one composition, a given amount of one component or a homogeneous mixture was added to vary the composition. In this case, the uncertainty of the volume measurement was ±0.05 mL. Therefore, the uncertainty of the calculated volume fraction was estimated to be ±0.05. Without measuring the composition of each phase, the type of phase separation could be easily judged by measuring the change in the volume ratio of the separated phases.

**Phase Composition.** Quantitative analyses of the composition in a phase were performed through $^1$H NMR. To analyze a water-rich layer, deuterized water was used to prepare an equilibrated mixture. The molar and weight ratios of the components were calculated based on the residual proton of the deuterized solvent as a reference. To analyze a TBAX-rich layer or a benzene-rich layer, an aliquot of the layer was added to a given amount of methanol-$d_4$ and the composition of the layer was determined based on the residual proton in the methanol. To analyze the water-rich layer of the three-component system that did not contain NaX, methanol-$d_4$ was also used to determine the concentration of TBAX in the phase. Besides a NMR analysis, the total halide ion concentration in the

oil-rich phase or in the TBAX-rich phase was determined by a GLC analysis of decyl halide that was formed by the reaction of decyl methanesulfonate with an aliquot of the halide-containing phase. The water content was also determined by Karl–Fisher titration.

## Results and Discussion

**Phase Equilibrium of TBAX/Benzene/Water Three-Component Systems.** A heterogeneous benzene–water mixture could be transformed to a homogeneous solution by adding a certain amount of a quaternary salt. We define the resulting homogeneous liquid phase as the M phase. An addition of TBAX (X = Cl, Br, and I) to benzene/water mixture (1 : 1 volume ratio) formed an M phase at 60 °C when the weight fraction of TBAX became higher than 0.49 (Cl), 0.63 (Br), and 0.73 (I), respectively. The minimum amount of quaternary salt required for the transformation strongly depended on the water–oil ratio. As shown in Fig. 1, the system of TBABr/benzene/water at 60 °C afforded an M phase region, under which a broad liquid–liquid two-phase region was observed. Hypothetical phase boundary lines are also drawn by dotted lines in the diagram. The M-phase region was attached to both the zero oil line and to the zero water line via two narrow regions (Wm and Om),[16] where the system would be assumed to be homogeneous, even in the absence of TBABr. Two dotted lines that hypothetically separate the M phase from the Wm and Om phases were drawn by connecting the TBABr corner with the two points corresponding to the benzene–water mutual miscibility. The tie lines in the 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). Similar phase diagrams have been reported for ternary liquid systems, such as ethanol/benzene/water or acetic acid/benzene/water systems.[18–20] The difference was the slope of the tie lines, which became very steep with a decreasing water content for this system. This means that the composition of the O phase varies little and TBABr is predominantly partitioned to the lower layer (M). Thus, an incremental addition of TBABr to a benzene/water system increases the volume of the bottom layer and its TBABr content, while the volume of the upper layer (O) decreases with a small change in its composition. It was impossible to determine whether and where a plait point is present. However, the most right-hand tie line obtained in the O–M region shows that the TBABr weight fraction in the O phase was as low as 0.001. We could not observe any tie lines below this water content. The position of the plait point is therefore near to the benzene corner, if present. An addition of water to a given TBABr solution in benzene thus leads to a phase separation of type O–M unless the TBABr concentration is too low. Further addition of water decreases the volume and oil content of the bottom layer (M). Therefore, the phase separation induced by the water addition is caused not by a simple saturation of water in the TBABr-containing benzene, but by the liberation of excess benzene from the M phase. On the other hand, the phase separation induced by the addition of benzene to a TBABr aqueous solution is caused by the liberation of excess benzene, leading to the formation of O–M (or O–W when TBABr content is low). The W phase is distinguished from the Wm phase because the former is unable to contain an excess amount of benzene beyond the mutual solubility between water and benzene.

The three-component system of TBACl/benzene/water at 60 °C was assumed to give a phase diagram similar to that of TBABr/benzene/water (Table 1). However, the phase diagram of TBAI/benzene/water at 60 °C was greatly different. As shown in Fig. 2, there is a broad region of a three-liquid-phase region of O–M–W, above which a two-liquid-phase region (M–W) is present. The regions of an O phase and a W phase were confined to the vicinities of the benzene and water corners, respectively. There is a distinct O–W region below

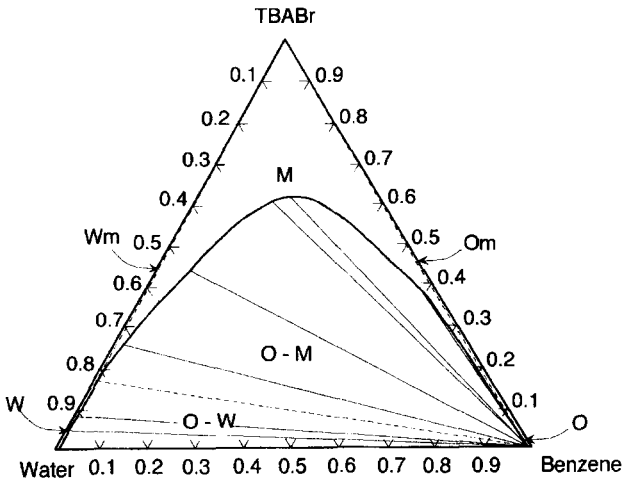



Fig. 1. Phase diagram of a TBABr/benzene/water ternary system at 60 °C. The composition is shown in weight fraction of component. A dashed line shows a hypothetical boundary that divides a liquid–liquid two-phase between O–M and O–W regions. The lines in O–M or O–W regions represent tie lines actually obtained by NMR analyses of the coexisting two phases.

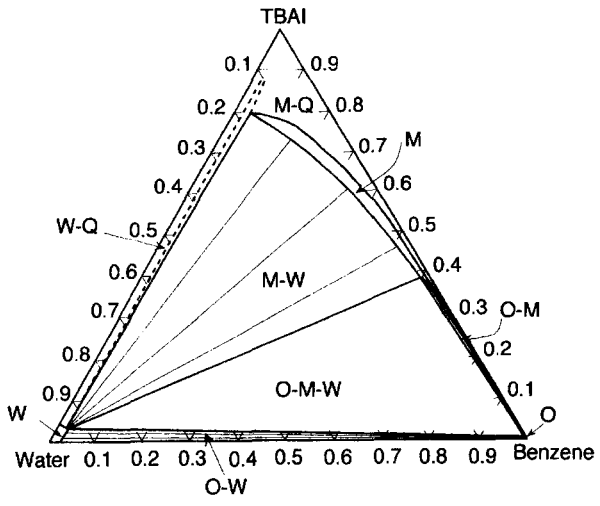



Fig. 2. Phase diagram of a TBAI/benzene/water ternary system at 60 °C. The composition is shown in weight fraction of component. The tie lines in M–W and O–W regions were drawn based on NMR analyses of the W phase.

the O–M–W region. In addition, we find a narrow M-phase region that is extended to the benzene corner while the region is attached neither to the zero oil line nor to the zero water line. There is a very narrow O–M region that is adjacent to the O–M–W and M regions. The occurrence of an O–M–W state clearly shows that the presence of an inorganic salt is not always a prerequisite for forming a so-called "third liquid phase." 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 (TBAI, benzene, water) by weight fraction was O ($< 0.01$, $> 0.99$, $< 0.01$), M (0.39, 0.59, 0.02), and W (0.02, 0.02, 0.96). Because the solubility of TBAI is low at 60 °C both in water and in benzene,[16] there were liquid-solid two-phase regions, W–Q and O–Q (M–Q), which were adjacent to the zero oil line and to the zero water line, respectively.

**Phase Diagram of TBAX/Water/NaX Three-Component Systems.** A phase diagram of the TBABr system at 60 °C is shown in Fig. 3. There is a wide liquid–liquid two-phase Wm–W region, above which a three-phase Wm–W–S region is present. The S phase is solid sodium halide. The Wm phase is an aqueous liquid that richly contains quaternary salts. This phase is able to imbibe a certain amount of benzene beyond the mutual solubility between water and benzene. The W phase is another aqueous liquid that contains most of the added NaX, while the content of TBAX is much lower than the Wm phase. Approximate tie lines are drawn by dashed lines based on the change in the relative volumes of the coexisting W and Wm phases. The bending point, n′, on the boundary line kn′w′ probably corresponds to a plait point of Wm–W. At a critical point of k, the Wm phase contacts to the Wm–W–S three-phase region. TBACl gave a similar diagram though the w′ point is closer to water corner in its position due to a low solubility of NaCl in water. Correspondingly, the regions of Wm–W and Wm–W–S shifted downward (Table 1). At temperatures higher than 70 °C, TBAI was assumed to give a similar diagram, except that a Wm–W region was attached to the zero NaI line and a Q–W or Q–Wm–W region was present above the Wm–W region. The W phase is not continuous to the Wm phase irrespective of the NaI content. At temperatures lower than 70 °C, the three-component system of TBAI/water/NaI was too complex to draw a diagram, because the solid TBAI phase coexisted with solid NaI over a wide area of the compositions.

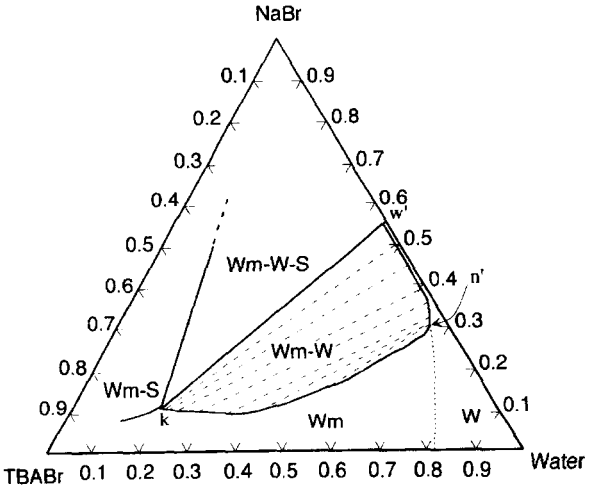



Fig. 3. Phase diagram of a TBABr/water/NaBr ternary system at 60 °C. The composition is shown in weight fraction of component. The dashed tie lines in Wm–W region was estimated based on the change in the volume ratio of the coexisting two phases.

**Phase Equilibrium of Four-Component Systems.** Figures 4 and 5 show two examples of the typical change in state when we add NaBr to a TBABr/benzene/water three-component system. In Fig. 4, where the TBABr content is relatively low, the state is varied from O–M, through O–M–W, to O–M–W–S with an increasing amount of NaBr. The O–M–W–S four-phase equilibrium consisted of an almost pure oil phase (O), a TBAX-rich layer (M), an almost saturated NaX aqueous solution (W), and a solid NaX phase (S). Therefore, it is easily understood that the TBAX-rich phase

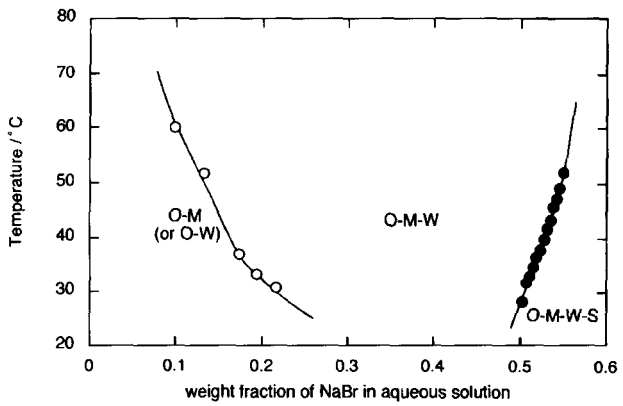



Fig. 4. Effect of NaBr on the phase transitions of TBABr/benzene/water/NaBr system. NaBr was added to the mixture of 0.5 mmol (0.162 g) of TBABr, 2.0 mL of benzene, and 1.0 mL of water.

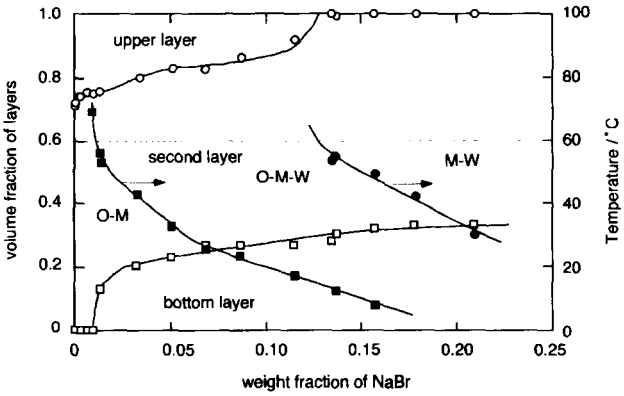
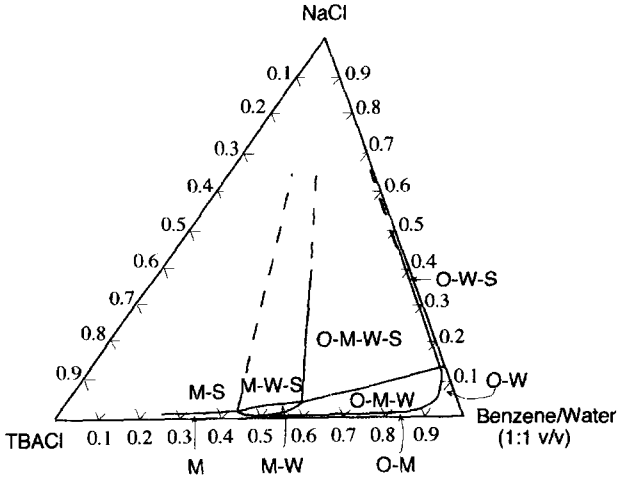



Fig. 5. Change in volume fractions among layers that coexist in a TBABr/benzene/water/NaBr system at 60 °C and temperature of phase transitions. NaBr was added to the mixture of 0.5 g of TBABr, 2.0 mL of benzene, and 2.0 mL of water.

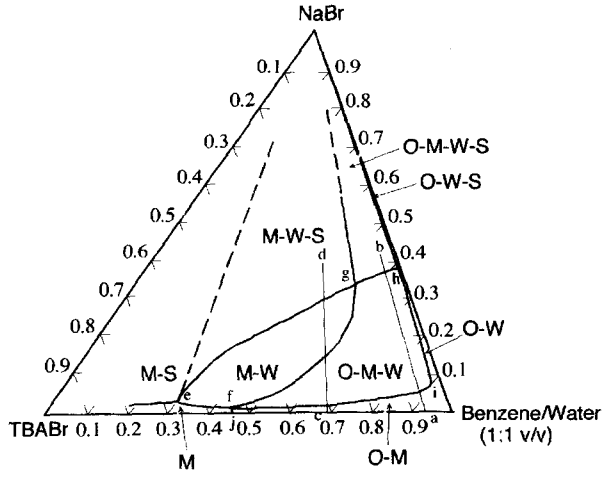
represented as the M phase in this paper coincides with the "third phase" of the PTC field. The state of the four-component system was also dependent on the temperature. The system tends to change its state from O–M to O–M–W with an increase in temperature. A different change in state is shown in Fig. 5, where the TBABr content was relatively high. The addition of NaBr induced a change in the state from O–M, through O–M–W, to M–W. The change in the volume ratio of each phase at 60 °C is also shown in Fig. 5. An aqueous phase (W) was suddenly liberated at a certain NaBr content from the lower M phase of an O–M state, resulting in the formation of an O–M–W equilibrium. The W phase exists as the bottom layer. The M–W type of phase separation appeared when the upper layer (O) of the O–M–W three-liquid-phase disappeared, as if it was absorbed into the middle layer (M). A further increase in NaBr resulted in the formation of a liquid–liquid–solid three-phase separation (M–W–S). An excess amount of solid NaBr was precipitated as an S phase. In this case, a four-phase equilibrium was never observed. With an increase in temperature, the system tends to change from O–M to O–M–W and from the O–M–W to the M–W state. Furthermore, the transition temperature from an O–M to O–M–W state or from an O–M–W to M–W state is lowered with an increase in the weight fraction of NaBr. The boundary line between O–M and O–M–W is closely related to the cloud point of the TBABr/NaBr aqueous solution system, though the cloud point was observed at much higher temperature and NaBr content.[16]

One composition of a four-component system is represented by a point within a regular tetrahedral diagram with four vertexes of the four components. It is possible to draw an arbitrary plane section of a tetrahedral diagram in order to show the phase diagram of the four-component system. The phase diagram of the TBAX/benzene/water three-component system, which we have already shown, is one of the base triangles. When an O–M–W–S four-phase body is present in the tetrahedral diagram, four three-phase bodies, that is, O–M–W, O–M–S, O–W–S, and M–W–S always appear. The four three-phase bodies should be adjacent to the corresponding triangle faces of the O–M–W–S tetrahedron. Six two-phase bodies (O–M, O–W, O–S, M–W, M–S, and W–S) which extend from the six edges of the O–M–W–S tetrahedron, are adjacent to the corresponding two three-phase bodies. Four single-phase bodies (O, M, W, and S), which extend from the vertexes of the O–M–W–S tetrahedron, are attached to the corresponding three-phase bodies at curved lines and two-phase bodies at curved surfaces.

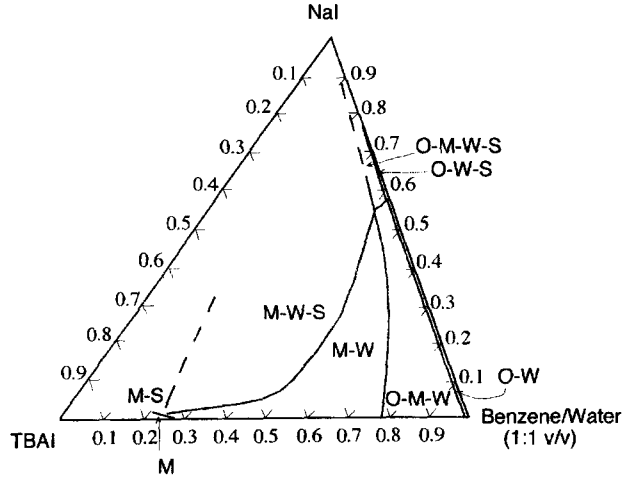
The phase- equilibrium state of the TBAX/benzene/water/NaX systems may be understood most clearly by a plane triangle that passes the NaX vertex, TBAX vertex, and the middle point of benzene–water line. The results at 60 °C are shown for the TBACl, TBABr, and TBAI systems in Figs. 6a, 6b, and 6c. The benzene/water volume ratio is fixed at 50 : 50. All systems of TBAX/benzene/water/NaX gave a liquid–liquid–liquid–solid four-phase equilibrium state (O–M–W–S). We found the same regions of equilibrium states in these phase diagrams, though the positions




(a) TBACl / Benzene / Water / NaCl




(b) TBABr / Benzene / Water / NaBr




(c) TBAI / Benzene / Water / NaI

Fig. 6. Phase diagram of a TBAX/benzene/water/NaX system at 60 °C. The benzene/water volume ratio is 50 : 50. The composition is shown in weight fraction of component. (a) TBACl/benzene/water/NaCl system. (b) TBABr/benzene/water/NaBr system. (c) TBAI/benzene/water/NaI system.

and areas of each equilibrium state were greatly different. There is a wide O–M–W–S area in the TBACl system. For the TBAI system, the M–W area was the widest among the three systems but the O–M–W–S area was the narrowest. An O–M–S three-phase region was never seen for the three diagrams, although the presence of the equilibrium state was easily clarified by adding water to a TBAX/benzene/NaX mixture. These results indicate that the M positions of the O–M–W–S four-phase body are all located at the benzene side of the plane section, and that the M position of the TBACl system is closest to the plane section. The difference observed among TBAX diagrams of Fig. 6 was that the regions of O–M–W and M–W of the TBAI system were attached to the base line, corresponding to the presence of an O–M–W region for a TBAI/benzene/water three-component system (Fig. 2). For the TBAI system, therefore, we could not find any O–M region in Fig. 6c.

Although it is not the main subject of this paper, the influence of oil is considerable to the phase behavior of a four-component system. In the corresponding plane section of the TBABr/decane/water/NaBr system, for example, there is a region of O–M–S instead of M–W–S that is adjacent to the O–M–W–S region (Fig. 7). The region of M–W disappeared from the diagram. These results mean the M composition of O–M–W–S phase equilibrium is located at the water-side of the plane section; the M phase is richer in water than in decane.

The three TBAX phase diagrams clearly show some other important facts. First, a certain amount of NaX is soluble in the M phases. Although the fact that the "third phase" in the phase-transfer system contains some amount of inorganic salt has already been pointed out by other reports,[7–10] the results in Fig. 6 indicate that the M phase does solubilize an inorganic salt irrespective of the presence of other phases. Even when tetramethylammonium salts, TMAX (X = Cl, Br, or I), were used instead of NaX, O–M–W–S four-phases were also formed. In these systems, the presence of TMAX in the M phase of an O–M–W–S system was readily ascertained by NMR analyses. There was a singlet peak corresponding to a methyl proton of the TMA cation.

Second, Fig. 6 shows that, according to the content of TBAX, the different types of changes in the state should be observed when NaX is added to a TBAX/benzene/water three-component system. It has been conventionally assumed that a phase-transfer catalytic system adopts either O–W or O–W–S equilibrium, where the quaternary salts in the oil layer are not in aggregated form. However, it is obvious that this is the case only when the content of TBAX is extremely small. Along the line ab in Fig. 6b, the state is varied from O–M, through O–M–W, to O–M–W–S with an increasing amount of NaBr. Along line cd, which corresponds to the change in Fig. 5, however, a different change in state was observed from O–M, through O–M–W, to M–W.

Putting together the information about some other sections enables us to draw a rough tetrahedral diagram. The system of TBABr/benzene/water/NaBr is shown schematically in Fig. 8. The thick dashed lines represent the loci of the M compositions of three-phase bodies. The plane-triangle section corresponding to Fig. 6b is also shown, in which each region is divided by dotted lines. The points e, f, g, h, i, and j are all present in this section and correspond to the points in Fig. 6b. The tie triangle in the M–W–S body moves from the M–W–S face (triangle mws) of the O–M–W–S tetrahedral body to the kw's triangle in the TBABr/water/NaBr three-component system with a decrease in the benzene content. The locus of the M composition is given by line 1, which passes along mek. The compositions of the W and S phases vary little, while the M phase changes its composition considerably, and finally turns to a Wm phase at extremely low contents of benzene. The locus of the M apex in the O–M–W

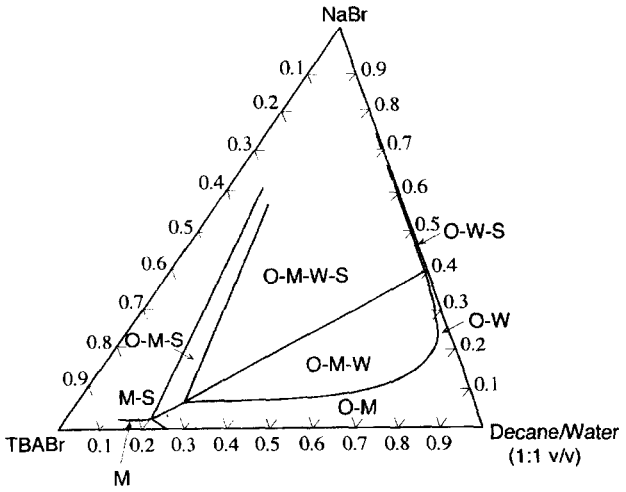



Fig. 7. Phase diagram of a TBABr/decane/water/NaBr system at 60 °C. The composition is shown in weight fraction of component. The decane/water volume ratio is 50 : 50.

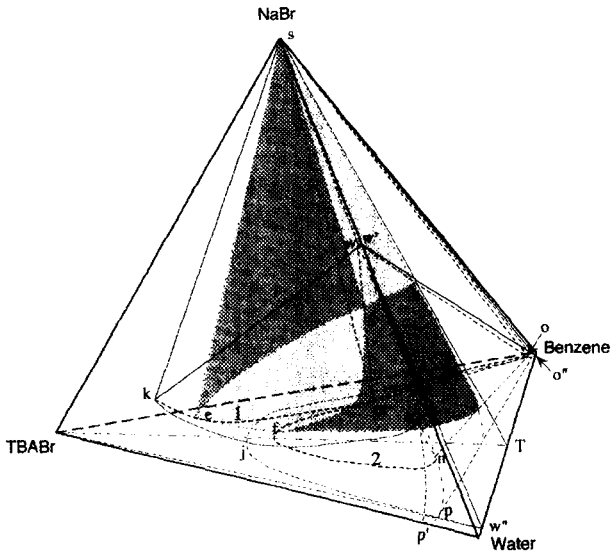



Fig. 8. Schematic representation of phase diagram of a TBABr/benzene/water/NaBr system at 60 °C. The loci of M phase composition of three three-phase bodies (M–W–S, O–M–W, and O–M–S) are given by lines, 1, 2, and 3, respectively.

body is shown by line 2 (mfn). The W apex of the tie triangle moves downward with a decreasing amount of NaBr along the wn line, while the apex O moves only slightly. The M and W vertexes of the O–M–W tie triangle fuses together at the n point and the M–W side disappears. Therefore, the composition of the "third phase" (M) varies considerably, particularly just after a "third phase" appears from O–M (or O–W) two-phase by the addition of NaX. The M composition of the tie triangle of the O–M–S body moves on line 3. It was impossible to determine whether the M–S and O–S sides of the tie triangle may fuse or not, because of an abrupt change in the volume of the M phase within a minimal change in the water content. The composition of the M phase of this O–M–S state also varies with the water content. The O–W–S three-phase body extends from the ows face of the O–M–W–S body to the o″w′s triangle in the benzene/water/NaBr three-component system. The composition of each phase varies little in this case. The five two-phase bodies (M–W, O–M, O–W, O–S, and W–S) and the three uniphase bodies (M, O, and W) are easily seen in Fig. 8. The M-phase body lies near to the base plane of TBABr/benzene/water system. It extends slightly upward along the surface of the O–M two-phase body, and contacts with the M–W two-phase body overlying it.

**Microstructure and Nature of the M Phase Formed by TBAX.** We have suggested the existence of two types of aggregates that are formed by TBAX: Om and Wm.[16] The Om phase (or Wm) is formed 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 (Fig. 1). As TBAX aggregates in the Om and Wm phases, it is reasonably assumed that TBAX also aggregates in the M phase. It may be anticipated that the microstructure (the aggregation form of TBAX) changes continuously from Om, through M to the Wm phase. In the M phase, the structure of the microemulsion may vary from w/o, via bicontinuous, to an o/w surface. There are two other homogeneous phases, an O phase and a W phase, in which TBAX is assumed to be present with a more-or-less non-aggregated form. The O phase hardly dissolves water beyond the mutual solubility between benzene and water, and vice versa for the W phase. In other words, the presence of TBAX hardly enhances the mutual solubility between benzene and water in these phases, probably due to being present almost as an isolated ion-pair in the O phase and as a dissociated form in the W phase. In fact, the $^1$H NMR water peak of an O phase with TBABr is coincident in position to that of water dissolved in pure benzene (0.46—0.60 ppm). In an M phase, however, the water peak considerably shifted to a lower field ranging from 1.4 to 2.95 ppm, depending on the TBABr and water concentrations. The bodies of these five liquid phases for the TBACl or TBABr system are continuous without any well-defined boundary in a tetrahedral diagram. However, it is clear that the Om and Wm phases never coexist. The M phase does not coexist with the Om or Wm phase either. The mixing of an M phase with an Om phase results in the formation of either another homogeneous phase (M or Om) with a different composition or a new O–M two-phase equilibrium. In the same way, the mixing of an M phase with a Wm phase forms either another uniphase (M or Wm) or a new O–M two-phase equilibrium. It is noted that these mixings never yield an M–W two-phase equilibrium.

An elevation of the temperature induces a separating-out of the W phase from the M phase and a mixing-in of the O phase to the M phase (Fig. 5). Therefore, a system tends to change its state from O–M, through O–M–W, to M–W with an increase in temperature. This behavior should be related to the change in the aggregate structure of TBAX in the M phase. It is well known that an elevation of temperature increases the value of the packing parameter, $pp$ ( = $v/al$), which has been used for an evaluation of phase behavior in surfactant chemistry.[21—23] The symbols of $v$, $l$, and $a$ represent the volume of the surfactant tail, the length of the tail, and the area of the surfactant head group, respectively. If this concept of a packing parameter is also applicable to our system, it is easy to explain the M-phase behavior. At high temperatures, the value of $pp$ is so large that TBAX prefers to form a w/o interface, suggesting the formation of oil-continuous microemulsions, such as reverse spherical or reverse rod-like structures. This facilitates more oil to be imbibed from the O phase. At low temperatures, TBAX may form an o/w interface due to a decrease in $pp$. Since TBAX has a relatively large $pp$ in itself, normal spherical micelles may not be formed, and other type of aggregates may be preferred. The effect of NaX has some resemblance to that of temperature. With an increase in the molar ratio of NaX to water in the M phase, the value of $pp$ increases and TBAX tends to prefer a w/o interface. The molar ratio is increased with the NaX concentration in a W phase that coexists with the M phase. Thus, an increase in the NaX content of a four-component system will transform an O–M–W equilibrium to an M–W equilibrium if the M phase can absorb all oil from the O phase.

On the other hand, an M phase also imbibes water from a W phase that coexists with the M phase. The amount was decreased with the NaX concentration of the W phase. The molar ratio of water to TBAX, the $R_w$ value, was reduced. The $R_w$ value is closely related to the minimum temperature above which the M phase is miscible with the O phase in any proportion.[16] Depending on the $R_w$ value, in other words, there is a certain limit to the amount of oil that the M phase can absorb. The water content in the M phase of an O–M–W three-phase reaches a minimum when the tie triangle approaches the triangle omw in Fig. 8 with an increasing NaX content. The $R_w$ value is ca. 1.4 at this point for TBABr, which is too high to insure complete miscibility between the O and M phases at 60 °C.[16] Phase separation takes place at low-weight fractions of TBABr. This is the reason why a TBAX/benzene/water/NaX system affords an O–M–W–S four-phase state. The four-phase body, therefore, locates at parts of lower TBAX contents in the tetrahedral diagram. If an inorganic salt has a high dehydrating power toward an

M phase, or if an oil has a high miscibility to an M phase, an O–M–W three-phase may be converted to an M–W two-phase by the addition of an inorganic salt, even at a very low content of quaternary salt. In a particular case, the transition would occur over the whole range of the quaternary salt concentration and, therefore, the O–M–W–S four-phase body would disappear from such a tetrahedral phase diagram.

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