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Tautomerization and Dissociation Equilibria of β-Diketones in Microemulsions

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The keto–enol tautomerization and dissociation equilibria of benzoylacetone, benzoyltrifluoroacetone, and 2-naphthoyltrifluoroacetone were studied in anionic, cationic, and nonionic microemulsions by means of UV spectrophotometry. The enol fraction in the microemulsions, which increased with an increase of the volume fraction of the organic components, was explained by the distribution model of the β-diketones between the pseudophases. The apparent dissociation constants in the cationic microemulsions were larger than those in the anionic or nonionic microemulsions. This result is discussed based on the distribution of the enolate form into the interphase, which was significantly affected by the surface charge of the microemulsions.

Microemulsions are microheterogeneous, optically transparent and thermodynamically stable liquids which are prepared by mixing water, a surfactant, a cosurfactant such as an alcohol and oil. They exist as oil in water, water in oil, or bicontinuous structures depending on the microemulsion composition. Recently, the characteristic properties of solvents of ionic and nonionic substances has attracted attention in both fundamental and practical fields of separation chemistry.[1,2] Recently, we reported the utility of o/w microemulsions as novel media in a capillary electrophoresis.[3] The solubilization phenomena in microemulsions, however, are still obscure and fundamental studies on the mechanisms of solubilization are now required.

In the present study, the nature of microemulsions from the solution behavior of β-diketones was examined. β-Diketone is known to show keto–enol tautomerism and the enol fraction at equilibrium reflects the nature of the microenvironment in the solvent in which it was dissolved. For example, it has been shown that the keto–enol equilibria of acetylacetone and *n*-alkyl substituted β-diketones can be used as an index of the solvent polarity of water–organic solvent mixtures.[4]

Experimental

Chemicals. Benzoylacetone (BA), Wako G.R., was purified by recrystallization three times from diethyl ether. Benzoyltrifluoroacetone (BFA), Wako G.R., was purified by sublimation under 2 mmHg (1 mmHg=133.322 Pa) at 35—38 °C. 2-Naphthoyltrifluoroacetone (NFA), Aldrich, was also purified by sublimation under 1 mmHg at 56—60 °C. The purity of these β-diketones was confirmed by melting point measurements. Sodium dodecyl sulfate (SDS), Wako biochemical grade, sodium bis-2-ethylhexylsulphosuccinate (Aerosol-OT, abbreviated as AOT), Wako, cetyltrimethylammonium bromide (CTAB), Nacalai G.R., and polyethylene glycol mono-*p*-octylphenyl ether (*n*≒10) (Triton X-100, abbreviated as TX100), Tokyo Kasei, were used as purchased. Heptane, Wako G.R., was fractionally distilled after treating with a mixture of sulfuric acid and nitric acid. Other chemicals used were of reagent grade. Water was purified by the Millipore Milli Q-II system.

Microemulsions were prepared by mixing a weighed amount of each component and the compositions were represented by the weight percent. The single phase microemulsion region in the phase diagram of SDS/1-butanol/heptane/water was confirmed at 25 °C by adding heptane to a mixture of the rest of the components (Fig. 1). The compositions of the representative microemulsions are listed in Table 1. The volume fraction of the organic components was calculated from the densities; 1.160 g cm^{-3} for SDS,[5] 0.806 g cm^{-3} for 1-butanol, 0.680 g cm^{-3} for heptane, 0.698 g cm^{-3} for octane, 1.029 g cm^{-3} for TX100, and 0.997 g cm^{-3} for CTAB.[6]

The pH measurements were carried out by a TOA HM-5B pH meter. UV spectra were recorded on a JASCO Uvidec 430 spectrophotometer. All of the measurements were carried out in a thermostated room controlled at 25±1 °C.

Results and Discussion

Equilibrium Fractions of Enol Forms. The spectra of the β-diketones showed two principal maxima in the UV

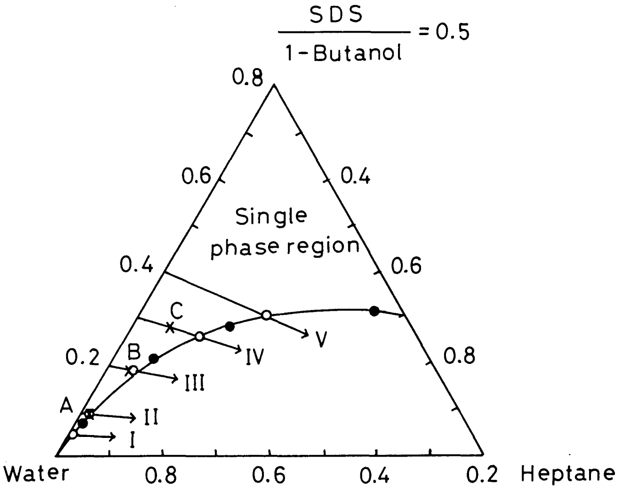

Fig. 1. Single phase microemulsion region in the phase diagram of water/SDS/1-butanol/heptane at 25 °C. Titration paths of heptane are shown by arrows I—V. Phase boundary is denoted by (○) from this work and (●) from Ref. 12. The SDS-ME A, B, and C are indicated by A, B, and C.

Table 1. Compositions of the Representative Microemulsions (wt%)

Microemulsions	H_2O	Surfactant	1-Butanol	Hydrocarbon
SDS-ME A	89.30	SDS 3.31	6.61	Heptane 0.80
SDS-ME B	76.02	SDS 6.34	12.67	Heptane 5.00
SDS-ME C	65.14	SDS 9.30	18.59	Heptane 6.97
TX100-ME	89.30	TX100 9.92	0	Octane 0.80
CTAB-ME	89.30	CTAB 3.31	6.61	Octane 0.80

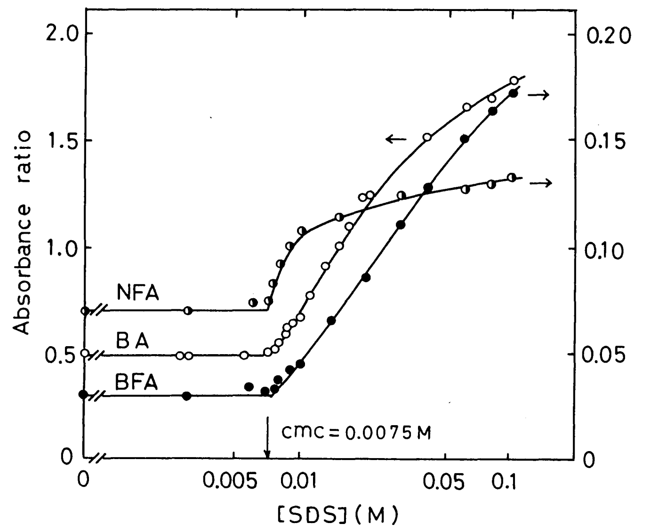

Fig. 2. Effect of SDS micellar solution on the absorbance ratio of the β-diketones. Absorbance ratio: A(315 nm)/A(250 nm) for BA, A(324 nm)/A(250 nm) for BFA and A(343 nm)/A(252 nm) for NFA.

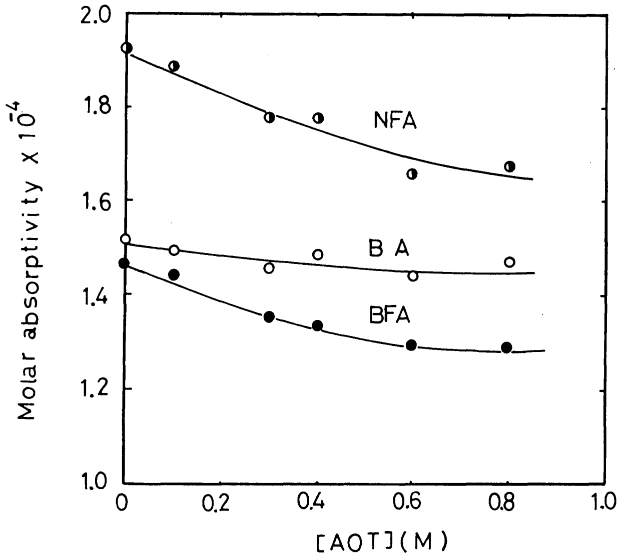

Fig. 3. Decrease of the apparent molar absorptivity of the β-diketones in AOT w/o microemulsions in a constant ratio of $[H_2O]/[AOT]=20$.

region. The maximum absorption around 300—350 nm was assigned to the enol form and the one around 250 nm to the sum of the enol, keto, and/or keto-solvated forms. The ratio of the two absorbance maxima reflected the degree of enolization. In Fig. 2, it is demonstrated that the absorbance ratio of the two maxima reflects the microstructure of the SDS solution through the preferential solubilization of the enol form into the micelles. This kind of experiment has previously been proposed as a spectrophotometric method for the determination of the cmc.[7] In the w/o microemulsions of AOT (AOT-ME), the increase of the microemulsion concentration at a constant ratio of $[H_2O]/[AOT]=20$ decreased the enol form as shown in Fig. 3.

The absorbance of β-diketones in the microheterogeneous systems is represented by the following equation, under acidic conditions in which the dissociation of the β-diketones is negligible,

$$A=\varepsilon_K\{[HL]_T-(E)(1-\phi-\phi_i)-(E)_o\phi\} + \varepsilon_E\{(E)(1-\phi-\phi_i)+(E)_o\phi\} \quad (1)$$

where ε_E and ε_K are, respectively, the molar absorptivities of the enol form and the keto and/or keto-solvated form, $[HL]_T$ is the total concentration of β-diketone in the whole system, (E) and $(E)_o$ are, respectively, the local concentrations of the enol form in pseudo-aqueous and pseudo-organic phases, and ϕ and ϕ_i are, respectively, the volume fractions of the pseudo-organic phase and the interphase between the pseudo phases. The medium effect on ε_K and ε_E and the adsorption of the enol form at the interphase are neglected in Eq. 1. The apparent enol fraction is defined and calculated by the next equation,

$$f(\mathrm{app})=\frac{(E)(1-\phi)+(E)_o\phi}{[HL]_T}=\frac{\varepsilon_a-\varepsilon_K}{\varepsilon_E-\varepsilon_K} \quad (2)$$

where ε_a equals $A/[HL]_T$ and $1-\phi \gg \phi_i$ is assumed.

In the o/w microemulsions of SDS (SDS-ME), the values of f(app) increased with an increase of heptane as shown in Fig. 4. The increment in the f(app) values with the addition of heptane is larger in the microemulsions with higher water contents. The f(app) values of the three β-diketones in the representative systems are listed in Table 2.

Considering the distribution equilibria of the β-diketones, HL, in the microheterogeneous systems, the distribution constant, $K_D=(HL)_o/(HL)$ and the adsorp-

Table 2. Apparent Enol Fractions and Distribution Parameters of β-Diketones in Microemulsions

Solvent	ϕ	BA			BFA[a)]				NFA[a)]		
		f(app)	K_D[b)]	$K_D'\phi_i$[c)]	f(app)	f_o	K_D[b)]	$K_D'\phi_i$[d)]	f(app)	f_o	$K_D'\phi_i$[e)]
0.10 M SDS	0.023	0.83	98	<0.1	0.11	1.0	51	8.4	0.13	1.0	1.9×10^2
0.44 M SDS	0.108	0.89	98	0.7	0.14	1.0	51	32	0.16	1.0	7.0×10^2
SDS-ME A	0.120	0.88	112	1.3	0.29	0.54	83	7.6	0.37	0.52	60
SDS-ME B	0.270	0.96	108	0.8	0.47	0.57	78	3.6	0.48	0.53	31
SDS-ME C	0.389	0.98	103	0.3	0.49	0.59	78	6.0	0.48	0.54	61
TX100-ME	0.107	0.81	112[f)]	2.3	0.22		—			—	
CTAB-ME	0.127	0.87	112[f)]	1.7	0.18		—			—	
AOT-ME	0.856	0.99	98	1.2	0.87	1.0	51	6.2	0.83	1.0	2.2×10^2

a) Aqueous solution contained 10^{-3} M $HClO_4$ (1 M=1 mol dm^{-3}). b) K_D values for SDS micelles and AOT-ME were approximated from those in heptane–water. c) f=0.325 and f_o=1.0 were used. d) f=0 was used. e) f=0 and K_D=1.26×10^3 (Ref. 11) were used. f) K_D value for SDS-ME A was assumed.

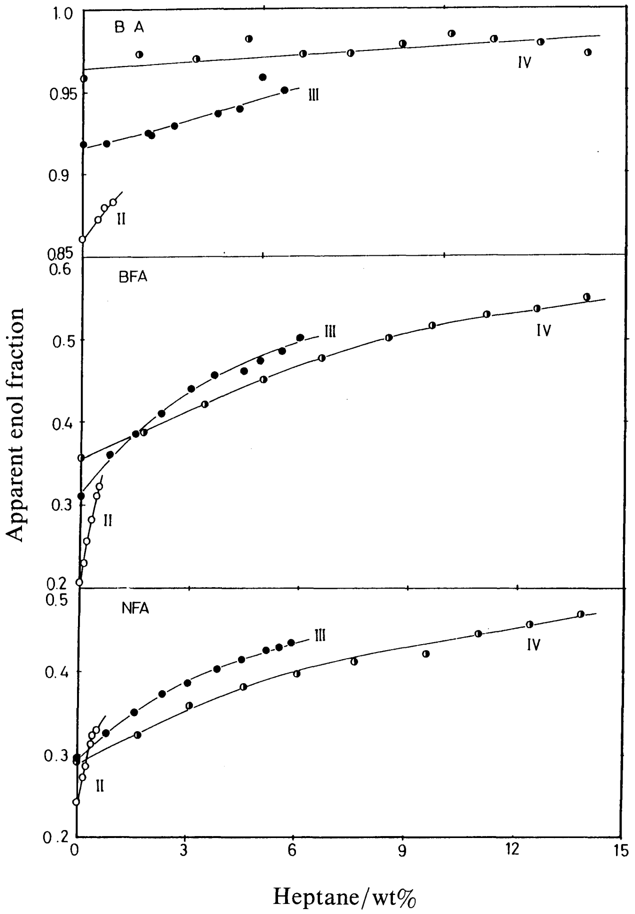

Fig. 4. Increase in the apparent enol fraction with heptane added along paths II, III, and IV, which are shown in Fig. 1.

tion constant, $K_D'=(HL)_i/(HL)$, of HL are defined, where the parentheses represent the pseudo-phase concentrations and the subscripts o and i refer to the pseudo-organic phase and the interphase between the pseudo-phases, respectively, and no subscript refers to the pseudo-aqueous phase. Then, Eq. 2 can be rewritten as,

$$f(\text{app}) = \frac{f(1-\phi)+f_oK_D\phi}{1-\phi+K_D\phi+K_D'\phi_i} \tag{3}$$

where f and f_o refer, respectively, to the enol fractions in the pseudo-aqueous phase and the pseudo-organic phase. Equation 3 suggests that f(app) is governed by ϕ, f, f_o, K_D, and $K_D'\phi_i$. In Table 2, the values of $K_D'\phi_i$ are listed for the cases where the values of f, f_o, and K_D were available. The values of f_o and K_D for SDS-ME were approximated from the experiments employing heptane–1-butanol mixtures of corresponding compositions to the pseudo-organic phases. In BA, the values of $K_D'\phi_i$ were smaller than those of $1-\phi+K_D\phi$, and the contribution of the interphase on its distribution was not serious. Thus, the enol fraction of BA was primarily governed by the distribution between the pseudo-aqueous and the pseudo-organic phases. In BFA and NFA, the values of f(app) were smaller than those for BA in all systems studied and the values of $K_D'\phi_i$ were larger than those for BA. These results suggested a significant contribution from the interphase. The increasing order of $K_D'\phi_i$, BA<BFA<NFA, may correspond to that of the interfacial adsorptivity of the keto and keto-hydrated forms, which may also coincide with the order of the hydrophobicity expected from the distribution constants.

Dissociation of β-Diketones. When the pH was increased, the dissociation of β-diketones in the micelles and microemulsions was observed as the increase of the absorbance of the enolate anion, L^-.

The distribution scheme of β-diketones in this situation is written as,

$$\begin{tikzcd} HL \arrow[r, shift left] \arrow[d, shift left] & HL_i \arrow[l, shift left] \arrow[r, shift left] & HL_o \arrow[l, shift left] \\ L^- \arrow[u, shift left] \arrow[r, shift left] & L^-_i \arrow[l, shift left] & \\ + & & \\ H^+ & & \end{tikzcd} \tag{4}$$

The concentrations of HL and L^- in the whole microemulsion system can be written as,

Table 3. Apparent Dissociation Constants and Adsorption Parameters of β-Diketones at 25 °C

Solvent	ϕ	BA		BFA		NFA	
		pK_a (app)	$K_L'\phi_i$	pK_a (app)	$K_L'\phi_i$	pK_a (app)	$K_L'\phi_i$
0.10 M SDS	0.023	9.98±0.77	—	6.88±0.67	1.9	7.33±0.61	18
SDS-ME A	0.120	9.93±1.07	0.04	6.60±0.17	8.6	6.89±0.41	50
SDS-ME C	0.389	10.29±0.71	0.44	6.84±0.30	10	6.89±0.11	1.3×10^2
TX100-ME	0.107	9.73±0.87	0.52	6.11±0.30	63	—	
CTAB-ME	0.127	8.27±0.60	44	4.38±0.12	2.8×10^3	—	
pK_a		8.70$^{a)}$		6.31$^{b)}$		6.27$^{b)}$	

a) Ref. 10. b) Ref. 11.

$$[HL]=(HL)(1-\phi-\phi_i)+(HL)_o\phi+(HL)_i\phi_i, \qquad (5)$$

$$[L^-]=(L^-)(1-\phi-\phi_i)+(L^-)_i\phi_i.$$

The adsorption constant, $K_L'=(L^-)_i/(L^-)$, and the dissociation constant, $K_a=(L^-)(H^+)/(HL)$, are defined for the above scheme.

The absorbance of the solution at a certain wavelength is given by the next equation,

$$A=\{\varepsilon_{HL}(HL)+\varepsilon_L(L^-)\}(1-\phi-\phi_i)+\varepsilon_{HL}{}^{\circ}(HL)_o\phi + \{\varepsilon_{HL}(HL)_i+\varepsilon_L(L^-)_i\}\phi_i, \qquad (6)$$

where ε_{HL}, $\varepsilon_{HL}{}^{\circ}$, and ε_L are, respectively, the molar absorptivities of HL in the pseudo-aqueous and pseudo-organic phases and L^- in the pseudo-aqueous or interphase. At higher pH values, the apparent molar absorptivity, ε, reached a constant value, which equaled ε_L for L^-. The pH dependence of ε was analyzed by the next equation,

$$\log\{(\varepsilon-\varepsilon_a)/(\varepsilon_L-\varepsilon)\}=\mathrm{pH}-\mathrm{p}K_a(\mathrm{app}), \qquad (7)$$

where K_a(app) is the apparent dissociation constant defined by,

$$K_a(\mathrm{app})=\frac{[L^-](H^+)}{[HL]}=\frac{1-\phi+K_L'\phi_i}{1-\phi+K_D\phi+K_D'\phi_i}K_a, \qquad (8)$$

Equation 8 can be used for the calculation of $K_L'\phi_i$ if K_a(app), K_a, K_D, and $K_D'\phi_i$ are known. Then, the dissociation constant in the interphase, $K_a'=(L^-)_i(H^+)/(HL)_i$, may be evaluated from the relation,

$$K_a'=K_aK_L'/K_D'. \qquad (9)$$

The plots of the apparent molar absorptivity against pH showed sigmoidal curves. Analyses of the results by Eq. 7 afforded the values of pK_a(app), which are listed in Table 3. The values of pK_a and pK_a(app) of BFA and NFA were smaller than those of BA, because of the electron-withdrawing effect of the trifluoromethyl group. It was also noticed that the pK_a(app) in the o/w microemulsion of CTAB (CTAB-ME) was smaller than that in the o/w microemulsion of TX100 (TX100-ME) and that pK_a(app) in SDS-ME was larger than that in TX100-ME. According to the electrostatic theory on the surface potential of micelles[8] and microemulsions,[9] we can postulate the next equation for the interfacial dissociation constant,

$$\mathrm{p}K_a'=\mathrm{p}K_a'^{\circ}-F\psi/2.303RT \qquad (10)$$

where p$K_a'^{\circ}$ is the pK_a' in the nonionic microemulsions, F is the Faraday constant and ψ is the surface potential. When the values of $K_D'\phi_i$ for SDS-ME A, TX100-ME and CTAB-ME were assumed to be equal, the surface potential was calculated by the equation,

$$\psi=0.0591\,(\log K_L'\phi_i-\log K_L'^{\circ}\phi_i) \qquad (11)$$

where $K_L'^{\circ}\phi_i$ is the $K_L'\phi_i$ in TX100-ME. Thus, the surface potentials of −68 mV and −51 mV for SDS-ME A and 114 mV and 97 mV for CTAB-ME were calculated, respectively, from the values of $K_L'\phi_i$ for BA and BFA. These surface potential values seemed quite reasonable as those of the anionic and cationic microemulsions reflecting the charges of the head groups of the surfactants.[8,9] Consequently, the solvent dependence of pK_a(app) was ascribable to the variation in the interfacial adsorptivity of L^- which was geverned by (i) the hydrophylic–lipophylic balance of L^-, which was observed in the TX100-ME system, and (ii) the electrostatic interaction between L^- and SDS or CTAB in the interphase.

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