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Partition Characteristics of Metal(II, III) Acetylacetonates between Sodium Dodecyl Sulfate Micelles and Water

Shoichi KATSUTA†* and Koichi SAITOH
Department of Chemistry, Faculty of Science, Tohoku University, Sendai 980

Partition coefficients of neutral acetylacetonates of Cr(III), Co(III), Rh(III), and Pd(II) between sodium dodecyl sulfate micelles and water were measured by micellar electrokinetic chromatography. The partition coefficients were much larger than those obtained between heptane and water. It was explained in terms of hydration of the complexes in the micellar phase.

Recently various analytical methods utilizing micellar media have been applied to the separation and/or determination of metal complexes as well as organic compounds.1) Although in these applications the partition of the solutes between the micelles and bulk solution is an important factor governing the analytical results, little information is available on the partition equilibrium of the metal complexes. In this study, we determined the partition coefficients of several neutral metal acetylacetonates between sodium dodecyl sulfate (SDS) micelles and water by means of micellar electrokinetic chromatography (MEKC), and discussed their cheracteristics by comparing with the liquid–liquid partition coefficient between heptane and water.

The migration time of an neutral solute (t_s) in MEKC is given as $t_s = (1 + k')t_0 /\{1 + (t_0/t_{mc})k'\}$ (1),2) where t_0 and t_{mc} are the migration times of the aqueous electroosmotic flow and the micelle, respectively, and k' is the capacity factor defined as a mole ratio of the solute in the micelle phase to that in the aqueous phase. When the micelle concentration is low, k' is expressed as $k' = P_{mc}V_{sf}\,(C_{sf} - \mathrm{CMC})$ (2),2) where P_{mc} is the partition coefficient defined as a molarity ratio of the solute in the micelle phase to that in the aqueous phase, V_{sf} the partial molar volume of the surfactant, C_{sf} the total concentration of the surfactant, and CMC the critical micelle concentration. Therefore, the plot of k' vs. C_{sf} should give a straight line with a slope of $P_{mc}V_{sf}$.

Inert complexes, tris(acetylacetonato)chromium(III) ($Cr(acac)_3$), -cobalt(III) ($Co(acac)_3$), -rhodium(III) ($Rh(acac)_3$), and bis(acetylacetonato)palladium(II) ($Pd(acac)_2$), were selected as the test compounds. Several organic compounds, benzene, *p*-xylene, phenol and acetophenone, were also tested for comparison. MEKC was performed in a fused-silica capillary (50 μm i.d. × 700 mm) filled with 0.010 M (1 M = 1 mol dm^{-3}) NaH_2PO_4–0.0020 M $Na_2B_4O_7$ buffer (pH 6.6) containing 0.025–0.10 M SDS at 25 °C. A sample solution of each compound (0.001–0.01 M) was injected by siphoning, and detected by spectrophotometry at 250 nm.

The capacity factors were calculated according to Eq. 1, where t_0 and t_{mc} were assumed to be equal to the t_s values of methanol and Sudan III, respectively. The k' was confirmed to be independent of the applied voltage 15.0–30.0 kV (current 14–32 μA). As was expected from Eq. 2, the plots of k' vs. C_{sf} gave straight lines with

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C_{sf}-axis intercepts of $(6.3\pm2.0)\times10^{-3}$ M, of which value was close to the CMC of SDS (4.6×10^{-3} M) in the present buffer solution determined by conductivity measurements. The P_{mc} values were determined from the slopes using the literature value of V_{sf} of SDS, 0.246 M^{-1}.[3]

The obtained P_{mc} values are listed in Table 1 together with the partition coefficients between heptane and water (P_{hep}). The P_{mc} values of the complexes increase as $Co(acac)_3 < Rh(acac)_3 < Cr(acac)_3 < Pd(acac)_2$ which is the same order in the P_{hep} values, however 62–830 times larger than the corresponding P_{hep} values.

The P_{mc} values of phenol and acetophenone are also much larger than their P_{hep}, whereas the P_{mc} values of benzene and *p*-xylene are closer to the P_{hep}. Benzene and *p*-xylene are known to be solubilized in the hydrocarbon part of the micelles,[4] therefore the comparable partition coefficients in the micelle/water and heptane/water systems are reasonable. On the other hand, phenol and acetophenone are located near the micellar surface and partially hydrated.[5] The transfer of these hydrophilic solutes from water to micelles should be thermodynamically favorable compared with that from water to heptane where they are dehydrated.

We investigated the UV absorption spectrum of $Co(acac)_3$ in 0.1 M SDS solution where a large portion of the complex was solubilized in the micelles. The d–π charge transfer band of the complex in the SDS solution (λ_{max} = 323 nm, $\varepsilon = 1.64\times10^3$ M^{-1} cm^{-1}) was closer to that in water (λ_{max} = 323 nm, $\varepsilon = 1.70\times10^3$ M^{-1} cm^{-1}) than that in heptane (λ_{max} = 321 nm, $\varepsilon = 1.48\times10^3$ M^{-1} cm^{-1}). This implies that the complex is hydrated near the micellar surface. It was previously reported the metal acetylacetonates have strong hydrogen-bond acceptor ability on their ligand oxygen atoms.[6] In conclusion, the metal complexes as well as the organic compounds, which possess the hydrophilic sites, are hydrated even in the micelles and have much larger partition coefficient in the micelle/water system than in the alkane/water system.

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Table 1. Partition coefficients of metal acetylacetonates and aromatic compounds in SDS-micelle/water (P_{mc}) and heptane/water (P_{hep}) systems at 25 °C

Solute	log P_{mc}	log P_{hep}	Solute	log P_{mc}	log P_{hep}
$Cr(acac)_3$	2.09	-0.43[a]	Benzene	2.02	2.29[b]
$Co(acac)_3$	1.89	-1.03[a]	*p*-Xylene	2.91	3.45[b]
$Rh(acac)_3$	2.05	-0.62[a]	Phenol	1.69	-0.90[b]
$Pd(acac)_2$	3.22	1.43[a]	Acetophenone	2.29	1.08[b]

a) Ref. 6. b) Ref. 7.

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