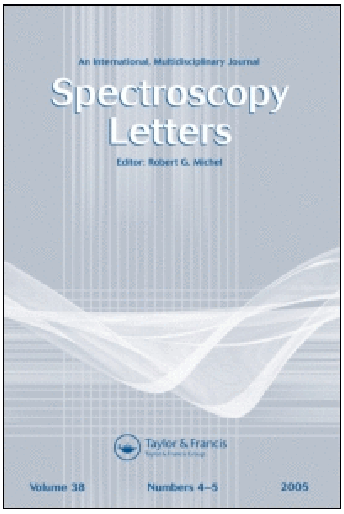

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Self-Indicating Surfactants: Potentially Micellar Solvatochromic Iron(II) Complexes

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SELF-INDICATING SURFACTANTS: POTENTIALLY MICELLAR SOLVATOCHROMIC IRON(II) COMPLEXES

Key Words: Iron(II) complexes; Schiff base ligands; solvatochromism; micelles.

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ABSTRACT

The preparation of ternary iron(II) complexes $[Fe(CN)_2(LL)_2]$ and $[Fe(CN)_4(LL)]^{2-}$, where LL = a Schiff base derived from 2-acetyl pyridine and a long chain amine $1\text{-}Me(CH_2)_nNH_2$ (n = 11, 15, 17), is described. These complexes exhibit strong solvatochromism and can thus be used to probe

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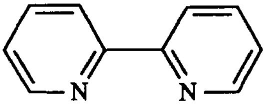
solvation in organised aqueous media, as in ternary water - Aerosol OT - hexanol mixtures. They also have a dramatic effect on the micellisation behaviour of the uncharged surfactant Triton X-100.

INTRODUCTION. Ternary low-spin iron(II)-diimine-cyanide complexes of the general type $[Fe(CN)_2(diimine)_2]$ and $[Fe(CN)_4(diimine)]^{2-}$ {where diimine = *e.g.* bipy, 2,2′-bipyridyl, *1*} are markedly solvatochromic[1-4]. Thus, for example, the maximum of the metal-ligand charge-transfer (MLCT) band of $[Fe(CN)_2(bipy)_2]$ shifts by over 100 nm on going from water to acetone as solvent. Such complexes[2] can thus be used as monitors of selective solvation in binary aqueous solvent mixtures[4-6]. We have recently shown that complexes of this type can be used to monitor micelle formation in surfactant-water media, with a large change of MLCT wavelength characterising the critical micelle concentration (c.m.c.)[7]. We therefore thought that it would be interesting to synthesise analogues of bipy containing long alkyl chains, to see if we could prepare complexes which spontaneously form micelles. The successful first stage in this project has been the preparation of complexes which co-micellise with surfactants, as evidenced by very large effects on the c.m.c. (critical micelle concentration) of surfactants such as Triton X-100 on the addition of small quantities of complex. This has been achieved by the preparation of complexes containing Schiff base ligands of type *2* in place of 2,2′-bipyridyl. We report here the syntheses of these complexes, their solvatochromic behaviour in single and mixed aqueous media, their effect on the c.m.c. of the surfactant, and their value in probing solvation in ternary water-oil-surfactant "organised media".



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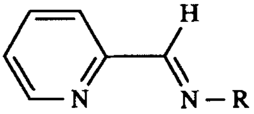

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EXPERIMENTAL. The complexes were prepared from the tris-ligand cations $[Fe(LL)_3]^{2+}$, themselves prepared from iron(II) ammonium sulphate, pyridine 2-carboxaldehyde, and the appropriate amine[8], by Schilt's method[9]. Treatment of the tris-ligand complex with potassium cyanide for a few hours gave water-insoluble species $[Fe(CN)_2(LL)_2]$, which could be filtered off, washed, and dried. Refluxing for several days gave the $[Fe(CN)_4(LL)]^{2-}$ anions, whose potassium salts could be obtained by evaporation of the reaction mixture to small volume. Potassium cyanide is very soluble in water, so the moderately soluble $K_2[Fe(CN)_4(LL)]$ products crystallise out first, and can be freed from potassium cyanide by washing repeatedly with small amounts of ice-cold water.

RESULTS AND DISCUSSION. Wavenumbers of maximum absorption for the lowest energy charge-transfer bands of the newly prepared complexes $[Fe(CN)_2(LL)_2]$ with LL = Schiff base ligand 2 with R = $(CH_2)_nMe$, n = 11, 15, and 17, are identical within experimental uncertainty in a given solvent. Their mean ν_{max}(MLCT) values for each medium composition are plotted against the respective values for the reference compound $[Fe(CN)_2(bipy)_2]$[2,3] in Figure 1 for a series of alcohol solvents and for methanol-water mixtures. These dicyano-complexes are effectively insoluble in water. The Figure 1 plot shows that their solvent sensitivity is 0.70 relative to the reference compound $[Fe(CN)_2(bipy)_2]$. As expected, these $[Fe(CN)_2(LL)_2]$

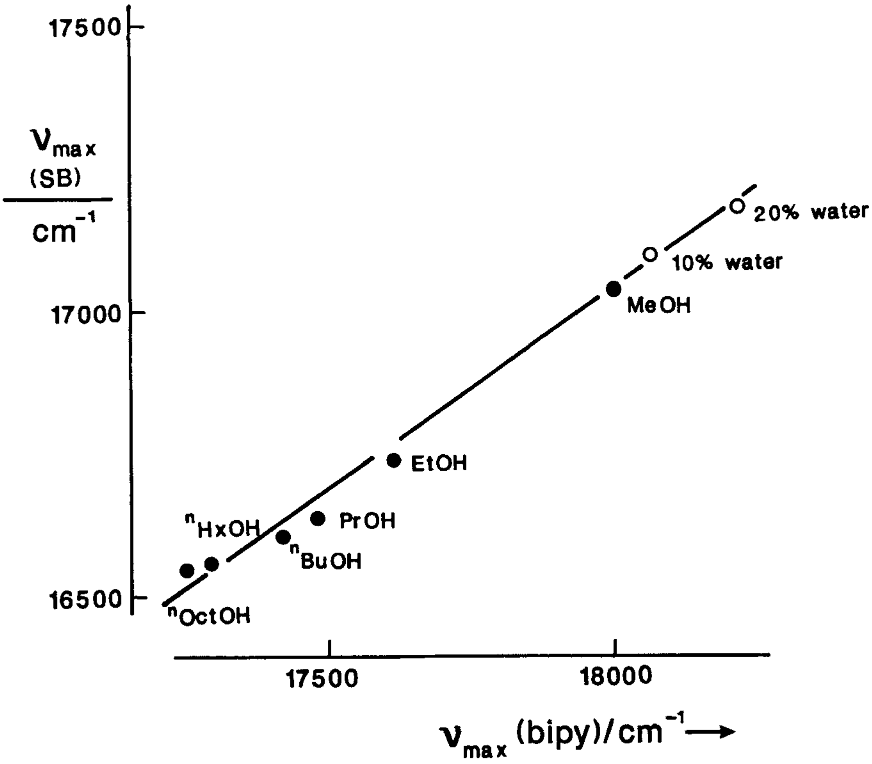

FIG. 1. Correlation of MLCT frequencies $\{\nu_{max}(SB)\}$ for the Schiff base complexes $[Fe(CN)_2(LL)_2]$ with those $\{\nu_{max}(bipy)\}$ for the reference compound $[Fe(CN)_2(bipy)_2]$.

species exhibit comparable solvent sensitivities to those established earlier[5] for analogues with ligands 2 containing short-chain alkyl groups R.

The solvatochromic behaviour of the octadecyl derivative in water-hexanol-Aerosol OT (AOT) media is illustrated in Figure 2, where the inset shows the optically transparent region (stippled). The trend

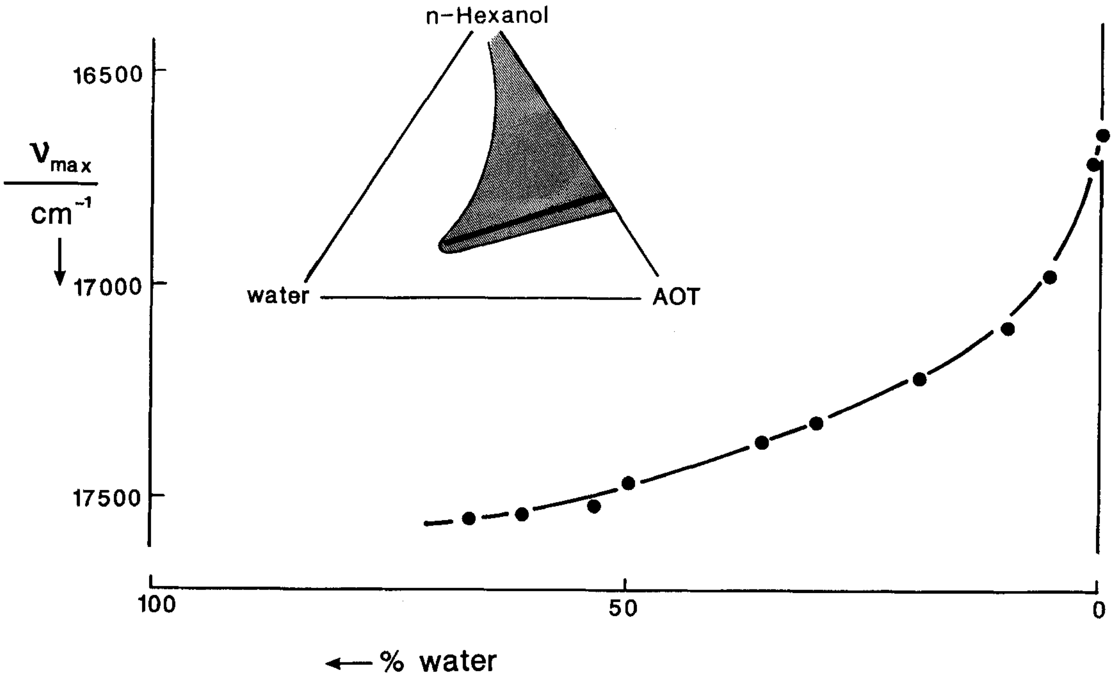

FIG. 2. Dependence of MLCT frequencies for the octadecyl Schiff base complex, $[Fe(CN)_2(LL)_2]$ with LL = 2 with R = $(CH_2)_{17}Me$, on water content (over the range of compositions indicated by the line shown in the inset) in water – Aerosol OT – 1-hexanol ternary solvent media.

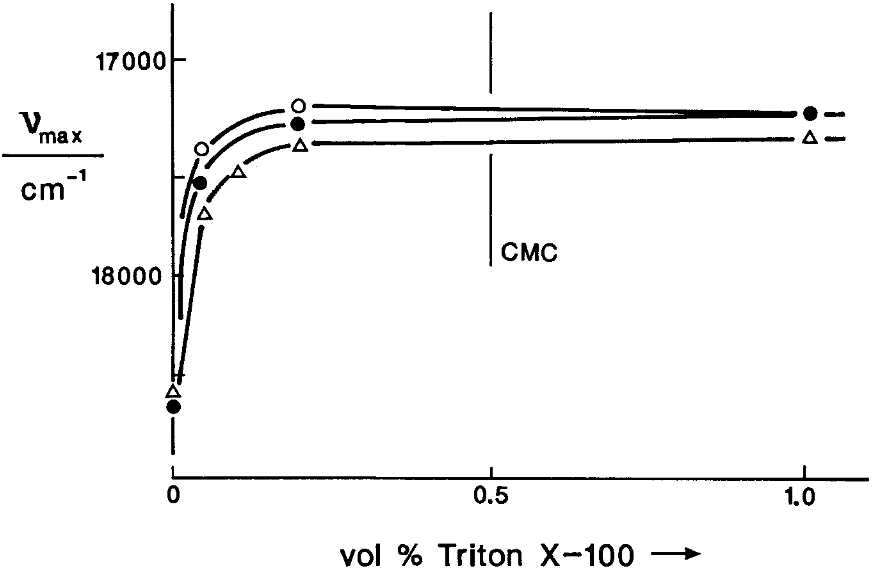

FIG. 3. Dependence of MLCT frequencies for the Schiff base complexes $[Fe(CN)_4(LL)]^{2-}$, LL = 2 with R = Δ $(CH_2)_{11}Me$, ● $(CH_2)_{15}Me$, o $(CH_2)_{17}Me$, on surfactant concentration in aqueous solutions of Triton X-100. CMC = critical micelle concentration for aqueous Triton X-100 in the absence of the complexes.

shown in this Figure indicates strong hydration of the complex, presumably at the two coordinated cyanides, causing marked shifts in the MLCT absorption band as soon as a little water is added to the hexanol-AOT solution. Presumably the iron complex is situated with its hydrophilic cyanide groups in the water pools of the reversed micelles in these microemulsions, with the alkyl chain aligned parallel to those of adjacent alkyl chains of the surfactant molecules in the micelle wall.

For the investigation of micellar effects in predominantly aqueous media it is necessary to switch from the water-insoluble dicyano-complexes to the water-soluble tetracyano-complexes. Trends in ν_{max}(MLCT) with increasing concentration of the surfactant Triton X-100 in aqueous solution are shown in Figure 3. It is clear that the introduction of the iron(II) complex has had a dramatic effect on the critical micelle concentration (c.m.c.), reducing this by an order of magnitude. These complexes are not themselves able to form micelles spontaneously, but it seems that they can comicellise with Triton X-100, in the process markedly affecting its own micellisation behaviour (the concentration of complex in these systems is approximately 10^{-4} mol dm^{-3}). We have not observed similar effects on the c.m.c. for the charged surfactants AOT and CTAB; in the case of the latter observations were made difficult by opalescence in the surfactant-complex-water mixtures.

It is obviously not possible to determine trends of the sort shown in Figure 3 for the dicyano-complexes, but it is of interest to note that Triton X-100 has a marked solubising effect on the complexes $[Fe(CN)_2(LL)_2]$ beyond its c.m.c. (i.e. beyond about 0.5 volume %). Favourable interactions between the hydrocarbon chains in complex and surfactant increase the solubility of these complexes sufficiently for the obtaining of satisfactory visible absorption spectra. The three complexes investigated in this study have ν_{max}(MLCT) = 16890 over the concentration range 0.5 to 1.0 volume % Triton X-100.

The lyotropic phase behaviour of the very similar complex $[Fe(CN)_4(OH_2)(C_{12}H_{25}NH_2)]^{2-}$ {which is actually more likely, from the synthesis described, to be dodecylaminepentacyanoferrate} has recently been described[10]. Sadly, no information was vouchsafed on the spectroscopic properties of this complex.

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