Solid state and solution behaviour of novel transition metal containing surfactants

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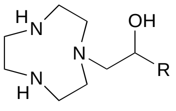
The micellation properties of first row transition metal containing surfactants derived from aza-macrocyclic ligands is described; the structure of one of the surfactants in the solid state has been determined by X-ray crystallography; the dimensions and morphology of micelles formed by a nickel(II) surfactant have been investigated by small-angle neutron scattering (SANS).

Surfactants containing transition metal ions have only recently begun to be investigated, and to date no attempt has been made at the rigorous determination of their structure–property relationships. Typical cationic amphiphiles, such as cetyltrimethylammonium bromide (CTAB), display surface activity but are essentially ‘innocent’ in their chemical reactivity. Our interest in this area is ultimately directed towards the preparation and application of surfactants which contain ‘non-innocent’ transition metal complexes as the head-group. The use of a transition metal ion in the head-group not only imparts charge, but also permits the incorporation of useful properties such as colour (*i.e.* a chromophore), paramagnetism, variable charge and pH sensitivity. However, most importantly, transition metal complexes possess a wide range of reactivity, such as redox behaviour and catalytic activity. Thus transition metal containing surfactants provide a method for localising redox or catalytic activity at an interface.

Here, we report our preliminary results on the synthesis and characterisation of a range of nickel(II) and copper(II) based surfactants. For the purposes of this paper we define the systems under investigation as cationic metallo-surfactants in which a (transition) metal ion forms an integral part of the head-group. Earlier work by other groups on metallo-surfactants has tended to concentrate on the lyotropic phase behaviour of non-labile metal complexes for example a $[\mathrm{Ru^{II}(terpy)_2}]^{2+}$ system.[1] An example of micellation in a $[\mathrm{Co^{II}(polyamine)}]^{3+}$ system has been reported,[2] but again the metal centre is non-labile. Of systems with kinetically labile metal ions, there has also been an elegant investigation into the micellation of a diaza-18-crown-6 based surfactant (an annelide) in the presence of s-block cations by a range of techniques,[3] and a recent report of a copper(II) cryptand which forms unilamellar vesicles.[4] The work presented here describes the solution and solid state behaviour of a ligand system which produces surface active complexes from non-surface active ligands upon coordination of a labile metal centre.

Initially we sought simple ligand systems in which the various components of the resulting complex amphiphile could easily be modified to accommodate different alkyl chain lengths and numbers, variable head-group size and a range of d- and f-block metal ions. Also we required a ligand system which formed stable complexes in which the metal ion remained strongly bound to the head-group of the amphiphile. This prevents the complication of metal–ligand dissociation affecting the composition of the system. Metal–ligand dissociation would not only increase the ionic strength of the solution but would also lower c.m.c. values by the introduction of the largely hydrophobic free ligand. We therefore prepared the range of ligands $\mathrm{L^1R}$ based upon 1,4,7-triazacyclononane ($[9]\mathrm{aneN_3}$). The synthesis of these ligands was achieved in gram quantitites by reacting 20 equiv. of 1,4,7-triazacyclononane with 1,2-epoxyalkanes in ethanol solution. The free ligands were isolated in quantitative yield after removing the excess 1,4,7-triazacyclononane by distillation. To date these ligands represent the first reported examples of aza-macrocycles bearing a single pendant alcohol donor.



$\mathrm{L^1R}$

$\mathrm{R = C_{\mathit{n}}H_{2\mathit{n}+1}}$
$n = 6, 8, 10, 12, 14, 16$

The ligands $\mathrm{L^1R}$ are poorly soluble in water, but readily dissolve upon the addition of nickel(II) salts to afford blue/purple solutions. The electronic spectra of these solutions indicate that the coordination geometry at the metal centre is octahedral and it is probable that an $\mathrm{N_3O_3}$ (*i.e.* $\mathrm{L^1R}$ and two molecules of water) donor atom set is present. The single crystal structure of $[\mathrm{Ni^{II}(L^1R)(H_2O)_2}]\mathrm{Cl_2}$ ($\mathrm{R = C_{10}H_{21}}$) was determined.[‡] The structure of the cation is illustrated in Fig. 1. This confirms the $\mathrm{N_3O_3}$ coordination sphere at a slightly distorted octahedral metal centre, with the macrocycle in its typical face capping mode and the pendant-arm alcohol also coordinated to the metal centre. The alkyl chain is found to be in the fully extended conformation. The packing diagram (Fig. 2) indicates that a lamellar structure is formed with an antiparallel arrangement of the cations. We have prepared ligands $\mathrm{L^1R}$ in both racemic and optically active forms. The structure presented here was prepared with racemic material and the crystal structure contains alternating layers of (*R*) and (*S*) material. It is worth noting that single crystals of the complexes $[\mathrm{Ni^{II}(L^1R)(H_2O)_2}]\mathrm{Cl_2}$ were found to be remarkably easy to obtain by cooling or concentrating stock solutions containing an excess of $\mathrm{NiCl_2(aq)}$. The facile nature of the crystallisation process is attributed to a Krafft point effect, with the approximate Krafft temperatures for the complex $[\mathrm{Ni^{II}(L^1R)(H_2O)_2}]\mathrm{Cl_2}$ being 35 °C ($\mathrm{R = C_{10}H_{21}}$) and 65 °C ($\mathrm{R = C_{16}H_{33}}$).

Characterisation of the interfacial behaviour of $[\mathrm{Ni^{II}(L^1\text{-}R)(H_2O)_2}]\mathrm{Cl_2}$ ($\mathrm{R = C_{,\mathit{n}}H_{2\mathit{n}+1}}$, $n = 6, 8, 10, 12, 14, 16$) has been undertaken to determine its critical micelle concentration, c.m.c. Surface tension measurements were determined by the Du Noüy platinum ring method. A typical plot of surface tension *vs.* concentration is illustrated in Fig. 3 for $[\mathrm{M^{II}(L^1R)\text{-}(H_2O)_2}]\mathrm{Cl_2}$ ($\mathrm{R = C_{10}H_{21}}$), ($\mathrm{M = Ni^{II}, Cu^{II}}$). Using this method,

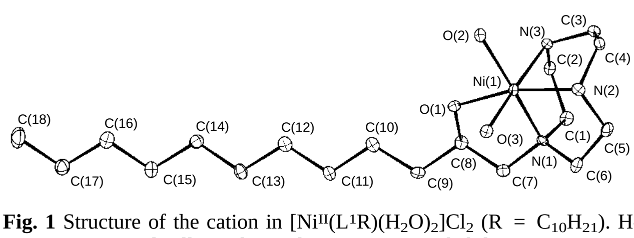


Fig. 1 Structure of the cation in $[\mathrm{Ni^{II}(L^1R)(H_2O)_2}]\mathrm{Cl_2}$ ($\mathrm{R = C_{10}H_{21}}$). H-atoms are omitted. Ellipsoids are drawn at 50% probability.

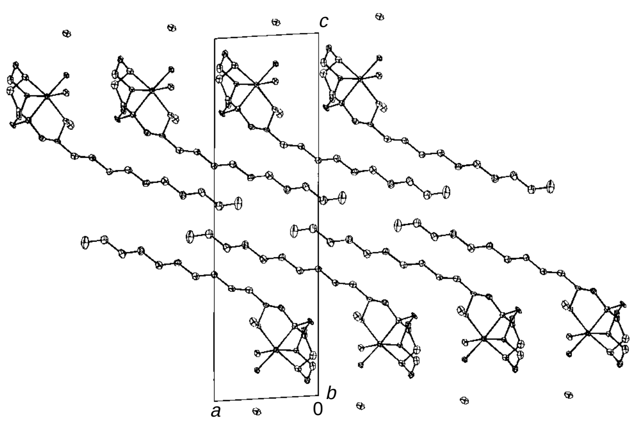


Fig. 2 Packing diagram in [$Ni^{II}(L^1R)(H_2O)_2]Cl_2$ (R = $C_{10}H_{21}$). View is along the *b* axis. Ellipsoids are drawn at 50% probability.

the c.m.c.s of the surfactants are 1.5 ± 0.2 mM (M = Ni^{II}) and 0.8 ± 0.1 mM (M = Cu^{II}). The adsorbed amount and hence, area per molecule at the surface, calculated *via* the Gibbs equation, $d\gamma/d \ln c = -\Gamma/RT$ is the same for both surfactants; 50 ± 5 Å^2. The c.m.c. values are lower than expected for a doubly charged amphiphile, which may be explained by noting that the head-group itself contains eight additional carbon centres, and hence reducing the overall hydrophilicity. The lower c.m.c. value of the copper complex is attributed to the tendency for Cu^{II} to adopt five-coordinate geometries. This would result in a marginally smaller head-group. Furthermore, it has been shown[5] that Cu^{II} can increase the acidity of a bound alcohol group so as to permit deprotonation. This process, even if occurring to a limited extent, would reduce the charge on the head-group and permit alkoxide to alcohol hydrogen bonding to occur between head-groups. This interaction between head-groups would reduce the effect of electrostatic repulsion of the head-groups, further lowering the c.m.c. value. Thus it can be seen that a very subtle change in the metal centre from Ni^{II} to Cu^{II} has a significant effect on the micellation properties of these surfactants.

The structures formed in the bulk solution slightly above the c.m.c. have been investigated by small-angle neutron scattering (SANS). The scattering from surfactant systems contains three important terms; the form factor, the structure factor and a constant term, essentially the intensity per micelle. The form factor describes the size and shape of the scattering body. The structure factor describes the spatial distribution of the scattering bodies and is determined by their interaction potential. For dilute cases, the structure factor may be neglected. A full analysis of the comprehensive SANS study will be presented shortly, but some data referring to the [$Ni^{II}(L^1R)(H_2O)_2]Cl_2$ (R = $C_{10}H_{21}$) surfactant are presented here.§ A typical set of scattering data and a fit to a spherical micelle model are shown in Fig. 4. Given the resolution of the data, we have made no attempt to break the scattering down into its component 'core' (alkyl tails) and 'shell' (head-group) contributions. The radius of the micelle is found to be 34 ± 3 Å with an aggregation number of 50 ± 10. This radius is somewhat larger than might be expected from a surfactant which has an all-*trans* length of *ca.* 20 Å and it therefore appears that the micelles are either very diffuse in nature or display a degree of non-sphericity. This anomaly is currently the subject of further SANS experiments.

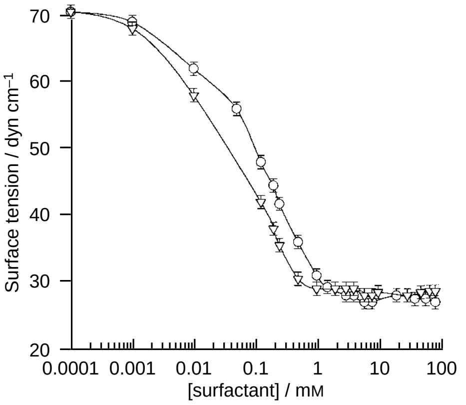


Fig. 3 Surface tension *vs.* concentration for [$M^1(L^1R)(H_2O)_2]Cl_2(aq)$ (R = $C_{10}H_{21}$) where M = Ni^{II} (○) or Cu^{II} (▽)

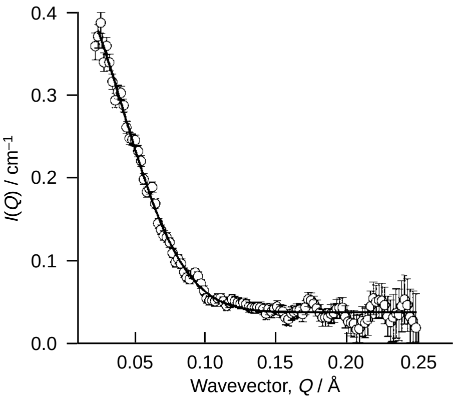


Fig. 4 SANS data for [$Ni^{II}(L^1R)(H_2O)_2]Cl_2$ (in D_2O) and the fit to a spherical micelle model. Concentration of [$Ni^{II}(L^1R)(H_2O)_2]Cl_2$ = 10 mM. (The quantity *Q* is given by $Q = (4\pi/\lambda) \sin(\theta/2)$, and is the modulus of the scattering vector, the resultant between the incident and scattered wavevectors.)

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Notes and References

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‡ *Crystal data* for $C_{18}H_{43}Cl_2N_3NiO_3$, M = 479.16, triclinic, space group $P\bar{1}$, a = 7.0430(6), b = 7.4080(8), c = 23.795(3) Å, α = 98.660(14)°, β = 90.670(14)°, γ = 106.010(5) (by least squares refinement of the setting angles for 250 reflections within θ = 2.60–25.13°). U = 1177.9(2) Å^3, Z = 2, D_c = 1.351 g cm^{-3}, T = 150 K, μ(Mo-Kα) = 10.72 cm^{-1}, $F(000)$ = 516, crystal size = 0.24 × 0.18 × 0.16 mm. Data were collected on a FAST TV Area detector diffractometer following previously described methods.[6] From the ranges scanned, 5038 data were recorded ($2.60 < \theta < 25.13°$; index ranges $-7 < h < 7, -6 < k < 8, -26 < l < 26$) and merged to give 3244 unique (R_{int}) = 0.0726). The structure was solved *via* direct methods[7] and refined on F_o^2 by full matrix least squares[8] using all unique data corrected for Lorentz and polarisation factors. All non-hydrogen atoms were anisotropic. The hydrogen atoms were inserted in idealised position with U_{iso} set at 1.5 U_{eq} of the parent. The weighting scheme used was $w = 1/[\sigma^2(F_o)^2 + (0.0219P)^2]$, where $P = [\text{Max.}(F_o)^2 + 2(F_c)^2]/3$; this gave satisfactory agreement analyses. Final R_1 (F) and $wR2$ (F_o^2) values were 0.0671 and 0.1016 for all 3244 data and 245 parameters. The corresponding R-values were 0.0419 and 0.0978 for 2038 data with $I > 2\sigma(I)$. Sources of scattering factors as in ref. 8. CCDC 182/756.

§ SANS measurements were performed on the LOQ diffractometer at the ISIS Spallation Source, Oxfordshire, UK.

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