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SURFACTANTS AND MACROSCOPIC INTERFACES

Surface and colloid properties of cyclic amides III. Surface activity and micellization of N-butyl-2-pyrrolidone in water Anjing Lou, Brian A. Pethica*, P. Somasundaran and Aixing Fan Langmuir Center for Colloids and Interfaces, Room 911, S.W. Mudd,

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Abstract

The aggregation and surface activity of N-butyl-2-pyrrolidone (BP) in water is investigated using surface tension, solubilization, fluorescence and NMR methods. The micelle point is high (~1.0 M) as expected for the butyl chain length, and the aggregation number is approximately 5, with pre-association below the c.m.c. Despite the low aggregation number, the fluorescence data indicate that the interior of the aggregate is similar to pure liquid BP. The adsorption of BP at the solution/air interface goes to a maxmum near the c.m.c., corresponding to an area of 45 ± 1 Å²/molecule.

Introduction

Because of the industrial interest in these compounds, the adsorption behavior, surface activity and micellization properties of N-alkyl-2-pyrrolidones have attracted recent attention[1]. Phase separation, surface activity and micellization of N-hexyl-2-pyrrolidone in aqueous solution have recently been reported[2]. Unlike the longer chain pyrrolidones such as the N-octyl or Ndodecyl compounds, which have been reported to show no micelles in solution[3-5], N-hexyl-2pyrrolidone forms micelles in aqueous solution at all temperatures from the freezing point up to the lower consolute temperature LCT (19.1 °C) and up to 25 °C in the water-rich phase above the LCT. Surface activity and adsorption of a series of N-alkyl-2-pyrrolidones at the air/solution interface at low surface pressures have been reported and interpreted in terms of two-dimensional virial coefficients and lateral intermolecular forces in the monolayers[6]. The properties of the interfaces of mixtures of the partially miscible short chain alkyl pyrrolidones with paraffins have been studied and the adsorption of the longer-chain pyrrolidones at these non-aqueous liquid/liquid interfaces have also been reported[7].

In this work, the surface activity and micellization of N-butyl-2-pyrrolidone (BP) in aqueous solution are reported using surface tension, NMR and fluorescence spectroscopic methods. It is found that BP forms micelles at a relatively high concentration and pre-aggregates below the apparent critical micellar concentration (c.m.c.). A small aggregation number is estimated from the ¹³C NMR chemical shifts of the BP solutions and confirmed by the surface tension measurements.

Materials and Methods

<u>Materials</u>: The N-butyl-2-pyrrolidone was provided by International Specialty Products Inc. with a purity of 99.6% from peak areas using GLC. The residual impurities were short chain homologs or compounds with a methyl group substituted in the pyrrolidone ring. These impurities are unlikely to interfere with the surface and micellar properties. Pyrene (Aldrich Chemicals) was recrystallized from ethanol-water mixtures. Water was triply distilled with the second stage from alkaline permanganate.

<u>Methods:</u>

Surface tension Surface tensions were measured at room temperature $(23.5 \pm 0.1 \text{ °C})$ mostly with the drop volume method using the Harkins and Brown corrections[8]. Measurements were also made with a platinum Wilhelmy plate coupled to a Cahn microblance. It was found that at higher BP concentrations, the plate method was inapplicable due to the onset of a finite contact angle. At lower concentrations (0.1 molal and below) the two methods for the surface tension agreed well. The water surface tension was checked using both the drop-volume and Wilhelmy plate methods. Both methods give $72.25 \pm 0.05 \text{ mNm}^{-1}$ at $23.5 \pm 0.1 \text{ °C}$.

Fluorescence Fluorescence spectra were recorded on a Photo International PTI-LS 100 spectrometer. A pyrene stock solution was prepared by stirring solid pyrene in water for 24 h and filtering off the excess probe. This solution was added as required to BP solutions for the polarity parameter I_3/I_1 ratio measurements[9], for which the pyrene concentration was kept constant. For the I_3/I_m measurements[10] pyrene concentrations were measured by UV spectrometry.

Solubility of pyrene Pyrene solubilities in BP/water mixtures were measured by adding excess solid pyrene to the chosen mixtures, shaking overnight, filtering and estimating the pyrene concentration by UV spectrometry.

¹³C NMR The ¹³C NMR spectra were obtained using a VXR Varian-400 M Hz NMR spectrometer at 25 °C. Deuterium Oxide (D₂O) with 99.9% purity obtained from Cambridge Isotope Laboratories (CIL) was used as received. Benzene was used as the external reference.

Results and discussions

Micelle formation Air/solution surface tensions (measured by the drop volume method to avoid contact angle problems at high BP concentrations) at 23.5 °C are shown across the whole range of concentration in Fig. BP is surface active, and the air/solution surface tension can be decreased to about 33 mNm⁻¹ at a plateau in the range from approximately 15 to 40% w/w. The results suggest the formation of aggregates of BP in solution above about 8.5%. However, above 40%BP, the surface tension decreases from the plateau value. This indicates clearly that the structure of mixtures above about 40% is no longer one of simple aggregates of BP in water. The aggregate formation can be seen more clearly on Fig. 2, which shows the surface tension plotted on a logarithmic concentration scale.

The large increase in the solubility of pyrene at room temperature above a BP concentration of about 1 Molal in Fig. 3 also suggests micelle formation. The trend of the surface tension with BP



Fig. 1. Surface tension of BP/water mixtures at 23.5 °C using the drop volume method

concentration (log scale, Fig. 2) below the c.m.c. and the corresponding form of the increase in pyrene solubility (Fig. 3) suggest that pre-aggregation occurs below the c.m.c., and that the micillization range is more diffuse than for hexyl pyrrolidone. Fig. 4 shows the polarity parameter (I_yI_1) of the pyrene spectrum[9] as a function of BP concentration in water. The ratio initially increases almost linearly with the concentration, but with a sharp change in trend over a narrow concentration range near 1.0 molal to a constant value at high BP concentrations. The onset of the constant I_yI_1 region corresponds with the micelle point as observed by surface tension and other measurements mentioned above. The region of linear increase in the I_yI_1 ratio below the c.m.c. is not usually seen with surfactants such as SDS[11], which micellize at low concentration. The trend for BP may be associated with the decrease in dielectric constant as BP ($\epsilon = 40$) is added to the



Figure 2. Surface tension of BP in water at 23.5 °C

water, since the c.m.c. for BP is higher than typical long chain surfactants. Above the c.m.c., the I_3/I_1 ratio value is ~ 0.78, which is lower than that for pyrene in SDS micelles (~0.9), but almost identical with the I_3/I_1 ratio value for pyrene in pure BP. This result suggests that the interior of the BP micelles is a similar environment to liquid BP, that is, more polar than the liquid paraffins which represent the interior of SDS micelles. This conclusion is supported by fluorescence measurements on pyrene excimer formation.

When the concentration of pyrene in a solution is increased, an excited state pyrene Py^* can interact with a ground state pyrene Py to form an excimer Py_2^* . The ratio of pyrene excimer to monomer emission intensities (Ie/Im) is a useful measure of excimer concentration, and hence of local pyrene concentration[10]. The Ie/Im ratios for pyrene dissolved in pure BP and 30wt% BP in



Figure 3. Solubility of pyrene in N-butyl-2-pyrrolidone/water mixtures at 23.5 °C

water are shown in Fig. 5. The ratio is much higher for a given overall concentration for 30wt% BP in water than for pure BP. If we assume that in 30wt% BP the pyrene is almost entirely partitioned into the micelles, and that above the c.m.c. (approximately 12% w/w) the monomer concentration is constant, the effective concentration of pyrene in the micelle is higher than the overall concentration in the mixture by a factor of 100/18 or 5.56. In fact (Fig. 5), for a given pyrene concentration in the 30% w/w BP solution, I_e/I_m is very close to the ratio observed at a concentration 5 times higher in pure BP. This shows that the pyrene is concentrated in the micelles and that the micelle interior is similar to liquid BP.

Figure 6 shows the dependence of the chemical shift for carbon 7 of BP on the concentration.



Figure 4. Variation of I Λ_1 ratio of pyrene as a function of BP concentration



The chemical shift for carbon 7 increases sharply above one molal BP indicating aggregation, in agreement with the c.m.c. obtained using the other methods as discussed above. The smaller increase of the chemical shift below the c.m.c. may correspond to premicelle aggregation or reflect other aspects of the non-ideality in that region.

Aggregation number The aggregation number of butyl pyrrolidone (BP) in aqueous solution may be estimated from the concentration dependence of the carbon 7 ¹³C NMR chemical shifts (δ)



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Figure 5. Excimer/monomer fluorescence ratio (Ie/Im) for pyrene dissolved in pure BP and 30% w/w BP in aqueous solution

shown in Fig. 6. The determination of micellar aggregation numbers from the ¹³C chemical shift data rests on the following assumptions[12]: the BP molecules are assumed to exist in two states; "free", as monomers, and "bound" in a micelle with aggregation number N. The chemical shifts are different in the two states and the monomer and micelle shifts, δ_{mono} and δ_{mic} , respectively, are assumed to be independent of surfactant concentration. Applying a single step mass-action equilibrium model, and assuming that the surfactant monomer S is in equilibrium with micelles S_N of aggregation number N, the equilibrium constant K of the association NS = S_N is given by

$$K = C_{mic} / C^{N}_{mono}$$
 (1)

where C indicates concentration. Taking $\delta_{mono} = 0$, and expressing the other δ values relative to δ_{mono} , the following equation can be derived.[13]



Figure 6. ¹³C NMR dependence of the chemical shift of carbon 7 of BP on the reciprocal concentration.

$$\log(C_t \ \delta_{obs}) = \operatorname{Nlog}[C_t \ (\delta_{mic} - \delta_{obs})] + \log K + \log N - (N-1) \log \delta_{mic}$$
(2)

where C_t is the total surfactant concentration ($C_t = C_{mono} + NC_{mic}$), δ_{obs} is the observed chemical shift, δ_{mic} is obtained by extrapolation of δ_{obs} to $1/C_t = 0$, and K and N are determined from the plot of $\log(C_t \delta_{obs})$ vs $\log[C_t (\delta_{mis} - \delta_{obs})]$

As indicated in Fig. 1, micelles are probably not formed when the concentration of BP in water exceeds 45% (corresponding to 0.17 on the reciprocal concentration scale in Fig. 6). Therefore, it is necessary to use the chemical shifts in the reciprocal concentration range between 0.17 to 1 (see the two vertical lines in Fig. 6) to evaluate omic. Based upon the evaluated δ_{mic} , and equation (2), a plot of log($C_t \ \delta_{obs}$) vs log[$C_t (\delta_{mic} - \delta_{obs})$] is given in Fig. 7. The aggregation number estimated from the plot is 5.2 ± 0.6 . The estimated error range for the aggregation number was obtained by drawing reasonable limits for the required intercept and slopes.



Figure 7. Estimation of the aggregation number of BP in water using the single-step model based on the chemical shift data

The aggregation number was also estimated approximately using the plot of surface tension vs concentration of BP in solution as shown in Fig. 2. The ratio of the slope of $d\gamma/d \log m$ (where m is the molal concentration) below the c.m.c. and above the c.m.c. from Fig. 2 gives an estimate of the aggregation number of 5 ± 0.6 , which is close to the value obtained from the chemical shift result

Adsorption of BP at the air/solution interface Since the c.m.c. for BP is at approximately 1 molal, estimation of the adsorption excess at the air/solution interface from the Gibbs equation requires activity corrections at the higher surface pressures. Freezing points for BP/water mixtures were measured to 0.01 °C to obtain the osmotic coefficients. Separation of distinct ice crystallites was observed at concentrations up to the c.m.c., but at higher concentrations the solid phase separating on cooling was amorphous in appearance, and the osmotic coefficients would appear to

be correspondingly unreliable. Heats of dilution (to be reported separately) fall off to zero at concentrations below c.m.c., and the osmotic coefficients obtained from the freezing points can be applied at 23.5 °C to calculate the BP activity up to the c.m.c. region. The results are shown on Fig. 2. Application of the Gibbs equation gives a maximum adsorption of BP at the air/solution interfaces as equivalent to 45 ± 1.0 Å²/molecule. This packing is larger than that for N-hexyl pyrrolidone for an equivalent surface pressure of 39 mNm⁻¹ (38 Å²/molecule). For both molecules the close packing is mostly defined by the ring head group.

Conclusions

In this study the principal finding is that N-butyl-2-pyrrolidone forms micelles in aqueous solution with a high c.m.c. and a small aggregation number. Pre-aggregation is also observed. These results are expected for the rather short alkyl chain of the molecules. Suprisingly for such a small aggregation number, the environment of the interior of the micelles is comparable to pure liquid BP as judged from the fluorescence results. The maximum adsorption of BP corresponds to a packing of 45 Å²/molecule.

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