Surfactant Property of Linear Alkanes with Two Pyrrolidone Moieties in Both Termini

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Linear alkanes with two pyrrolidone groups in both termini [abbreviation: 1,n-dipyrrolidonyl alkane (1,n-DPA) (n = 3, 5, 9, and 12)] were synthesized. Their surface activities were evaluated in terms of surface tension, and compared with those of a few kinds of surfactants. Among 1,n-DPAs, 1,3-, 1,5-, and 1,9-DPAs were fully soluble in water and surface-active: especially 1,9-DPA showed a surface tension value of γW/A 32.8 mN/m at 5.9 × 10^{-2} mol/L or 1.7 wt% and was suggested as a nonionic surfactant with simple structure and moderate activity. Critical miceller concentration (CMC) of 1,9-DPA was 1.45 × 10^{-2} mol/L. Surface tension values of 1,5- and 1,9-DPAs were lower than those of the corresponding monofunctional pyrrolidones, N-propyl and N-pentylpyrrolidones. Minimum area per surfactant molecule (A_{min}) decreased with increase of methylene chain length in the series of 1,n-DPAs. The results suggested that 1,n-DPA favorably chooses a loop structure at air/water interface.

KEY WORDS: **Bifunctional pyrrolidone, 1,n-dipyrrolidonyl alkane, nonionic surfactant, surface tension.**

We have studied adsorption of active hydrogen compounds such as phenol on polymers having cyclic amide or carbamate moieties in the side chain (1–3). In order to study the adsorption by complex formation based on hydrogen bonding, linear alkanes with two pyrrolidone moieties at both termini (1,n-DPAs) have been selected as the model compounds (4,5). In connection with the adsorption behavior in water, we have independently examined surface activities of 1,n-DPAs. These compounds can be regarded as amphiphiles owing to their unique structures consisting of a hydrophobic methylene chain and two terminal hydrophilic groups.

Nonionic surfactants have many advantages as detergents, emulsifiers, and for chemical studies, because they indeed do not ionize in aqueous solution. Several types of non-polymer nonionic surfactants are known, such as sulfoxides, amine oxides, ethylene oxides, alcohols, and pyrrolidones (6–12). Studies on a few ionic surfactants with two hydrophilic groups at both termini of hydrophobic group have been reported (13–19). However, there seems to be no study on nonionic surfactant with two hydrophilic groups at both termini of a hydrophobic group, except polymer surfactants.

This article deals with the synthesis and surfactant nature of these dipyrrolidonyl alkanes (1,n-DPAs).

EXPERIMENTAL PROCEDURES

Materials. Commercially available 2-pyrrolidone and dimethylformamide (DMF) were dried over calcium hydride, distilled under reduced pressure, and stored over molecular sieves.

Synthesis of 1,n-DPA; a typical procedure (for 1,3-DPA): To a suspension of sodium hydride (55 wt% mineral oil dispersion, 9.0 g, 0.18 mol) in 150 mL of dry DMF was added dropwise 2-pyrrolidone (12.8 g, 0.15 mol) dissolved in 50 mL of dry DMF with stirring at room temperature. The mixture was kept at 40–45°C for 5 hr. 1,3-Dibromopropane (15.2 g, 0.075 mol) dissolved in 50 mL of dry DMF was added dropwise to the resulting solution with stirring at room temperature and the mixture was stirred for 20 hr at that temperature. After DMF was removed by distillation under reduced pressure, the residue was extracted with acetonitrile and n-hexane. The acetonitrile layer was evaporated and the residue was distilled under reduced pressure, where bp = boiling point, IR = infrared, and NMR = nuclear magnetic resonance. Yield 41% (yellow viscous oil). Bp 168–173°C/0.8mmHg (lit. (20,21) 177°C/0.36mmHg). IR (neat) 1678 cm^{-1}(C=O). ^{1}H-NMR(CCl_4) 3.54–2.89(m, 8H $4\times\text{-}CH_2\text{-}N\text{=}$), 2.40–1.37(m, 10H, $3\times\text{-}CH_2\text{-},2\times\text{-}CH_2\text{-}\overset{\overset{O}{\|}}{C}\text{-}$) ppm.

Unknown 1,5- , 1,9-, and 1,-12-DPAs were prepared according to the similar procedure as mentioned above for 1,3-DPA where EA = elemental analysis and mp = melting point.

1,5-DPA: Yield 51%. Bp 198–201°C/0.8mmHg. IR(neat) 1668 cm^{-1} (C=O). ^{1}H-NMR(CCl_4) 3.83–2.93(m, 8H, $4\times\text{-}CH_2\text{-}N\langle$), 2.56–1.73(m, 8H, $2\times\text{-}CH_2\text{-}$, $2\times\text{-}CH_2\text{-}\overset{\overset{O}{\|}}{C}\text{-}$), 1.73-0.92(m, 6H, $3\times\text{-}CH_2\text{-}$) ppm. EA calc'd(C 65.52%, H 9.31%, N 11.75%), found(C 64.41%, H 9.35%, N 11.37%).

1,9-DPA: Yield 58%. Bp 220–226°C/0.6mmHg. IR(neat) 1682 cm^{-1}(C=O). ^{1}H-NMR(CCl_4) 3.79–2.82(m, 8H, $4\times\text{-}CH_2\text{-}N\langle$), 2.50–1.80(m, 8H, $2\times\text{-}CH_2\text{-}$, $2\times CH_2\text{-}\overset{\overset{O}{\|}}{C}\text{-}$), 1.80–0.91(m, 14H $7\times\text{-}CH_2\text{-}$) ppm. EA calc'd(C 69.35%, H 10.27%, N 9.51%), found(C 68.99%, H 10.57%, N 9.29%).

1,12-DPA: Yield 53%. Bp 230–236°C/0.2mmHg. Mp 39–41°C. IR(neat) 1682 cm^{-1} (C=O). ^{1}H-NMR(CCl_4) 3.73–2.82(m, 8H, $4\times\text{-}CH_2\text{-}N\langle$), 2.46–1.79(m, 8H, $2\times\text{-}CH_2\text{-}$, $2\times\text{-}CH_2\text{-}\overset{\overset{O}{\|}}{C}\text{-}$), 1.79-0.77(m, 20H, $10\times\text{-}CH_2\text{-}$) ppm. EA calc'd(C 71.38%, H 10.78%, N 8.32%), found (C 71.22%, H 10.98%, N 8.18%).

Measurements. Surface tension values were measured in water at a few different concentrations with a Kyowo Kagaku CBVP A-3 surface tentiometer, based on Willhelmy method at 20°C. Critical miceller concentration (CMC) of 1,9-DPA was determined by calculating several data obtained at various

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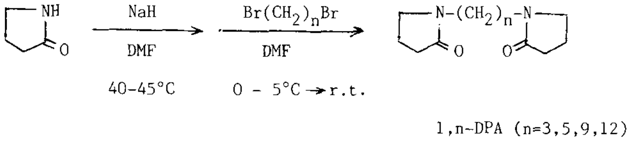
concentrations. ^{1}H-NMR spectra were recorded on a JNM PMX-60si NMR spectrometer (60 MHz) using tetramethylsilane as an internal standard. FT-IR (Fourier transform infrared detection) spectra were obtained with a JASCO FT-IR/3 spectrometer.

RESULTS AND DISCUSSION

1,n-Bispyrrolidone-terminated alkanes [1,n-DPAs (n = 3,5,9, and 12)] were prepared by the reaction of 2-pyrrolidone and the corresponding 1,n-dibromoalkanes in the presence of sodium hydride in DMF according to the reported method for 1,3-DPA with some modifications (Scheme 1) (11,12). The purified products were obtained as viscous oils (1,3-, 1,5-, and 1,9-DPAs) and crystals (1,12-DPA). The structures of the DPAs were determined by IR and NMR spectra and elemental analyses for unknown DPAs (n=5,9,12).



SCHEME 1

In order to evaluate the activities of the DPAs as nonionic surfactants, the surface tension values (γW/A) were measured in the aqueous solution. Although 1,12-DPA was partially soluble in water, 1,3-, 1,5-, and 1,9-DPAs were completely soluble in water and were surface-active. Plots of the surface tension vs log of the surfactant concentration for the DPAs and N-alkylpyrrolidones (mAPs) are shown in Figure 1. Table 1 summarizes some surface properties of the DPAs and mAPs, along with those of several selected surfactants for comparison. Maximum surface excess concentrations (Γ_{max} in mol cm^{-2}) and minimum areas per surfactant molecule (A_{min} in nm^2), at water/air interface, were calculated from the surface tension data by the following equations:

$$\Gamma_{max} = -S_{max}/2.303RT \qquad [1]$$

$$A_{min} = 10^{14}/N\Gamma_{max} \qquad [2]$$

where S_{max} is the slope of the surface tension vs log concentration plots at 20°C (Fig. 1), R = 8.314Jmol^{-1}K^{-1}, and N is Avogardo's number (8). The calculated data are listed in Table 1.

Figure 1 and Table 1 indicate that the γW/A value decreases as the methylene chain length increases in the series of 1,n-DPAs. Similar tendency is observed in the case of mAPs. Among the DPAs, 1,9-DPA showed the lowest surface tension value (γW/A=32.8 mN/m at a concentration of [C]=5.9 × 10^{-2} M or 1.7 wt%), which is compared to that of sodium salt of lauric or stearic acid at 70°C. The γW/A value of 1,9-DPA is higher than those of ionic surfactants such as sodium palmitate (at 70°C) and a nonionic polymer surfactant (Table 1), and seems to be fairly satisfactory as that of a nonionic surfactant.

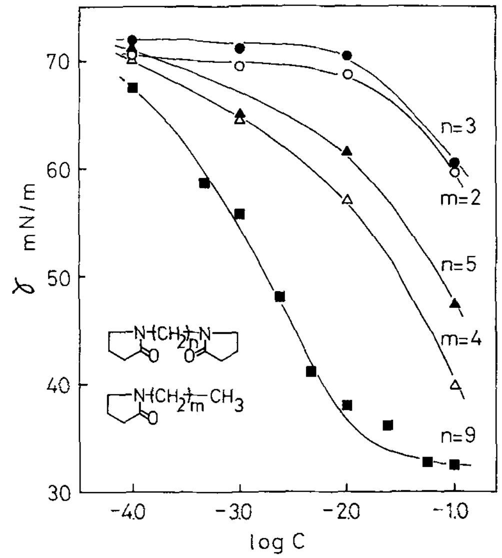


FIG. 1. Surface tension of 1,n-DPAs and mAPs in water at 20°C. (●) n=3 (•) n=9 (ι) m=2 (△) m=4.

The important thing is that γW/A value of each of 1,n-DPAs (n=5,9) is lower than that of the corresponding monofunctional derivative mAP (m=2 or 4). This result would suggest that terminal functionalization of a hydrophobic group with two hydrophilic groups effectively contributes to the increase of surface activity. It can be explained by the difference between structures of 1,n-DPA and mAP in the air-water interface, which will be discussed later. However, it has been reported that in block copolymer systems, ABA block copolymer was slightly less surface active than BAB and AB block copolymers (A:hydrophilic group, B:hydrophobic group) (23–25). On the other hand, CMCs of DPAs were calculated and listed in Table 1. CMC of 1,9-DPA was 1.45 × 10^{-2} M (or 4.27 g/L) which was compared to that of sodium laurate ([C] = 2.0 × 10^2 M), and presumably lower than those of nonionic polymer surfactants ([C]= < 10 g/L) (Table 1).

Inspection of data of Table 1 reveals that A_{min} of 1,n-DPA clearly decreases with increase of its methylene chain length, in good accordance with that of mAP. Further, the A_{min} values of 1,n-DPAs are much smaller than those of similar type of bifunctional ionic surfactants, 1,n-*bis*(sodium sulfophenoxy)alkanes (1,n-DSA). Above all, it is of importance that the increase of methylene chain length of 1,n-DSA causes increase of A_{min} value, although temperature on measurement is different. Clearly this behavior of 1,n-DSA is reverse to that of 1,n-DPA. These results seem to reflect the obvious difference of air/water interface behavior between 1,n-DPAs and 1,n-DSAs. Namely, it can reasonably be explained by assuming that 1,n-DPA takes a loop structure at air/water interface while 1,n-DSA is lying flat in the interface like mAP does, as illustrated by Figure 2. Although the exact reason of the difference is not clear, the behavior of 1,n-DSA may be

TABLE 1

Surface Properties of 1,n-DPAs, mAPs, Disulfonates, and Related Substances in Water

Compound		Temp. °C	γW/A mN/m	Γ_{max} mol/cm² × 10^{10}	A_{min} nm² × 100	CMC mol/L
1,n-DPA	n=3	20	60.6[a]	1.75	94.9	>1.0 × 10^{-1}
	n=5	20	47.7[a]	2.53	65.7	>1.0 × 10^{-1}
	n=9	20	33.5	3.12	52.9	1.45 × 10^{-2}
mAP	m=2	20	59.9[a]	1.64	101.3	>1.0 × 10^{-1}
	m=4	20	40.0[a]	3.12	52.9	>1.0 × 10^{-1}
	m=7[b]	25	33.0[a]	4.38	37.9	—
	m=9[b]	25	28.4[a]	4.61	36.0	—
	m=11[b]	25	27.5[a]	5.08	32.7	—
$NaO_3SC_6H_4O(CH_2)_6OC_6H_4SO_3Na$[c]		25	—	—	460	4.3 × 10^{-3}
$NaO_3SC_6H_4O(CH_2)_{10}OC_6H_4SO_3Na$[c]		60	—	—	750	2.0 × 10^{-3}
$NaO_3SC_6H_4O(CH_2)_{12}OC_6H_4SO_3Na$[c]		70	—	—	760	1.0 × 10^{-3}[d]
$C_{11}H_{23}COONa$[e]		70	36.0	—	—	2.0 × 10^{-2}
$C_{15}H_{31}COONa$[e]		70	31.0	—	—	3.8 × 10^{-4}
$C_{17}H_{35}COONa$[e]		70	28.0	—	—	5.6 × 10^{-5}[f]
ABA block copolymer $(NCH_2CH_2)X(NCH_2CH_2)_y(NCH_2CH_2)_z$[g]		20	35.8	—	—	—
BAB block copolymer $(NCH_2CH_2)X(NCH_2CH_2)_y(NCH_2CH_2)_z$[h]		20	31.3	—	—	—

[a] Measured minimum value.
[b] Ref (8).
[c] Ref (18).
[d] 0.558 g/L.
[e] Ref (22).
[f] 0.155 g/L.
[g] Ref (23)(x=6.5, y=9.0, z=5.6).
[h] Ref (23) (x=6.0, y=10.9, z=5.2).

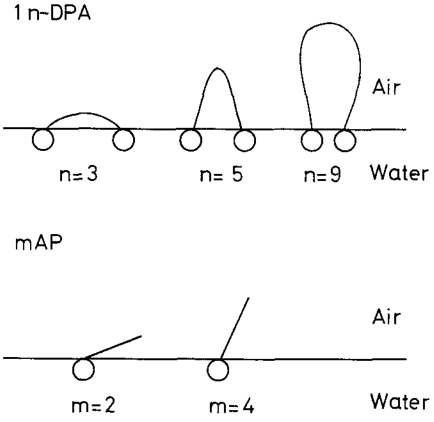


FIG. 2. Speculated structures of 1,n-DPA and mAP in air/water interface.

attributed to existence of electrostatic repulsion between the two ionic hydrophilic groups. If it is true, easy formation of the loop structure appears to be the characteristic nature of the bifunctional **nonionic** surfactants such as 1,n-DPAs which may not show serious electrostatic repulsion between the two terminal hydrophilic pyrrolidone groups in the interface.

In summary, 1,n-DPAs were synthesized and their surfactant properties were evaluated in terms of γW/A, CMC, and A_{min}. 1,9-DPA was demonstrated to be a new type of nonionic surface active agent with a simple structure. Good surface activity of 1,9-DPA is probably due to the formation of the loop structure in air/water interface, which may be characteristic of nonionic surfactants having two hydrophilic groups at both termini of a hydrophobic group.

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