Some Synergistic Properties of N-Alkyl-2-pyrrolidones, a New Class of Surfactants[1]

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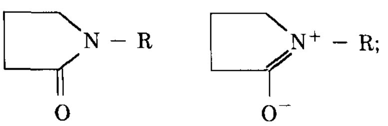
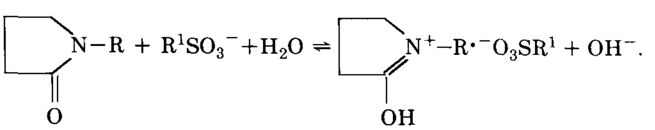
N-Alkylpyrrolidones, a new class of commercial surfactants, interact synergistically with anionic surfactants. Mixtures of the N-2-ethylhexyl-(C2,6P), N-octyl-(C8P), N-decyl-(C10P), and N-dodecyl-(C12P) pyrrolidones with commercial linear sodium alkylbenzenesulfonate (LAS) were investigated. Measurements of the molecular interaction parameters, β^σ, and β^M, for mixed monolayer formation and mixed micelle formation, respectively, in these mixtures indicated that the first three compounds show synergism in surface tension reduction efficiency and all four compounds show synergism in surface tension reduction effectiveness, when mixed in the proper proportions with LAS. This was confirmed experimentally. The N-alkylpyrrolidone-LAS mixtures also exhibit synergism in Ross-Miles foaming and in Draves (skein) wetting.

Recently, a new type of surfactant, N-alkyl-2-pyrrolidones, has become available commercially (1). The materials of this surfactant are available as essentially single components, in contrast to most commercial surfactants, which are mixtures of isomers and homologs. Because of their purity, structure/property relationships can be clearly seen in these compounds and, as a result, we have conducted an extensive investigation of their fundamental properties at various interfaces: aqueous solution/air, aqueous solution/liquid hydrocarbon, and aqueous solution/hydrophobic solid (2,3).

From their chemical structure, a resonance hybrid of the nonionic and zwitterionic forms,



these compounds in aqueous solution should interact with anionic surfactants in a manner similar to amine oxides, by accepting a proton to form an anionic-cationic salt.



These materials, therefore, have the potential to interact synergistically with anionic surfactants. Investigation of various mixtures of these materials showed that these materials do, indeed, interact synergistically with anionic surfactants at the various interfaces mentioned previously (3). The work described here covers their synergistic interaction with a commercial linear alkylbenzenesulfonate (LAS).

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MATERIALS AND METHODS

The N-alkyl-2-pyrrolidones were each of >99% purity by GC, used as received, and had n-dodecyl (C12P), n-decyl (C10P), n-octyl (C8P), and 2-ethylhexyl (C2,6P) alkyl chains as their hydrophobic groups. The LAS was a commercial grade (C-550, Vista, used as received).

Surface tension measurements were made by the Wilhelmy plate technique with a sandblasted platinum plate of ca. 5-cm perimeter. Instruments were calibrated against quartz-condensed water (specific conductivity 1.1×10^{-6} mhos cm^{-1} at 25°C) each day that measurements were made. Sets of measurements were taken at 15-min intervals until no significant change occurred.

Foaming was done by the Ross-Miles technique (4,5) at 25°C. Wetting was measured at 25°C by the Draves-Clarkson method (6).

Determination of interaction parameters. In order to determine whether mixtures of the N-alkylpyrrolidones with commercial LAS would show synergism in their surface properties, molecular interaction parameters, β^σ for mixed monolayer formation at the aqueous solution/air interface and β^M for mixed micelle formation in aqueous solution, were calculated from the surface tension-concentration curves of the individual surfactants and at least one mixture of them (Fig. 1) by the method that we have described in our previous publications on synergism (7–10). These parameters are used to predict whether synergism will exist in a mixture of two surfactants.

Synergism in surface tension reduction efficiency is present when the mixture of surfactants can reach a given surface tension at a lower concentration than the individual surfactants by themselves. The C8P-LAS mixture, at a mole fraction of N-alkylpyrrolidone in the total surfactant in the aqueous phase (α_p) = 0.412, in Figure 1 illustrates this.

The conditions for synergism in surface tension reduction efficiency are (7): (i) β^σ must be negative and (ii) $|\beta^\sigma| > |\ln C_1^0/C_2^0|$.

The parameters for the N-alkylpyrrolidone-LAS mixtures are listed in Table 1. From the data shown there, synergism of this type should exist in the C2,6P-LAS, C8P-LAS, and C10P-LAS systems. Some experimental data are shown in Table 2.

TABLE 1

Molecular Interaction Parameters for N-Alkylpyrrolidone-LAS Mixtures at 25°C

System	β^σ	$\lvert\ln(C_p^0/C_L^0)\rvert$	β^M
C2,6P-LAS	−4.0	1.87	−2.8
C8,P-LAS	−3.8	0.99	−2.6
C10P-LAS	−3.8	1.54	−2.3
C12P-LAS	−3.1	4.0	−1.7

C_p^0, C_L^0 = molar concs. of N-alkylpyrrolidone and LAS, resp., for γ = 36 dynes/cm.

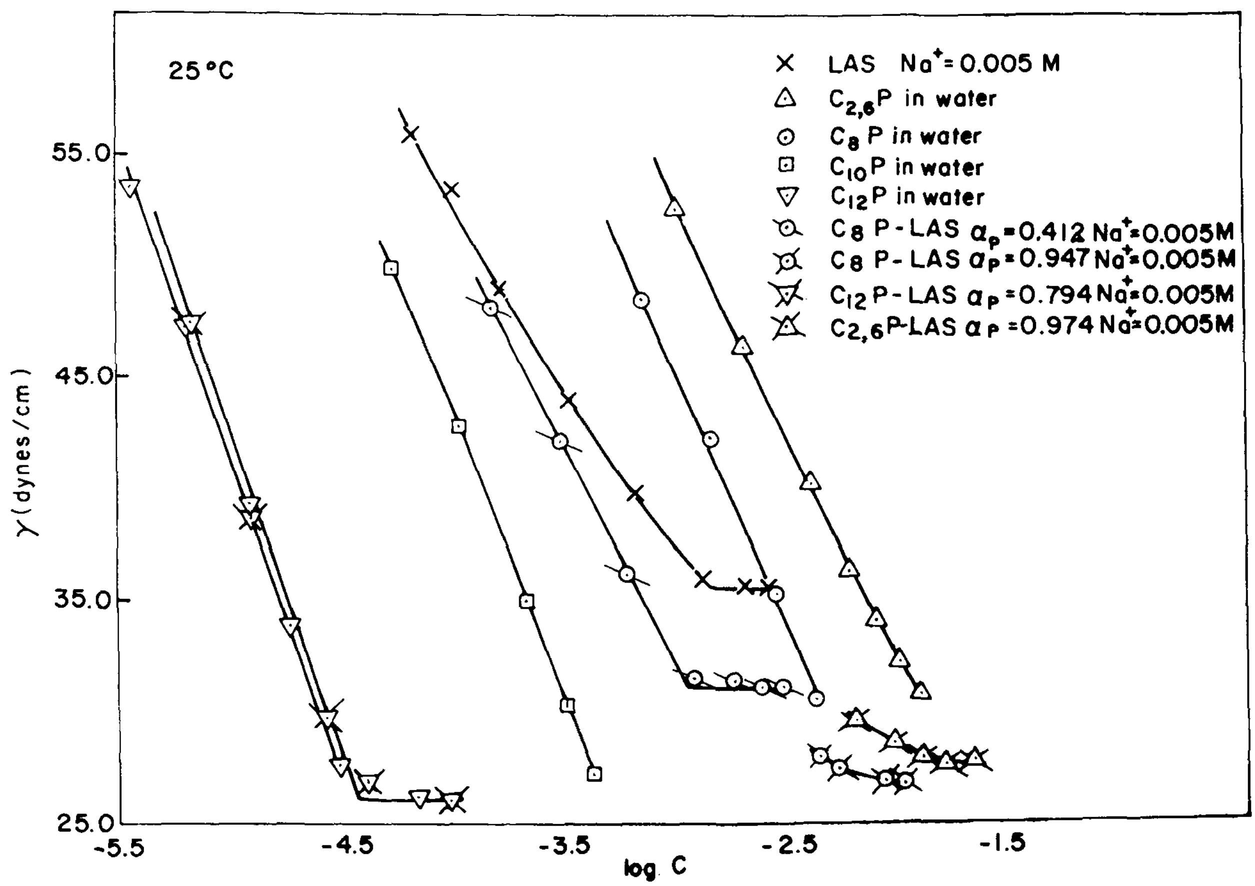

FIG. 1. Surface tension vs. log molar concentration of the surfactant in the aqueous phase.

TABLE 2

Synergism in γ Reduction Efficiency for N-Alkylpyrrolidone-LAS Mixtures (Molar concs. to yield γ = 36 dynes/cm, [Na+] = 0.005 M, 25°C)

Without LAS	Conc (M)	LAS:P (w/w)	Conc (M)
C2,6P	6.3×10^{-3}	4.4:1	8.3×10^{-4}
C8P	2.6×10^{-3}	2.5:1	6.0×10^{-4}
C10P	$1.9_1 \times 10^{-4}$	1.5:1	1.5×10^{-4}
LAS	$1.1_5 \times 10^{-3}$		

TABLE 3

Synergism in γ Reduction Effectiveness Parameters

System	$\beta^\sigma - \beta^M$	$\left\lvert \ln\left(\frac{C_1^{o,cmc} \cdot C_2^M}{C_2^{o,cmc}\ C_1^M}\right)\right\rvert$	LAS/P* (w/w)
C2,6P-LAS	−1.5	0.47	0.10:1
C8P-LAS	−1.6	0.41	0.10:1
C10P-LAS	−1.8	0.75	0.10:1
C12P-LAS	−1.3	0.67	0.35:1

Synergism in surface tension reduction effectiveness exists when the surfactant mixture at its critical micelle concentration (cmc) reaches a lower surface tension than that attained at the cmc of either surface-active component of the mixture by itslef. This is illustrated by the C2,6P-LAS and C8P-LAS mixtures at α_p = 0.947 in Figure 1. The conditions for synergism of this type to exist are (11): (i) $\beta^\sigma - \beta^M$ must be negative and (ii) $|\beta^\sigma - \beta^M| > |\ln (C_1^{o,cmc} \cdot C_2^M)/C_2^{o,cmc} \cdot C_1^M$ where $C_1^{o,cmc}$ and $C_2^{o,cmc}$ are the molar concentrations of surfactants 1 and 2, respectively; they are required to yield a surface tension value equal to that of any mixture of the two surfactants at its cmc; C_1^M, C_2^M are the critical micelle concentrations of surfactants 1 and 2, respectively. The pure, individual N-alkylpyrrolidones investigated here have limited solubility in water at 25°C and do not reach their cmcs. Therefore, the molar concentration of the N-alkylpyrrolidone at its maximum solubility in water (shown in Fig. 1) was used instead of the cmc value in condition 2 above.

The surface tension reduction effectiveness parameters are shown in Table 3. All the N-alkylpyrrolidone-LAS systems are capable of showing synergism in this respect at the proper ratio of the two surfactants. The ratios for maximum synergism (LAS/P*) in this respect (i.e., minimum surface tension, calculated by equations described in a previous publication [11]) are also shown in the table.

Table 4 shows some experimental surface tension data for these systems. The N-alkylpyrolidones form mixed

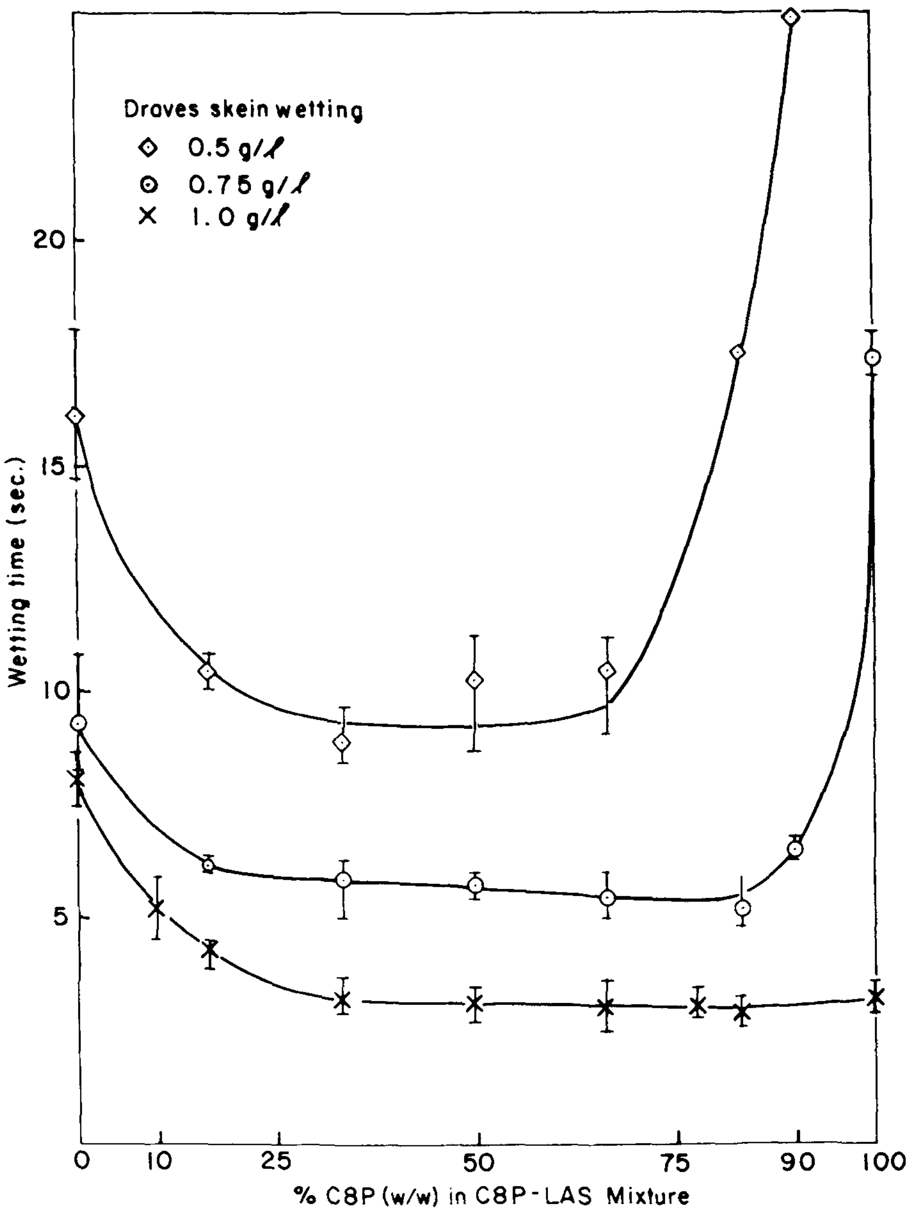

FIG. 2. Draves skein wetting time vs. percentage of C8P in C8P-LAS mixtures at various total surfactant concentrations.

TABLE 4

Synergism in γ Reduction Effectiveness, 25°C (γ, in dyne/cm)

System	γ_{min} (no LAS)	+LAS/P (w/w)	γ_{min}
C2,6P	31.8	0.10:1	27.7
C8P	31.3	0.10:1	26.8
C10P	27.2	0.10:1	26.4
C12P	27.2	0.35:1	26.1
LAS	35.5		

micelles with LAS, which increase their water solubility and permit them to reduce the surface tension of the solution to lower values. As can be seen from these data. the addition of 10-35% of LAS to the N-alkylpyrrolidone reduces the surface tension of the solution to values lower than that attainable with the individual surfactants by themselves.

Since such fundamental synergistic interactions should also result in synergism in performance properties, the foaming and wetting properties of mixtures of these materials with anionic surfactants were investigated.

Foaming. Synergism in foaming was investigated by the Ross-Miles method. Synergism in foam effectiveness exists when the initial foam height of the surfactant mixture at a given total concentration in the liquid phase exceeds that of the individual surfactants at the same concentration. A previous investigation of the relationship between synergism in the fundamental properties of mixed monolayer and mixed micelle formation and synergism in foaming (12) showed that synergism in

TABLE 5

Ross-Miles Foam Height: C8P + LAS (0.25% total surf. conc, 25°C, Na^+: 0.008 N)

Wt % C8P	Initial height (cm)	5 min (cm)
0	183	180
9.2	185	182
19.7	190	187
36.4	195	190
57.2	194	187
76.4	194	187
91.6	194	192
100	17	10

foaming effectiveness has a direct correlation with synergism in surface tension reduction effectiveness. That is, when a mixture of surfactants can reach a lower surface tension than either surfactant of the mixture by itself, then that mixture, at a given concentration in the aqueous phase, will show a Ross-Miles initial foam height greater than that attainable by either surfactant by itself, at the same concentration.

From our data on synergism in surface tension reduction effectiveness of the N-alkyl-2-pyrrolidone and their mixtures with commercial linear dodecylbenzenesulfonate (LAS), the N-octyl derivative shows the greatest degree of synergism in surface tension reduction effectiveness. It therefore has the greatest potentiality for synergism in foaming effectiveness. Some foaming data for C8P-LAS mixtures are shown in Table 5. The mixtures, at 0.25% total surfactant concentration in double-distilled water containing fixed 8×10^{-3} M total Na^+ concentration in all cases, show synergism in foaming effectiveness at weight percentages of C8P from 9–92% in the pyrrolidone-LAS mixture. It is noteworthy that the C8P, which has a very low initial foam height by itself, shows a higher foam height than LAS when only 8.4 percent of LAS is present in the mixture. Similar data on N-dodecyl-2-pyrrolidone (C12P)-LAS mixtures showed no synergism. C12P has very low solubility in water at room temperature and, at the 0.25% concentration used in these foaming studies, most of the C12P-LAS mixtures were not clear.

Wetting. Mixtures of these compounds with LAS also exhibit synergism in wetting. Synergism in wetting effectiveness exists when the wetting time of the surfactant mixture is shorter than that of the individual surfactants by themselves, at the same concentration in the liquid phase. Wetting times were measured by the Draves skein technique. Some data for C8P-LAS mixtures are shown in Figure 2. The synergism is particularly noticeable at 0.75 and 0.5 g/l total surfactant concentrations. C8P-LAS mixtures show the greatest degree of synergism, although C2,6P-LAS mixtures also show synergism in this respect.

Draves skein wetting by these mixtures appears to depend upon the surface tension of the aqueous solution at the wetting front. Investigations in our laboratory indicate that dynamic surface tension often parallels equilibrium surface tension. Therefore, it is reasonable that these mixtures, which show synergism in surface tension reduction effectiveness, also show synergism in wetting effectiveness.

ACKNOWLEDGMENT

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REFERENCES

1. Personal communication, GAF Chemicals Corp.
2. Rosen, M.J., Z.H. Zhu, B. Gu and D.S. Murphy, *Langmuir 4*:1273 (1988).
3. Rosen, M.J., B. Gu, D.S. Murphy, and Z.H. Zhu, *J. Colloid Interface Sci. 129*:468 (1989).
4. Ross, J. and G. Miles, *Oil and Soap 18*:99 (1941).
5. American Society for Testing and Materials, Method D 1173-53, Philadelphia, PA, 1953.
6. Draves, C.Z. and R.G. Clarkson, *Am. Dyestuff Rep. 20*:201 (1931).
7. Hua, X.Y., and M.J. Rosen, *J. Colloid Interface Sci. 90*:212 (1982).
8. Rosen, M.J., and X.Y. Hua, *J. Amer. Oil Chem. Soc. 59*:582 (1982).
9. Rosen, M.J., and D.S. Murphy, *J. Colloid Interface Sci. 110*:224 (1986).
10. Rosen, M.J., and B. Gu, *Colloids Surfs. 23*:119 (1987).
11. Hua, X.Y., and M.J. Rosen, *J. Colloid Interface Sci. 125*:730 (1988).
12. Rosen, M.J., and Z.H. Zhu, *J. Amer. Oil Chem. Soc. 65*:663 (1988).

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