Technical

Effect of Alkyl-2-pyrrolidone-5-carboxylate As an Additive on Emulsion Stability

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ABSTRACT

Alkyl-2-pyrrolidone-5-carboxylates (R-PCA), the derivatives of higher alcohols, were prepared and their properties as emulsion stabilizers were estimated using surface tension meter and Multiple Drop methods in the presence of sodium dodecyl sulfate (SDS) and were compared to those of another system containing a series of the corresponding alcohols as stabilizers. The R-PCA system markedly reduced the interfacial tension compared to a higher alcohol system, and the interfacial tensions for both R-PCA and higher alcohol systems decreased with the increase of carbon chain length. The stability of oil drops increased greatly by addition of R-PCA compared to higher alcohol system. In the higher alcohol system, the stability of oil drop showed the minimum at carbon 12. In the R-PCA system, the stability of oil drops increased greatly with the increase of carbon chain length. A series of R-PCA was found to be useful as emulsion stabilizers.

INTRODUCTION

Some higher fatty alcohols have been reported to be very useful as stabilizers of emulsions (1-9). Schulman and Cockbain (2) have found that the stability of Nujol-in-water emulsions increases markedly by an addition of cetyl alcohol, which results from a formation of intermolecular complexes with emulsifiers at oil-water interface. Davies and Mayers (3) also have reported that simultaneous adsorption of sodium dodecyl sulfate and cetyl alcohol to benzene-water interface results in a very high interfacial viscosity and then forms more stable emulsions compared to the system including only sodium dodecyl sulfate as an emulsifier. The reason emulsions become more stable by adding a small amount of higher fatty alcohols has so far been explained by more stable complex formations between alcohols and emulsifiers.

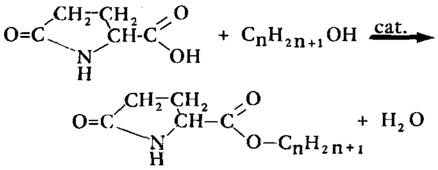
We are interested in some effects of alcohol derivatives of DL-2-pyrrolidone-5-carboxylic acid (PCA) as emulsion stabilizers, these being regarded as some of the most important natural moisturizing factors (10-13). Some workers have reported that a superior moisturizing effect is contributed to the properties of cosmetic emulsions by an addition of a small amount of stabilizers such as PCA salts or their derivatives (such as higher fatty alcohol esters of PCA) (14-17). However, their studies have not been made systematically for higher alcohols and their PCA derivatives. A higher alcohol ester of PCA can be expected to have better properties as an emulsion stabilizer than the higher alcohol.

In this study, PCA esters of alcohols with chain length of 8-16 carbon atoms are prepared. Their effects as emulsion stabilizers for the toluene-in-water emulsion system are discussed on the basis of experimental results obtained by Wilhelmy-type surface tension meter and Multiple Drop methods. These are compared to results for the corresponding higher alcohols.

EXPERIMENTAL PROCEDURES

Materials

Alkyl-2-pyrrolidone-5-carboxylate (R-PCA) was prepared by usual esterification of DL-2-pyrrolidone-5-carboxylic acid with corresponding higher alcohol in a toluene solvent using *p*-toluene sulfonic acid as a catalyst.



Water formed as a byproduct was separated as the toluene azeotrope and measured volumetrically. The endpoint of reaction was found from the amount of water as byproduct. The unreacted PCA and a trace of catalyst were removed from toluene solution by adding ca. 1 M (10 wt%) sodium carbonate solution. After the toluene was distilled, the reaction product was purified by crystallization 3 times from n-hexane. The purity of the sample was confirmed by IR and elemental analysis.

Sodium dodecyl sulfate (SDS) for biochemical use (Wako Pure Chemical Industries, Ltd., Tokyo) was extracted with petroleum ether for 100 hr to remove traces of alcohols, then purified by crystallization 3 times from ethanol and carefully dried in vacuo for 60 hr before use. The purity of the sample was confirmed by the absence of a minimum in the surface tension vs concentration curve. The CMC value of SDS, determined by conductivity method in water at 25 C, was 8.00 mmol/ℓ, in good agreement with the literature value at 25 C (18).

Higher fatty alcohols were the extra pure grade products (higher than 99%, Wako Pure Chemical Industries, Ltd., Tokyo) used without further purification.

Toluene was GR and used without further purification. The water used was passed through a Milli-Q Water Purification System (Nihon Millipore Co., Tokyo) until its specific conductivity fell below $10^{-7}\,\Omega^{-1}\,cm^{-1}$.

Apparatus and Procedure

The interfacial tension was measured with a Wilhelmy-type surface tension meter (Shimadzu Surface Tensiometer ST-1). The oil-soluble substance (higher alcohol or R-PCA) was dissolved in toluene as the oil phase, whereas SDS was dissolved in the water phase. The interfacial tensions at the toluene (oil-soluble substance containing)/water (SDS containing) interface were measured at various concentrations of the oil-soluble substances at 25 C. The concentration of SDS in the water phase was fixed at 8.00 mmol/ℓ

TABLE I

Characteristics of Additives Used

Chemical composition	Abbr.	Carbon chain length	Melting point (C)
Octyl-2-pyrrolidone-5-carboxylate	Oc-PCA	8	40
Decyl-2-pyrrolidone-5-carboxylate	De-PCA	10	52
Dodecyl-2-pyrrolidone-5-carboxylate	La-PCA	12	60
Tetradecyl-2-pyrrolidone-5-carboxylate	My-PCA	14	68
Hexadecyl-2-pyrrolidone-5-carboxylate	Ce-PCA	16	73
Octyl alcohol	Oc-OH	8	-15
Decyl alcohol	De-OH	10	7
Dodecyl alcohol	La-OH	12	24
Tetradecyl alcohol	My-OH	14	38
Hexadecyl alcohol	Ce-OH	16	50

near the cmc to obtain uniform and stable droplets for the measurements of the stability of the oil droplets (19). These measurements were started 10 min after initial contact between the 2 phases, since the equilibria at these interfaces were reached after 5 min (20).

To measure the stability or persistence of oil drops at the oil-water interface, an apparatus shown in Figure 1 similar to that of Cockbain and McRoberts was used (19).

The apparatus consists of vessel A (diameter 21 cm) in which the oil-water interface is made, a thermostated water jacket B and tip C to form the oil drop. Tip C has 3 parts: a syringe (capacity 2 ml), a syringe needle with flattened tip and a micrometer which is modified to push the syringe piston and then measure the distance travelled by the piston. As Cockbain et al. (19) found, the stabiltiy of the drops was hardly affected by volume in the range 0.0005-0.01 ml. Therefore, the size of the drop was maintained at ca. 2 x 10^{-3} ml by changing the needle size. The distance from the tip of C up to the interface was ca. 2 cm. After detaching a drop from the top of C, it ascends in vessel A and then comes into contact with a planar oil-water interface and finally coalesces with time. The time of coalescence or lifetime of the drops until 30 oil drops coalesce at the interface was measured at 25 C using a stop watch. When the last drop comes into contact with the oil-water interface, the measurement of lifetime was started. The formation of the 30 oil drops required 30 sec, but the time for setting of the oil drops did not affect the experimental data.

The experiment was made with the toluene-water system containing various concentrations of the oil-soluble substances in the toluene phase as additives and 8 mmol/ℓ of SDS in the water phase as an emulsifier. When the number of drops remaining without coalescence (N) was plotted in logarithmic scale against time (t), most plots were found to be linear in the range of part AB on the curve, as shown in Figure 2, in agreement with the results obtained by Cockbain et al. (19).

In general, the overall stability of droplet can be evaluated by the time required for half the droplets to coalesce (t 1/2) (19, 21-22); these half-life time values were used in order to estimate the stability of oil drops in this experiment.

RESULTS AND DISCUSSION

In general, it is necessary to satisfy the following requirements in order to make a stable emulsion: (a) small differences in density between the dispersed and continuous phases; (b) high viscosity of the continuous phase; (c) small interfacial tension between the dispersed and continuous phases; (d) expanded electrical double layer existing at the oil-water interface; and (e) mechanical strength in the adsorbed layer at the oil-water interface. In the presence of additives (oil-soluble substances), the most important factors affecting substantial emulsion stability seem to be interfacial tension and mechanical strength of the interfacial film. Therefore, coalescence of droplets and interfacial tension may be the most important factors in order to discuss the stability of emulsions.

Figure 3 shows the effects of addition of various alcohols and the PCA esters of corresponding alcohols as the oil-soluble substances on the interfacial tensions at the toluene/SDS solution. In both cases, the interfacial tensions decreased with increasing concentrations of alcohols or R-PCA, dissolved in the oil phase. The effectiveness in reducing the interfacial tensions in the R-PCA was larger than for the alcohols over the entire concentration range, as shown in Figure 3. Notably, the interfacial tension could decrease to as low as 2 dyn/cm even in a dilute toluene

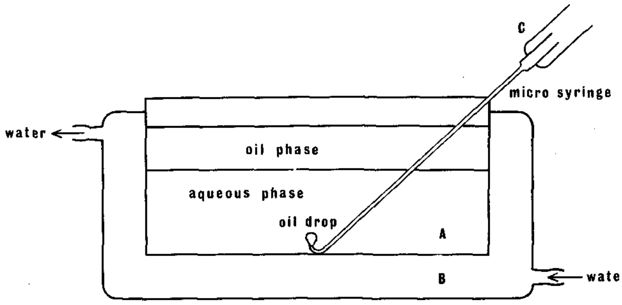


FIG. 1. Apparatus for determining the lifetime of oil drops.

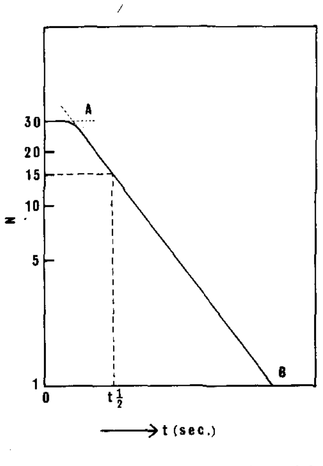


FIG. 2. Typical relationship between N (in logarithmic scale) and t.

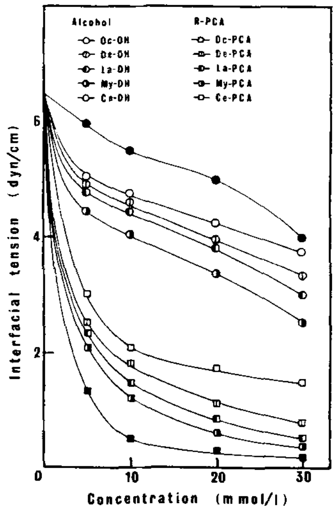


FIG. 3. Effect of oil-soluble substances on the interfacial tension at toluene/SDS soln interface. Water phase: 8 mmol/ℓ SDS soln.

solution of R-PCA. This suggests that SDS molecules interact with R-PCA molecules more strongly than higher alcohol molecules, probably because of the difference of the ion-dipole interactions between SDS and additives. To know the influence of the hydrophobic group in the additives (oil-soluble substances) on the interfacial tension, the interfacial tensions for 2 series of higher alcohols and R-PCA were plotted against the carbon numbers of the corresponding alcohols as shown in Figure 4.

Both these interfacial tensions decreased with increasing chain length except for the alcohols, where a minimum was observed at C_{14}; that is, the interaction of additives with SDS is found to increase with the increase in the effect of hydrophobic groups in the additives.

Figures 5 and 6 show the effect of additives (higher alcohol and R-PCA) on the stability of oil drop at the toluene/SDS solution interface. As shown in Figure 5 for higher alcohols, the stability of oil drop increased with additive concentration, but decreased at its high concentration. This result suggests that the surface of oil drop is completely occupied by the alcohol molecules, and then the adsorbed amount of SDS at the oil-water interface decreases. As shown in Figure 6 for R-PCA, the stability of an oil drop was remarkably increased above a certain concentration and the oil drops hardly coalesced. Oc-PCA showed behavior similar to the higher alcohol, but the effect of Oc-PCA on the stability of oil drop was larger than that of the higher alcohols. Therefore, it is recognized that oil drop can be markedly stabilized by the R-PCA system compared to the higher alcohol system at all concentrations. Furthermore, apparently SDS interacts with R-PCA more strongly than higher alcohol. It is concluded that a pyrrolidone ring plays an important role in making the oil drop stable. This also suggests that pyrrolidone rings have some ability to capture SDS molecules from aqueous solution into the surface of oil droplets. Accordingly, molecular association at an oil-water interface between SDS and R-PCA molecules can be considered to be different from those of higher alcohols.

Figures 7 and 8 show the effect of hydrocarbon chain lengths of higher alcohols and R-PCA, respectively, on the stability of oil droplets at the toluene/ aqueous SDS solution interface. The stability of oil droplets for the higher alcohol systems decreased with increased hydrocarbon chain length of carbon atoms 8-12, then increased with increased chain length from 12 to 16 and showed just a minimum at C_{12} corresponding to lauryl alcohol as shown in Figure 7.

This suggests that the polar groups in alcohols with carbon chain length below C_{12} interact with the ionic groups of SDS more effectively than with the hydrocarbon chain parts. The increase in the stability of the system using alcohols above C_{12} can be considered to result from stronger chain-chain interaction between alcohol and SDS. The minimum in Figure 7 appears at carbon 12 just where both effects of polar and hydrocarbon groups are compensated. In the R-PCA systems, the stability of oil drops depended on the hydrocarbon chain length and gradually increased with increasing chain length at all concentrations, then markedly increased above a certain carbon chain length, as shown in Figure 8. This apparently results from the stronger interaction between hydrocarbon chains of R-PCA and SDS.

According to Dervichian (23) it has been reported that the van der Waals forces between the hydrocarbon chains of emulsifier molecules primarily result in the regular arrangement of the molecules in mixed monolayers and also that emulsifier molecules cannot associate easily in surfactants with hydrocarbon chain below 8 C atoms. From these suggestions and experimental findings, it may be concluded that a molecular association between SDS and additives is dependent of the van der Waals forces between their hydrocarbon chains or on the ion-dipole interactions

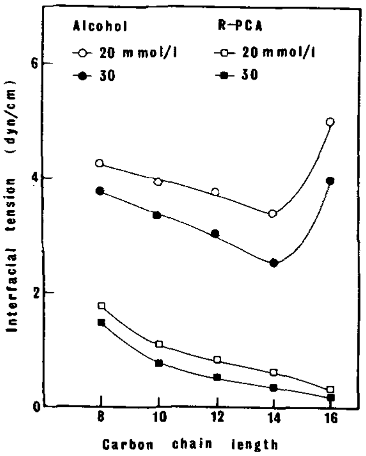


FIG. 4. Effect of hydrophobic group in oil-soluble substances on the interfacial tension at toluene/SDS soln interface.

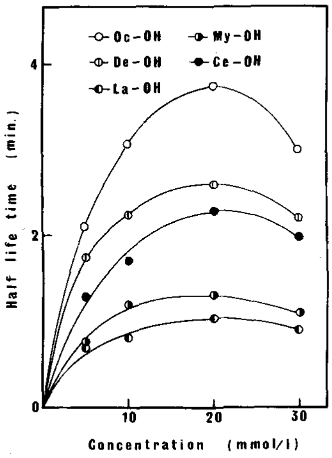


FIG. 5. Effect of higher alcohols on the stability of oil drop at toluene/SDS soln interface. Water phase: 8 mmol/ℓ SDS soln.

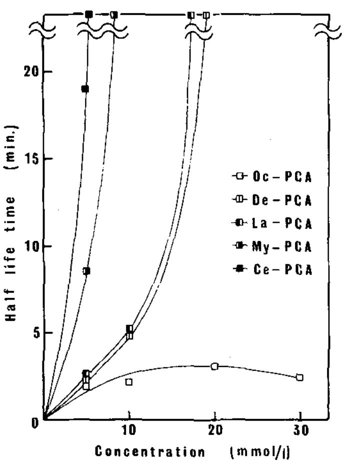


FIG. 6. Effect of R-PCA on the stability of oil drop at toluene/SDS soln interface. Water phase; 8 mmol/ℓ SDS soln.

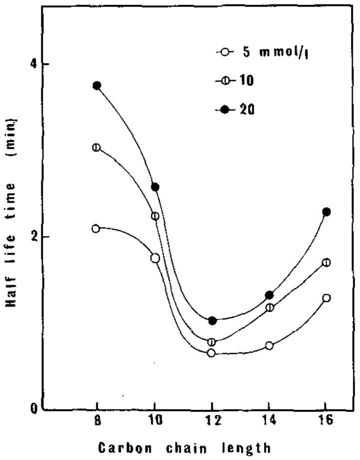


FIG. 7. Effect of hydrophobic group in higher alcohols on the stability of oil drop at toluene/SDS soln interface.

between their head groups, and also that the mechanically stronger interfacial film is formed because of stronger interaction between SDS and additive molecules.

In general, the ionic character of SDS has been reported to create an electrical double layer at the oil-water interface in addition to the film barrier, thus inhibiting coalescence. Therefore, it is considered that the stability of an oil drop depends on the adsorbed amount of SDS available for inhibition of coalescence. It is also recognized that a condensed mixed monolayer of SDS and additives on the surface of emulsion drops is necessary for the stability of the oil drop, and the instability of the oil drop is caused by an incomplete oil surface coverage. Many investigators have reported that higher alcohols form a stable complex with SDS at the oil-water interface (1-9), but it is expected that as SDS molecules are not sufficiently adsorbed at the oil-water interface because of their electric repulsion, even if SDS-alcohol complex is formed, a stable 2-dimensional complex is not formed. When R-PCA are used as additives in the oil phase, the stronger interfacial film is considered to be formed because parts of a charge on SDS will be neutralized by the dipole of R-PCA, and the adsorbed amount of SDS to the oil-water interface will be increased.

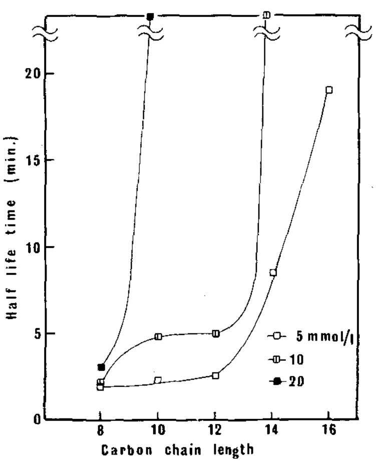


FIG. 8. Effect of hydrophobic group in R-PCA on the stability of oil drop at toluene/SDS soln interface.

REFERENCES

1. Schulman, J.H., and E.K. Rideal, Proc. R. Soc. (London) 46: 122B (1937).
2. Schulman, J.H., and E.G. Cockbain, Trans. Farady Soc. 36:651 (1940).
3. Davies, J.T. and G.R.A. Mayers, Ibid. 56:691 (1960).
4. Kung, H.C., and E.D. Goddard, J. Phys. Chem. 67:1965 (1963).
5. Carless, J.E., and G. Hallworth, J. Colloid Sci. 26:75 (1968).
6. Kung, H.C. and E.D. Goddard, J. Phys. Chem. 68:3465 (1964).
7. Vold, R.D., and K.L. Mittal, J. Colloid Interface Sci. 38:451 (1972).
8. Fukushima, S., M. Takahashi and M. Yamaguchi, Ibid. 57:201 (1976).
9. Elworthy, P.H., A.T. Florence and J.A. Rogers, Ibid. 35:34 (1971).
10. Laden, K., Amer Perfum. Cosmet. 82:77 (1967).
11. Laden, K., and R. Spitzer, J. Soc. Cosmet. Chem. 13:263 (1962).
12. Laden, K., and R. Spitzer, Ibid. 18:351 (1967).
13. Laden, K., and R. Morrow, Ibid. 21:417 (1970).
14. Yamagishi, M., Japan Patent Tokko 45-15392 (1970).
15. Ichikawa, T., Japan Patent Tokkai 50-22008 (1975).
16. Sumida, S., Japan Patent Tokko 51-35474 (1976).
17. Yunber, F., Japan Patent Tokkai 52-122637 (1977).
18. Hayase, K., and S. Hayano, Bull. Chem. Soc. (Japan) 50:83 (1977).
19. Cockbain, E.G., and T.S. McRoberts, J. Colloid Sci. 8:440 (1953).
20. Ogino, K., and M. Ota, Bul. Chem. Soc. (Japan) 49:1187 (1976).
21. Nielsen, L.E., R. Wall, and G. Adams, J. Colloid Sci. 13:441 (1958).
22. Edge, R.M., and M. Greaves, Inst. Chem. Eng. Symp. Series *26:63 (1967).*
23. Dervichian, D.G., in "Surface Phenomena in Chemistry and Biology," edited by P. Sherman, Academic Press, New York, 1968, pp.82-89.

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