Drug Development and Industrial Pharmacy, 24(1), 95–100 (1998)

COMMUNICATION

Influence of the Purification of Sodium Dodecyl Sulfate on the Physical Properties of Solutions and O/W Emulsions

C. Arias,[1,*] I. Gómez-Escalonilla,[1] C. Rueda,[1]
and C. Molina[2]

[1]*Departamento de Química Física Farmacéutica and*
[2]*Departamento de Farmacia y Tecnología Farmacéutica, Facultad de Farmacia, Universidad Complutense, Ciudad Universitaria, E-28040 Madrid, Spain*

ABSTRACT

The effect of the purification of sodium dodecyl sulfate (SDS) has been studied in aqueous solutions and in o/w emulsions. The physical properties (surface tension, conductivity, light dispersion, viscosity, and granulometry) depend on the degree of purity of surfactant. This effect is less important within the emulsion technology when thickener or cosurfactant agents are added to the emulsion.

INTRODUCTION

Sodium dodecyl sulfate (SDS) is used in many systems within pharmaceutical technology such as absorption, micellization, and binding to synthetic and natural macromolecules (1–3). Its addition to aqueous solutions of polymers allows the effective number of intramolecular links to be increased and therefore the size of aggregate is improved and the viscosity is increased (4).

However, the commercial SDS is often contaminated with impurities such as sodium dodecyl homologs, electrolytes, and small but significant amounts of free alcohol which can be difficult to eliminate (5,6).

The physical parameters, number of micelle aggregation, micelle volume, molecular weight (7), and ionization degree change according to the presence of impurities. Small amounts influence the physical properties of solutions, as can be detected in surface tension–concentration curves (8). Several works (9) justify the minimum

---

*To whom correspondence should be addressed.

detected in this curve due to the presence of dodecyl alcohol; even this compound causes a change of the hydrophobic region size due to its solubilization inside the micelle, and therefore the aggregation number and the critical micelle concentration decrease.

On the other hand, an increase of the ionic strength and a change in the intermicelle interactions is detected in the sample with the presence of electrolytes which influences the amount of surfactant used in each case.

The aim of this paper is to check if the degree of purity of SDS influences not only the dissolution properties but also the physical stability of emulsions where this is used as surfactant.

MATERIALS AND METHODS

Oil-in-water (o/w) emulsions were prepared. The surfactant agent was SDS with different degrees of purity. This surfactant was purified from the commercial SDS (95%) (Baker) by recrystallization from ethanol and extraction by diethyl ether (Merck) for 24 hr in soxhlet at 60°C. SDS was dried in vacuum at 50°C (10).

The emulsification process was carried out through a Politron homogenizer Pt-3000 at 20,000 rpm for 3 min. In all emulsions the internal phase is constituted by soy bean oil 10%.

Four types of emulsions were prepared in order to reach different aims. In the emulsions I, II, IV, we wanted to determine the influence of the purification of surfactant at different concentrations: from 10^{-4} M to 10^{-2} M, without thickener and cosurfactant agents (emulsion type I), with sodium carboxymethylcellulose 1% as thickener agent (emulsion type II), and with 1-pentanol 10% as cosurfactant agent (emulsion type IV).

From the results of our study, we chose the surfactant concentration 8×10^{-3} M to prepare the emulsion type III, where we wanted to determine the percentage of cosurfactant that is more suitable to promote higher stability of the emulsified system; therefore, we used 1-pentanol at different percentages: 1%, 2.5%, 5%, 7.5%, and 10%. To study the physical stability of emulsions, two techniques were employed: rotation viscosimetry, in which the shear rates varied from 11.16 sec^{-1} to 1731 sec^{-1}; and analysis of particle size, in which the Galay Cis-1 analyzer employed a scanning He-Ne laser beam for the time of transition measurements. The distribution of globules of internal phase allows the determination of the statistical diameter surface/volume.

On the other hand, different solutions of purified and commercial SDS (concentrations from 10^{-3} M to 10^{-2} M) in distilled water were prepared and the study was carried out by using three techniques: conductimetry (Metrohm AGCU-9100 Herisau, measurement range from 1 S to 100 mS), light scattering (P.G.D. 42000 Soffica model with polarized light from mercury steam lamp at $\lambda = 5460$ Å), and surface tension (Tensiometer K12, Kruss).

RESULTS AND DISCUSSION

SDS Solutions

Figure 1 shows the surface tension measurements versus surfactant concentration. As the concentration increases the surface tension decreases, still reaching a minimum value of 5×10^{-3} M. At higher concentrations the surface tension increases and only at concentrations higher than 2×10^{-2} M the surface tension tends to keep constant. This behavior is due to the presence of homologs and electrolytes in the surfactant. By this technique we can detect differences according to the degree of purity of surfactant. The surface tension is higher in the case of the purified SDS than in the commercial SDS. The purification process allows smaller changes of surface tension and therefore it is easier to determine the critical micelle concentration (CMC).

Light dispersion measurements allow the determination of the CMC at 5 mM (commercial SDS) and at 8 mM (purified SDS).

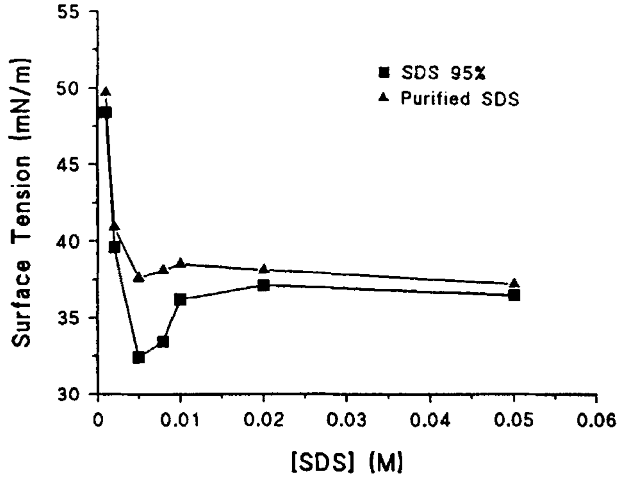

Figure 1. Surface tension versus surfactant concentration.

Table 1

opes Corresponding to the Specific Conductivity Versus SDS Concentration Before (S_1) and After (S_2) CMC

actant	$S_1/10^3$ μS m² mol⁻¹	$S_2/10^2$ μS m² mol⁻¹	α[a]
mercial SDS	1369.00	188.05	0.014
fied SDS	1316.22	184.24	0.014

egree of micellar dissociation.

onductivity measurements show the same results for
C. The relation between the specific conductivity
the surfactant concentration (Table 1) allows the
ee of micellar dissociation (α) to be calculated by
slope relation method (11).

able 2 shows the viscosity values at different shear
; in order to avoid the influence of shear rate, the
lts were obtained by extrapolating the shear rate to
. At lower concentrations (10^{-3} M) than CMC, the
rent viscosity of commercial SDS is higher than in
ase of purified SDS; however, at higher concentra-
s (10^{-2} M) than CMC, the opposite is true. The
tural numbers ($n - 1$) calculated according to the
ald equation are smaller than 1 in both solutions.
n these results we can conclude a dilatant behavior
therefore the micelle formation does not influence
ncrease of volume.

ecause the differences found between both SDS
entrations are not too large, we devised a statisti-
reatment in order to determine if there were significant differences between the viscosity values (Table 3). The results obtained from 62 samples show a normal distribution. The hypothesis test for α = 0.05 allows the significant differences to be checked and from these results, we can conclude that the viscosity measurements allow the presence of impurities in the solutions of SDS to be determined.

Emulsions

Emulsions Type I

Figures 2(a) and 2(b) show the particle size distribution at two concentrations 8×10^{-3} M [Fig. 2(a)] and 5×10^{-3} M [Fig. 2(b)]. A bimodal distribution of the globule size can be seen as the concentration increases. On the other hand, as the degree of purity increases, the distribution is more narrow with more homogenity in the particle size. Table 4 shows the mean diameter which decreases in the case of purified SDS compared to the value of commercial SDS.

Figure 3(a) shows the viscosity values versus shear rate according to the different surfactant concentrations. At concentrations higher than 10^{-3} M, the viscosity of emulsions with purified surfactant is higher than with commercial SDS.

With both surfactants a dilatant behavior can be detected because as the shear increases the viscosity increases. According to Stalidis et al. (12) in these types of o/w emulsions the stability can be justified due to the ionic surfactant absorption process which allows electrostatic interactions above 10^{-4} M.

Table 2

Apparent Viscosity (mPa·sec) Values Corresponding to Commercial and Purified SDS at Different Shear Rates (γ) and Concentrations[a]

	[SDS] = 10^{-3} M		[SDS] = 10^{-2} M	
γ (sec⁻¹)	SDS 95%	Purif. SDS	SDS 95%	Purif. SDS
557	0.69	0.30	0.59	0.64
747	0.75	0.59	0.65	0.70
983	0.83	0.67	0.77	0.79
1313	1.02	0.94	0.93	0.97
1731	1.21	0.94	1.07	1.13
γ = 0 sec⁻¹	0.40	0.21	0.38	0.40
$n - 1$	0.50	0.55	0.55	0.52
r	0.982	0.998	0.995	0.979

[a] Structural numbers ($n - 1$) and correlation coefficients (r).

Table 3

Statistical Values for 31 Samples of Commercial SDS and 31 Samples of Purified SDS at Different Shear Rates (γ)

	SDS 95%		Purified SDS	
γ (sec^{-1})	μ	σ	μ	σ
0[a]	0.38	0.06	0.43	0.06
557[b]	0.63	0.07	0.69	0.07
983[c]	0.79	0.05	0.81	0.03
1731[d]	1.12	0.08	1.17	0.05

$Z_{\alpha/2}$ = 1.96; statistical estimator: [a]3.22, [b]3.37, [c]2.38, [d]3.03; μ = mean value; σ = standard deviation.

Emulsions Type II

The presence of thickener agent allows the globule size to be reduced with regard to the size detected in emulsions type I (Table 4). At CMC, the statistical diameter surface/volume decreases from 7.81 μm ± 3.88 to 2.39 μm ± 1.03 (commercial SDS) and from 7.41 μm ± 3.75 to 2.02 μm ± 0.88 (purified SDS). In these emulsions, the presence of thickener agent has more influence on the particle size distribution than the degree of purity of surfactant, even though the percentage of smaller particles is larger with purified SDS than with commercial SDS [Fig. 2(c)].

The presence of sodium carboxymethylcellulose (13) changes the rheological behavior with regard to the emulsion type I. The flow is shear thinning and the viscosity increases [Fig. 3(b)]. The influence of the degree of purity is more important at concentrations 5×10^{-3} M and 8×10^{-3} M where the viscosity increases with the purification of surfactant.

Emulsions Type III

The different percentages (1, 2.5, 5, 7.5, 10%) of 1-pentanol were added to the aqueous phase in order to study its influence as cosurfactant. As the 1-pentanol concentration increases, the distribution of particle size is more narrow and homogeneous [Fig. 2(d) and 2(e)] and the statistical diameter surface/volume decreases. With 10% of cosurfactant the diameter is about 1 μm and therefore we chose this percentage to prepare the emulsions type IV.

Emulsions Type IV

The emulsified systems were prepared by adding 1-pentanol 10% to the aqueous phase constituted by distilled water and surfactant.

At surfactant concentration higher than 5×10^{-3} M, the degree of purity does not seem to be an important factor because the diameter (Table 4) and the distribution of particle size is similar in both surfactants; this could be due to the resolution power of the analyzer. We cannot see differences between both surfactants when the diameter is smaller than 0.82 μm [Fig. 2(f)].

As the shear rate increases the viscosity increases too, therefore we can conclude that the presence of cosurfactant does not change the dilatant behavior detected in emulsions type I, however the viscosity is higher in emulsions type IV.

CONCLUSIONS

An increase in the degree of purity of surfactant improves the physical stability of emulsions because the particle size distribution is more homogeneous, the per-

Table 4

Statistical Values of the Number Distributions Corresponding to Emulsions Type I, Type II, and Type IV

	Emulsion Type I				Emulsion Type II				Emulsion Type IV			
[SDS] (M)	SDS 95%		Purif. SDS		SDS 95%		Purif. SDS		SDS 95%		Purif. SDS	
	μ	σ	μ	σ	μ	σ	μ	σ	μ	σ	μ	σ
10^{-4}	2.44	2.61	2.22	2.32	1.89	1.32	2.15	1.46	1.91	1.38	1.96	1.33
10^{-3}	2.79	3.44	2.30	2.22	1.70	0.97	1.73	0.94	1.22	0.57	1.21	0.62
5×10^{-3}	2.73	2.65	1.16	1.35	1.56	0.78	1.44	0.69	0.86	0.24	0.82	0.20
8×10^{-3}	3.57	3.19	3.07	2.70	1.29	0.54	1.38	0.64	0.78	0.11	0.77	0.11
10^{-2}	3.44	2.98	3.38	2.82	-	-	1.35	0.61	0.77	0.09	0.77	0.09

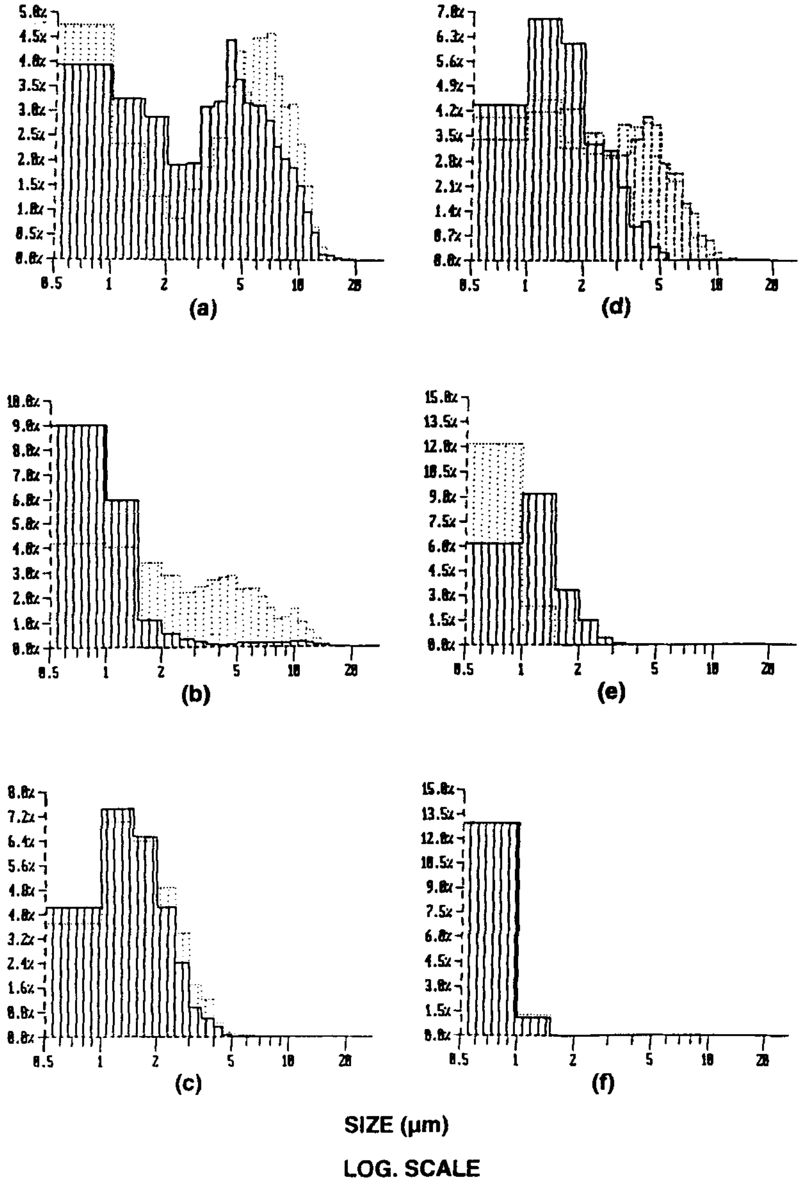

Figure 2. Probability number density graph versus size log scale for different types of emulsions. (a) Type I ([SDS] = 8 × 10^{-3} M); __ purified, . . . commercial. (b) Type I ([SDS] = 5 × 10^{-3} M); __ purified, . . . commercial. (c) Type II ([SDS] = 5 × 10^{-3} M, [Na-CMC] = 1% w/v); __ purified, . . . commercial. (d) Type III ([purified SDS] = 8 × 10^{-3} M); __ [1-pentanol] = 5% w/v, . . . [1-pentanol] = 2.5% w/v, ._._._ [1-pentanol] = 1% w/v. (e) Type III ([Purified SDS] = 8 × 10^{-3} M); __ [1-pentanol] = 7.5% w/v, . . . [1-pentanol] = 10% w/v. (f) Type IV ([SDS] = 8 × 10^{-3} M, [1-pentanol] = 10% w/v); __ purified, . . . commercial.

centage of particles with smaller size increases, and the statistical diameter surface/volume decreases and therefore we could deduce a higher level of bioavailability. The viscosity increases in the case of purified SDS and therefore the physical stability of emulsion increases too; however the rheological behavior does not change with the purity of surfactant.

Both parameters, particle size and viscosity, are more evident without thickener and cosurfactant agents, because with those compounds the particle size decreases

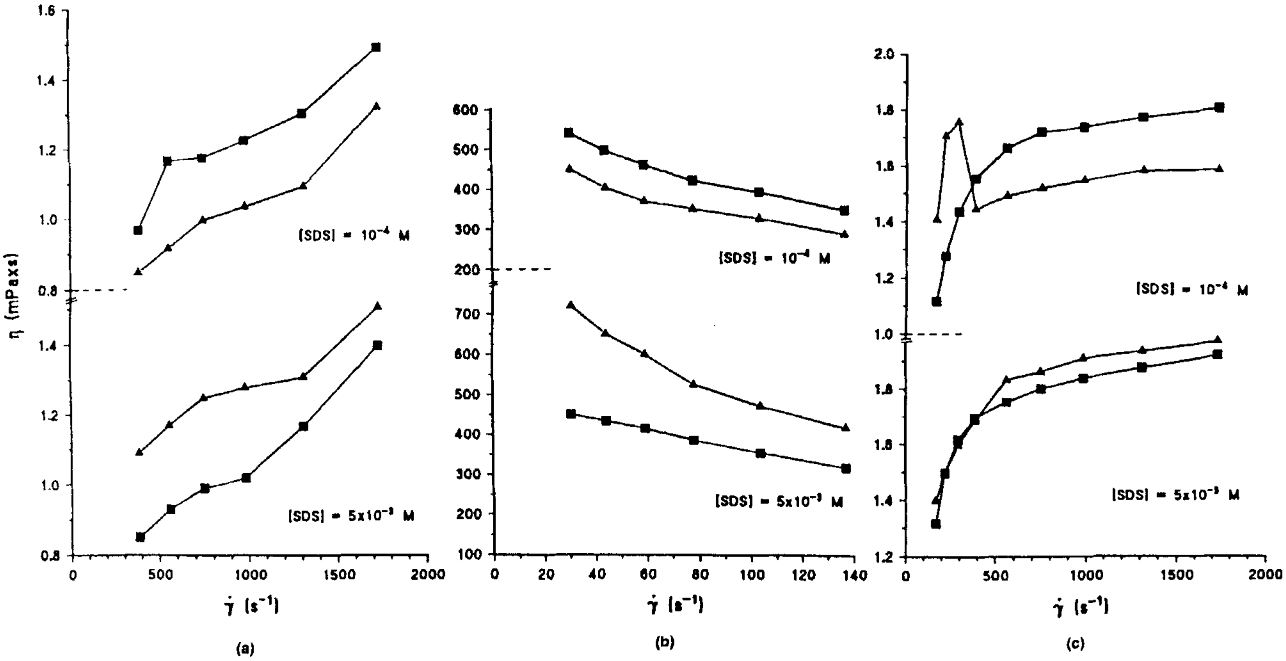

Figure 3. Viscosity curves of emulsions type I (a), type II (b) and type IV (c). (■) SDS 95% (commercial), (▲) purified SDS (at 20°C).

and differences cannot be seen between the two surfactants.

We can conclude that an increase in the degree of purity of surfactant improves the physical properties of the emulsion. Its effect is more evident without thickener and cosurfactant agents and therefore in those emulsions where it is needed, the use of these coadjuvants it is not necessary to purify the commercial SDS.

ACKNOWLEDGMENTS

This paper was partially supported by Dirección General de Investigación Científica y Técnica (M.E.C./ APC96-0013).

REFERENCES

1. M. N. Jones, *Biological Interfaces*, Elsevier, Amsterdam, 1975, pp. 101–130.
2. M. J. Rosen, *Surfactant and Interfacial Phenomena*, Wiley-Interscience, New York, 1978.
3. C. Tanford, *The Hydrophobic Effects: Formation of Micelles and Biological Membranes* (2nd ed.), Wiley-Interscience, New York, 1980, p. 131.
4. W. Binana-Limbele, F. Clouet, and J. Francois, Colloid Polym. Sci., 271, 748 (1993).
5. B. R. Vijayendran, J. Colloid Interface Sci., 60, 418 (1977).
6. A. Smith, J. Colloid Interface Sci., 66, 575 (1978).
7. R. J. McGreery and R. S. Schechter, J. Colloid Interface Sci., 127, 209 (1989).
8. G. Czichocki, D. Vollhardt, and H. Mach, J. Colloid Interface Sci., 95, 275 (1983).
9. J. S. Zhou and M. Dupeyrat, J. Colloid Interface Sci., 134, 320 (1990).
10. M. Nakamae, M. Abe, and K. Ogino, J. Colloid Interface Sci., 135, 449 (1990).
11. M. Valiente and E. Rodenas, Anales de Química, 85, 192 (1989).
12. G. Stadilis, A. Avranas, and D. Jannakoudakis, J. Colloid Interface Sci., 135, 313 (1990).
13. I. Cayre, C. Arias, and C. Rueda, Rev. Roum. Chim., 31, 727 (1986).