Anionic surfactant–water systems: Influence of lecithin addition on the rheological behavior

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Synopsis

The viscosity values of ternary systems containing anionic surfactant, lecithin, and water have been studied using sodium alkyl-ether-sulfate, sodium dodecylsulfate, and sodium dodecylbenzenesulfonate as surfactants. The highest concentrations of surfactant and lecithin studied were 30% and 3% in weight, respectively. The following conclusions may be drawn: (1) All the systems present Newtonian rheological behavior, except those containing: 30% sodium alkyl-ether-sulfate and 2% or more lecithin, 30% sodium dodecylsulfate and 3% lecithin. These non-Newtonian systems behave like pseudoplastic fluids. (2) The addition of lecithin improves the solubility of sodium dodecylsulfate in water, but diminishes the solubility of sodium dodecylbenzenesulfonate. (3) The systems containing sodium alkyl-ether-sulfate show an abnormal temperature dependence on viscosity, with maximum values at temperatures around 283–288 K. These viscosity maxima are related to the existence of ethylene oxide groups in surfactant molecules. (4) The addition of lecithin causes an increase in viscosity values of surfactant–water systems and also a shift of the maximum viscosity temperature toward higher values.

INTRODUCTION

The use of surfactants and some phosphatides is common in the cosmetic and food industries.[1] However, these systems have not been systematically studied from the point of view of their rheology and only limited references are available.[2–5] The phosphatides most frequently used are lecithins. These are the chemical compounds obtained when a triglyceride fatty acid radical is substituted by phosphoric acid esterified with choline. The greater fraction of the lecithins commercialized is

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obtained from soybean oil, and represents 20% of phosphatides production. Lecithin is obtained too from some other oils such as those from colza, peanut, and sunflower seeds, and some other sources like egg yolk.[6]

Lecithin is specially useful in food industries because of its emulsifying power and natural origin. It is used as a fat disperser. Another property of lecithin is its antioxidant capacity and due to this property, lecithins are used in small amounts to prevent the oxidation of some fats and cosmetic products.[7–10]

What is studied in this work are the effects of temperature and concentration on the rheological behavior of anionic surfactant–lecithin–water systems. The surfactants studied are anionics, of great industrial utilization, which have different chemical structure. From the knowledge of the rheological behavior we try to obtain information to suggest the micellar structure of the former systems.[11–19]

Egg yolk has been used because the high quality of the commercialized product.

EXPERIMENTAL

Products

Sodium alkyl-ether-sulfate (AES): This was based on a mixture of fatty alcohols (75% w/w in C_{12} and 25% w/w in C_{14}), with an average ethoxylation grade corresponding to two moles of ethylene oxide and containing 70% w/w surfactant in an aqueous system. The amount of total electrolytes and unsulfated fatty ether alcohols was 3% and 1%, respectively.

Sodium Dodecylsulfate (DS): This was prepared with a surfactant content of 31.7% in water, and a content of electrolytes and unsulfated fatty alcohols of 1.2% and 1.5%, respectively.

Sodium Dodecylbenzenesulfonate (LAS): This was prepared with a surfactant content of 66% in water, and a content of electrolytes and unsulfated fatty alcohols of 2.1% and 1.5%, respectively.

The surfactants used in the present work are commercial products, and the three have linear alkyl chain.

Lecithin: Egg lecithin was supplied by Merck, and was used without further purification. The study of its fatty acid composition gave the following results, in weight percentage:

Palmitic acid	33.5%
Stearic acid	14.0%

Oleic acid	35.0%
Linoleic acid	14.5%
Araquidonic acid	3.0%.

Preparation of the systems

Systems were prepared by weight, combining the amount of surfactant, distilled water, and lecithin required in each case.

The systems prepared contain 0%, 1%, 2%, or 3% of their weight in lecithin and 0%, 10%, 20%, or 30% in surfactant. Due to the abnormal behavior of the 30% AES systems, it was also studied at intermediate lecithin concentrations of 0.5%, 1.5%, and 2.5%.

In order to identify each of the systems, two numbers have been used: the first stands for the surfactant percentage and the second stands for the lecithin percentage. For example, systems LAS-20-1 contains 20% sodium dodecylbenzenesulfonate and 1% lecithin.

Viscometers

Two viscometers were used: a thermostatable falling-ball viscometer (Haake, model B/BH) and a thermostatable rotational viscometer (Haake, model RV-12) equipped with a programmer for shear rate variation and an automatic system for recording shearing stress. The dimensions of the rotational viscometer are given by cylinder radii of 10.10 and 11.15 mm and a height of 61.4 mm. The rotating cylinder is the smaller one.

In order to establish the rheological behavior of the systems, the thixotropic (T) loop[20] was employed. In the T loop, the shear rate is first ramped up to some maximum value ($D_{\max}$) and then is ramped down at the same rate back to zero. Thus, the T loop is characterized by two parameters, the loop time and the maximum shear rate. We have developed our experiments with a loop time of 3 min and a maximum value of shear rate of 28.48 s^{-1}. In these conditions, we have found that the measures were reproducible, except for some systems in which air bubbles were trapped. In such conditions, the measure was not possible.

Experimental results

Rheological behavior of the systems has been determined using the rotational viscometer, and those which presented Newtonian rheological behavior were then studied in the falling-ball viscometer.

Table I shows viscosity values (mPa s) for the Newtonian systems.

TABLE I. Viscosities (mPa s) and phase behavior of the (A) water/sodium alkyl-ether-sulfate/lecithin, (B) water/sodium dodecylsulfate/lecithin, and (C) water/sodium dodecylbenzenesulfonate/lecithin systems.

System	278 K	283 K	288 K	293 K	298 K	303 K	308 K	313 K
(A)								
AES-10-0	3.10	2.68	2.34	2.08	1.86	1.65	1.51	1.38
AES-10-1	3.38	2.92	2.56	2.24	2.02	1.83	1.65	1.49
AES-10-2	3.88	3.37	2.97	2.60	2.33	2.10	1.90	1.76
AES-10-3	4.71	4.20	3.65	3.24	2.86	2.60	2.42	2.27
AES-20-0	7.57	6.69	5.83	5.11	4.52	4.08	3.71	3.37
AES-20-1	8.40	7.36	6.40	5.69	5.03	4.53	4.14	3.78
AES-20-2	9.60	8.59	7.85	7.12	6.23	5.73	5.26	4.95
AES-20-3	11.1	10.3	9.50	8.75	8.03	7.49	7.03	6.60
AES-30-0	62.1	76.9	75.5	67.1	56.5	47.5	38.2	30.8
AES-30-0.5	105	131	131	116	98.6	83.3	67.4	52.6
AES-30-1	145	192	198	176	146	119	99.0	75.5
AES-30-1.5	193	260	278	251	204	167	131	99.2
AES-30-2	PP[a]	PP	PP	PP	PP	PP	c	c
AES-30-2.5	PP	PP	PP	PP	PP	PP	c	c
AES-30-3	VE[b]	VE	VE	VE	PP	PP	c	c
(B)								
DS-10-0	S[d]	S	B[e]	B	1.58	1.43	1.30	1.21
DS-10-1	S	S	B	B	1.67	1.51	1.39	1.27
DS-10-2	S	S	B	B	1.86	1.72	1.55	1.40
DS-10-3	S	S	B	B	2.58	2.27	2.00	1.78
DS-20-0	S	S	B	B	B	3.14	2.79	2.47
DS-20-1	S	S	S	B	5.17	4.53	3.91	3.29
DS-20-2	S	S	S	B	9.71	8.01	6.53	5.35
DS-20-3	S	S	S	B	21.3	16.7	12.5	9.60
DS-30-0	S	S	S	B	B	205	144	96.3
DS-30-1	S	S	S	B	B	354	228	145
DS-30-2	S	S	S	B	B	1175	723	436
DS-30-3	S	S	S	B	B	PP	PP	PP
(C)								
LAS-10-0	30.5	16.4	9.74	6.28	4.34	3.27	2.77	2.42
LAS-10-1	44.7	20.9	12.3	7.60	5.30	3.89	3.02	2.64
LAS-10-2	B	B	B	20.2	11.8	7.92	5.22	3.90
LAS-10-3	B	B	B	B	B	B	B	B
LAS-20-0	B	B	B	2136	1331	791	434	284
LAS-20-1	B	B	B	B	B	987	625	367
LAS-20-2	B	B	B	B	B	B	B	B
LAS-20-3	B	B	B	B	B	B	B	B
LAS-30-0	B	B	B	B	B	B	B	B
LAS-30-1	B	B	B	B	B	B	B	B
LAS-30-2	B	B	B	B	B	B	B	B
LAS-30-0	B	B	B	B	B	B	B	B

[a] Pseudoplastic.

[b] Viscoelastic.

[c] Measure was not possible due to the trapping of air in the sample.

[d] Solid.

[e] Biphasic.

TABLE II. Apparent viscosity (mPa s) of non-Newtonian systems, shear rate equal to 15 s^{-1}.

System	278 K	283 K	288 K	293 K	298 K	303 K	308 K	313 K
AES-30-2	853	2140	4533	8660	6 307	4 993	d	d
AES-30-2.5	3553	5507	6573	6867	8 287	8 727	d	d
AES-30-3	VE[a]	VE	VE	VE	32 933	33 227	d	d
DS-30-3	S[b]	S	S	B[c]	B	3 823	2438	1343

[a] Viscoelastic.
[b] Solid.
[c] Biphasic.
[d] Measure was not possible due to the trapping of air in the sample.

Non-Newtonian systems were found to be antithixotropic, and the values measured in the return run were always higher than those measured in the outward run. The antithixotropic behavior will be studied in a future paper.

Table II shows the apparent viscosities (mPa s) measured in the return run at shear rate equal to 15 s^{-1}, for the systems which present non-Newtonian behavior: AES-30-2, AES-30-3, and DS-30-3.

DISCUSSION

Study of Newtonian systems

Viscosity variation with composition

Solution's viscosity depends on the magnitude of the interactions between its particles (ions, molecules, micelles, insolubilized particles dispersed...).[11,21] If these interactions are shear rate dependent, the solution will behave as a non-Newtonian fluid.

Newtonian behavior of the systems studied is attributed to the presence of small spheroidal micelles, among which there are no interactions dependent on shear rate.[18,22]

As it is added to the surfactant systems, the lecithin becomes part of the micelles due to its amphiphylic character, the fatty radicals of the lecithin tending towards the inside of the micelle, while the phosphoric ester tend to go towards the micellar surface,[23,24] thus increasing its volume and even producing other types of aggregates.[25] This increase in micellar volume explains the viscosity increase observed in the surfactant–water systems, when the lecithin is added.

When studying the influence of the type of surfactant on the viscosity of the surfactant–water–lecithin systems, one finds that for the same lecithin and surfactant concentration (below 20%), the viscosity of the surfactant–water systems increases as follows: DS < AES < LAS; this sequence is maintained when lecithin is added to these systems. The viscosity of systems formed by spheroidal micelles increases with micellar size.[26] This fact may explain the sequence observed.

For a 30% surfactant concentration, viscosity value increases as follows: AES < DS, due to the different solubility of the two surfactants in water. This difference is due to the formation of hydrogen bonds between water and the ethoxy groups of AES,[17] diminishing its Kraft point.[27]

Viscosity variation with temperature

AES/lecithin/water systems. When studying the influence of temperature on viscosity values in AES/lecithin/water systems, one can find three behaviors clearly differentiated:[28]

(i) "Thermally normal Newtonian" systems, whose viscosity value decreases as temperature increases. Systems with 10% or 20% AES exhibit this behavior.

(ii) "Thermally abnormal Newtonian" systems, whose viscosity value increases with temperature, up to a maximum value, after which viscosity decreases as temperature increases. Systems AES-30-0, AES-30-0.5, AES-30-1, and AES-30-1.5 exhibit this behavior.

(iii) Non-Newtonian systems. Systems AES-30-2, AES-30-2.5, and AES-30-3 exhibit this behavior.

A relationship between viscosity and temperature, for Newtonian systems containing AES, may be given as follows:

$$\eta = A + Be^{D(1/T - 1/293)} + Ce^{E(1/T - 1/293)}, \qquad (1)$$

where A, B, and C are parameters of the equation, T is the absolute temperature, and D (7900 K) and E (7600 K) are parameters related to the flow activation energy. The sum of the parameters A, B, and C must correspond to the viscosity value measured at 293 K. Linear correlation coefficients were found to be greater than 0.995 in all cases.

Figure 1 shows the dependence of the viscosity with temperature. The points represent the experimental values and the lines represent the fit obtained for each system.

DS/lecithin/water systems. Two behaviors are observed in these systems:

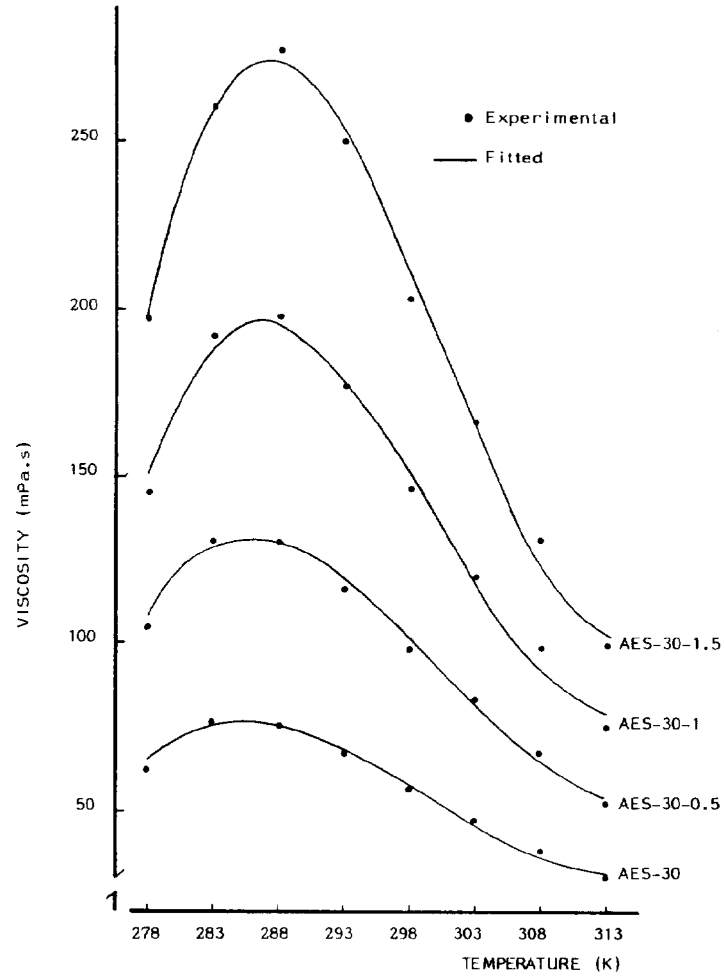

FIG. 1. Dependence of the viscosity with temperature.

(i) "Thermally normal Newtonian" systems, whose viscosity value decreases as temperature increases. All DS systems show this behavior, except DS-30-0.

(ii) Non-Newtonian system: DS-30-3 is a pseudoplastic fluid.

LAS/lecithin/water systems. All the systems prepared with LAS present thermally normal Newtonian behavior.

The decrease of viscosity values with temperature exhibited by thermally normal Newtonian systems, can be explained considering the fact that as temperature increases, the hydrodynamic radius of the micelles decreases.[29] This means a greater mobility of the micelle due to its smaller effective size. The decreases of viscosity are very pronounced at the lowest temperatures studied.

The maximum of viscosity in thermally abnormal Newtonian systems is explained by the action of two counterposed effects dependent on temperature.[30] As it increases:

(i) The hydrogen bonds between water and ethoxy groups are the first to break, which leads to an increase in micellar size and, consequently, in viscosity.

(ii) Structured water around the ionic groups in the micellar surface is released, causing the diminution of micellar effective size, and hence a decrease in viscosity.

At temperatures below that for the maximum viscosity, the first effect predominates, whereas at higher temperatures, the second predominates. At temperatures higher than those studied, viscosity values may be expected to approach asymptotically to a single value related to the minimum micellar size corresponding to a sphere of characteristic hydration radius for each type of surfactant.[31]

Another fact which must be pointed out in AES-30 systems is the shift of the maximum viscosity temperature towards higher values as lecithin concentration increases: AES-30-0 shows a maximum viscosity temperature at 283 K, whereas in the system AES-30-1.5, this temperature reaches 288 K. This fact is related with the solvation of the polar groups of the lecithin, placed in the micellar surface. For this reason, a slightly higher temperature is needed to produce an effective decrease in micellar size, and consequently, in viscosity. The maximum obtained by differentiating Eq. (1) also shows the shift of maximum viscosity temperature when lecithin concentration is increased.

Study of non-Newtonian systems

When the micelles surpass a certain volume, a change takes place in the rheological behavior of the system, from Newtonian to non-Newtonian.[30,32]

Thus, systems AES-30-2 (278 to 303 K); AES-30-2.5 (278 to 303

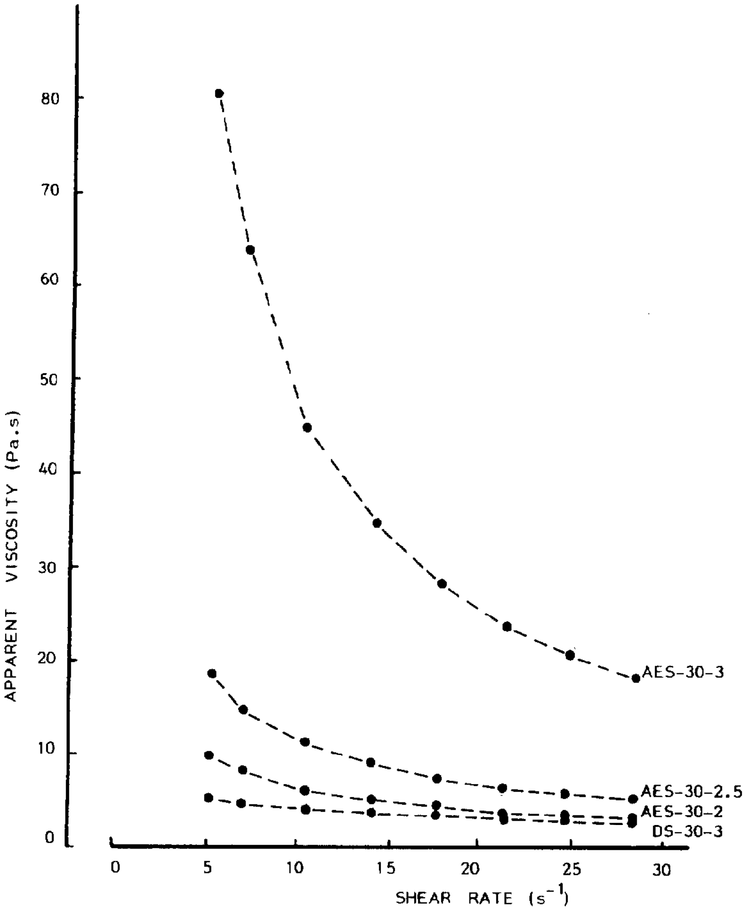

FIG. 2. Variation of apparent viscosity with shear rate, at 303 K, in pseudoplastic systems.

K); AES-30-3 (298 to 303 K); and DS-30-3 (303 to 313 K) exhibit pseudoplastic behavior, that is, micellar interactions depend on shear rate.

When the volume of the micelles surpasses that corresponding to the pseudoplastic behavior, mesomorphic phases appear in the systems, causing viscoelastic characters to arise. This fact takes place in the systems AES-30-3 in a temperature range from 278 to 293 K.

TABLE III. Parameters of Ostwald's equation (2).

Temperature	r	τ_M	b
System AES-30-2			
278 K	0.9999	12.8±0.1	0.87±0.01
283 K	0.9999	32.1±0.2	0.67±0.01
288 K	0.9998	67.7±0.3	0.30±0.01
293 K	0.9996	129.7±0.8	0.26±0.01
298 K	0.9995	94.1±1.1	0.30±0.01
303 K	0.9993	74.8±0.7	0.32±0.01
System AES-30-2.5			
278 K	0.9992	53.7±0.6	0.34±0.01
283 K	0.9962	83.1±1.2	0.20±0.01
288 K	0.9992	98.3±0.7	0.22±0.01
293 K	0.9995	103.2±0.7	0.25±0.01
298 K	0.9998	124.0±0.5	0.28±0.01
303 K	0.9992	130.4±1.1	0.27±0.01
System AES-30-3			
298 K	0.9982	493.7±3.5	0.12±0.01
303 K	0.9902	490.6±8.4	0.13±0.01
System DS-30-3			
303 K	0.9992	57.0±1.4	0.75±0.02
308 K	0.9990	35.9±1.0	0.83±0.01
313 K	0.9990	20.1±0.7	0.86±0.03

Figure 2 gives the apparent viscosity values (measured in the return run) versus shear rate, showing that the apparent viscosity diminishes as shear rate increases.

Experimental values of the shearing stress in pseudoplastic systems fit Ostwald's equation, suitably modified as follows:

$$\tau_v=\tau_M(D/D_M)^b, \tag{2}$$

where τ_v is the returning shear stress (Pa); D is shear rate (s^{-1}); D_M is a shear rate value in the range studied; b (pseudoplasticity coefficient); and τ_M are fitting parameters of the equation. In order to simplify comparisons, the value of D_M has been taken as 15 s^{-1} in all cases.

Table III shows the values of the fitting parameters for the systems which exhibits pseudoplastic behavior, at each of the temperatures studied, together with the linear correlation coefficients r, and the errors by which they are affected for a probability of 95%. Experimental values of τ_M are always within the error limits of this parameter.

Pseudoplasticity may be attributed to the existence of spheroidal micelles with mutual interactions dependent on shear rate, or to the presence of nonspheroidal aggregates and micelles or portions of mesomorphic phases which are oriented towards the shear direction when they receive the shear stress.[22] At this moment, we have not any optical evidence to determine which of the two models is the correct one. Our future goal is to realize an optical study of such systems in order to clarify this point and give physical sense to the diminution of viscosity with shear stress.

Table II also shows that the maximum viscosity in AES-30-2, AES-30-2.5, and AES-30-3 takes place at higher temperatures compared to the systems with lower lecithin concentration, as commented before.

System AES-30-3, between 278 and 293 K, exhibit viscoelastic behavior. The "Weissemberg effect" takes place; that is, the fluid goes up along the rotor axis when shearing is being carried out, creating a convex vertex. The displacement of fluid in the fixed cylinder of the rotational viscometer gives way to errors in the measurement of the shearing stress which cannot be quantified by this type of viscometer.[33]

CONCLUSIONS

(1) The addition of lecithin increases viscosity in all systems studied; the higher the lecithin concentration, the higher the viscosity increase.

(2) All the systems studied exhibit Newtonian behavior, except systems AES-30-2, AES-30-3, and DS-30-3.

(3) A decrease of viscosity with temperature is observed in all the systems, except those prepared with 30% AES, which exhibit "thermally abnormal" behavior.

(4) System AES-30-2 (278–303 K), AES-30-2.5 (278–303 K), AES-30-3 (298–303 K), and DS-30-3 (303–313 K) are pseudoplastic fluids, and fit Ostwald's equation.

(5) System AES-30-3 at 278–293 K exhibit viscoelastic behavior.

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