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Anionic Surfactants–Water Systems: Specific Refractive Index, Specific Volume and Viscosity

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ABSTRACT

Specific refractive index, specific volume and viscosity were studied in several systems containing sodium alkyl-ether-sulfate (10; 20; 25; 27.5 and 30% w/w), sodium dodecyl sulfate (5; 10; 15; 20; 25; 27.5 and 30% w/w) and sodium dodecylbenzenesulfonate (5; 7.5; 10; 12.5; 15; 17.5 and 20% w/w) in water for a temperature range of 278–313 K. Systems with concentrations above 20% w/w of sodium dodecylbenzenesulfonate were not studied, as biphasic systems occurred throughout the temperature range.

The study led to the following conclusions: (1) All systems studied showed Newtonian rheological behavior. (2) For concentrations equal to or below 20% w/w, the viscosity of systems with sodium dodecyl sulfate is lower than in systems containing sodium alkyl-ether-sulfate, at the same concentration and temperature; this tendency is reversed at concentrations above 20% w/w. (3) Systems with sodium dodecylbenzenesulfonate show the highest viscosity values, in comparison with the other two anionic surfactants studied, at the same concentration and temperature.

INTRODUCTION

The study of special rheological characteristics of surfactants requires that a pattern be established, allowing the prediction in general terms of their performance when faced with concentration and temperature changes during the manufacture of cosmetics, detergents, emulsions, etc. [1].

This paper describes the effects of two variables (concentration and temperature) on the specific refractive index, specific volume and viscosity values of three anionic surfactant–water systems of industrial interest.

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 of surfactant in an aqueous system. The average composition of surfactant, before the sulfatation and after ethoxylation was:

- 20% w/w fatty alcohols.
- 15% w/w fatty alcohols with 1 mol ethylene oxide.
- 15% w/w fatty alcohols with 2 mol ethylene oxide.
- 15% w/w fatty alcohols with 3 mol ethylene oxide.
- 35% w/w fatty alcohols with more than 3 mol ethylene oxide.

The maximum amount of total electrolytes and fatty-ether-alcohols insulfatation was 4 and 1% w/w, respectively.

Its rheological behavior can be defined as follows [2]:

(a) Systems containing up to 25% w/w of active matter behave like Newtonian fluids, i.e. their viscosity decreases as the temperature is raised. These are known as "thermically normal Newtonian" systems.

(b) Systems containing 27.5 and 30% w/w of surfactant behave like Newtonian fluids with viscosity increasing as the temperature is raised, till a maximum value is reached, from which point viscosity decreases with temperature. These systems are known "thermically abnormal Newtonian" systems.

Sodium dodecyl sulfate (DS): This was prepared with a surfactant content of 31.7% w/w in an aqueous system, and a maximum content of insulfatation and electrolytes of 1.5 and 1.3% w/w, respectively.

Sodium dodecylbenzenesulfonate (LAS): This was prepared with a surfactant content of 66% w/w in an aqueous system, and a maximum content of insulfatation and electrolytes of 2 and 2.1% w/w, respectively.

Systems containing sodium dodecyl sulfate or sodium dodecylbenzenesulfonate demonstrated "thermically normal Newtonian" rheological behavior.

The surfactants used in the present work are from industry and the three have a linear alkyl chain.

Preparation of the samples

Systems were prepared by weight, combining the weighed amounts of the surfactant and distilled water required for each concentration. The mixture was homogenized, with careful agitation to avoid the introduction of air.

Aqueous systems were prepared containing 10; 20; 25; 27.5 and 30% w/w of sodium alkyl-ether-sulfate; 5; 10; 15; 20; 25; 27.5 and 30% w/w of sodium dodecyl sulfate and 5; 7.5; 10; 12.5; 15; 17.5 and 20% w/w of sodium dodecylbenzenesulfonate.

Pycnometer

A 50 ml pycnometer, calibrated with double-distilled water, was used to measure density.

Refractometer

An Abbé type thermostatable refractometer, with a sensitivity of 0.0005 unit, was used in the present work.

Viscosimeter

A thermostatable falling-ball viscosimeter (Haake, model B/BH), and a thermostatable rotational viscosimeter (Haake, model RV-12) equipped with a programmer for shear rate variation and an automatic system for recording shearing stress were used.

Values obtained with the rotational viscosimeter were based on the measurement of shearing stress for different shear rates. These shear rates are proportional to the gyration rates and the shearing stress is proportional to the applied torque (0.015 N m), and to the sensor system of viscosity which is formed by a fixed cylinder (external) and another, movable cylinder (internal); its characteristics are: internal radius 10.10 mm; height 61.40 mm, and external radius 11.55 mm.

Experimental results

Specific volume (ml g^{-1}) and refractive index values corresponding to the systems studied could be calculated using reported values for the density and refractive index of water at the required temperature and the parameter values w [Eqn (1)] and q [Eqn (2)].

The viscosity values (mPa s) obtained for these systems are shown in Figs 1–3.

To determine the monophasic or biphasic character of the systems, these were maintained at the temperature studied for 24 h.

DISCUSSION

Specific volume

For each concentration of surfactant and temperature, specific volume increases as follows: LAS < AES < DS, due to the shapes and sizes of the micelles and the tighter packing of the micelles as follows: DS < AES < LAS. All this is due to the different molecular structure of the surfactants.

For the systems studied, linear regressions were conducted for plots of specific volume (v) versus the weight fraction of surfactant (x) at different temperatures. These regressions can be expressed as follows:

$$v = k + w \cdot x \qquad (1)$$

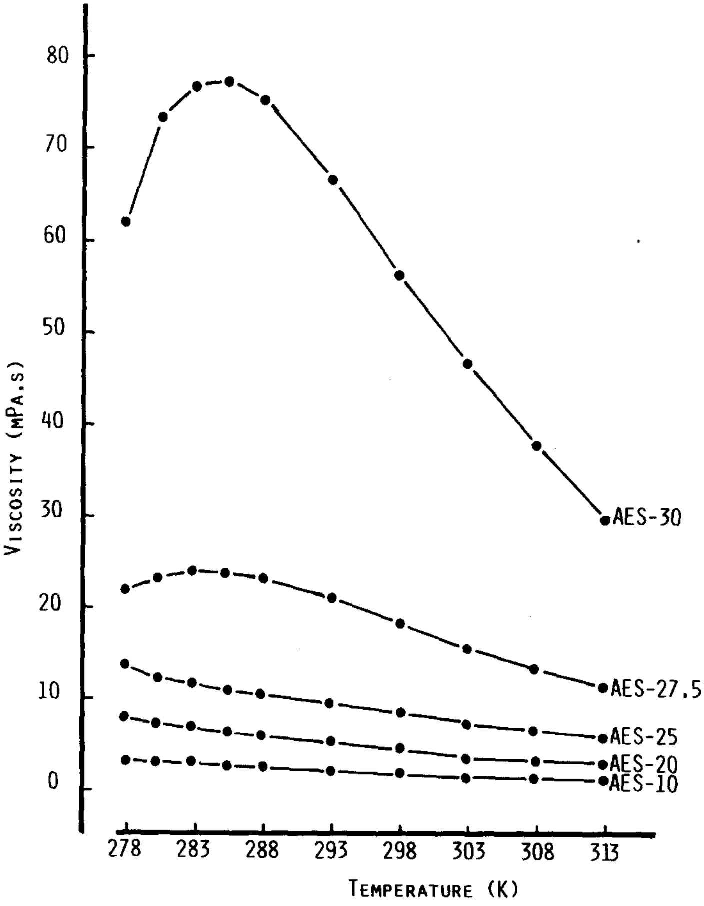

Fig. 1. Viscosity values of systems containing sodium alkyl-ether-sulfate (AES).

where *k* and *w* are the regression parameters.

Assuming an ideal character for these systems, *k* must correspond to the specific volume of water determined experimentally at each temperature. The results do not show any significant differences between the values of *k* obtained for the different systems studied and the values corresponding to water. Table 1 shows the parameter values $-w$ of the different regressions. Maximum deviations of the experimental values are less than ±0.1%.

Regression analysis was carried out to obtain the single value of the parameter $-w$ given in Table 1, for those systems remaining monophasic over the entire concentration range used for each surfactant and at all temperatures studied.

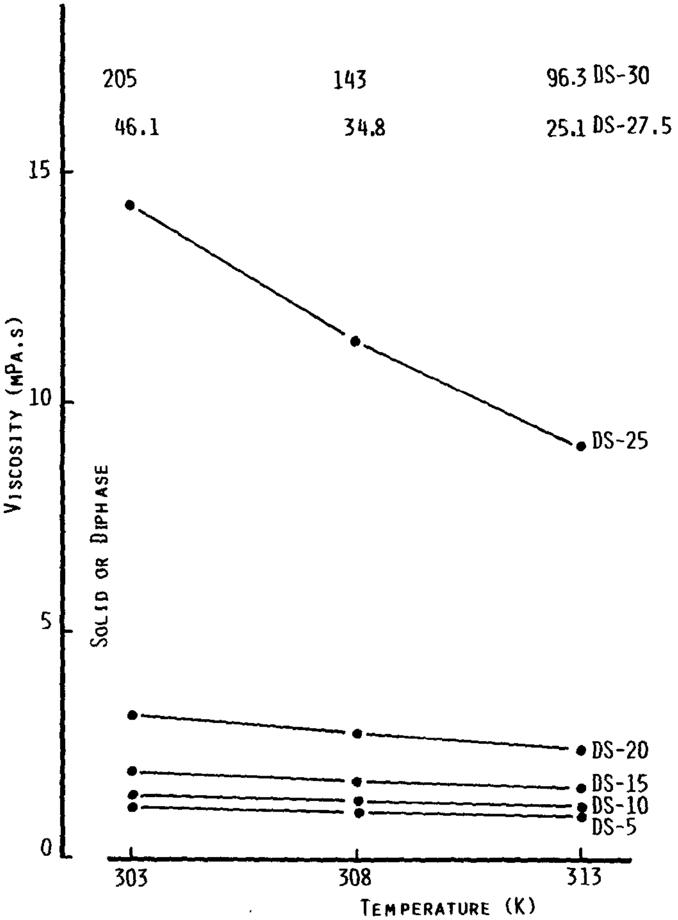

Fig. 2. Viscosity values of systems containing sodium dodecyl sulfate (DS).

Specific refractive index

Values of refractive index, for the same concentration of surfactant and temperature, increase as follows: DS < AES < LAS. The order is related to the volume and structure of the micelles.

Specific refractive index values of the systems for each concentration do not vary significantly with temperature at the chosen probability level $P=0.05$, indicating that no structural modifications take place in the systems with temperature variations. For these systems, linear regressions were dertermined for specific refractive index (R) versus the weight fraction of surfactant (x). These regressions can be expressed as follows:

$$R=p+q\cdot x \quad (2)$$

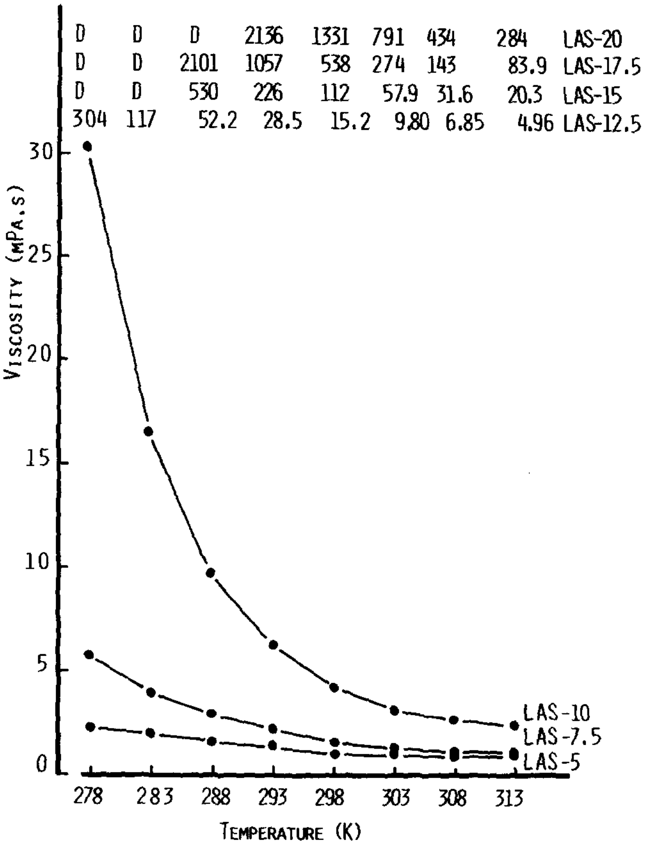

Fig. 3. Viscosity values of systems containing sodium dodecylbenzenesulfonate (LAS).

where p and q are the regression parameters.

Assuming an ideal character for the systems studied in relation to this porperty, p should correspond to the specific refractive index of water determined experimentally. The results show that no significant differences exist between the values of p corresponding to the systems studied and specific refractive index value of water (0.2070 ml g^{-1}). The parameter values q of the different regressions are 0.034, 0.037 and 0.060 for AES, DS and LAS, respectively. Maximum deviations of the experimental values are less than ±0.3%.

Similarly, it appears that they are straight lines with the same intercept and with slopes which increase in the order: AES < DS < LAS. Therefore specific refractive index is related to the greater intermolecular and intermicellar interactions in the afore-mentioned order.

Micelles in systems with AES are the most stable with regard to phase sep-

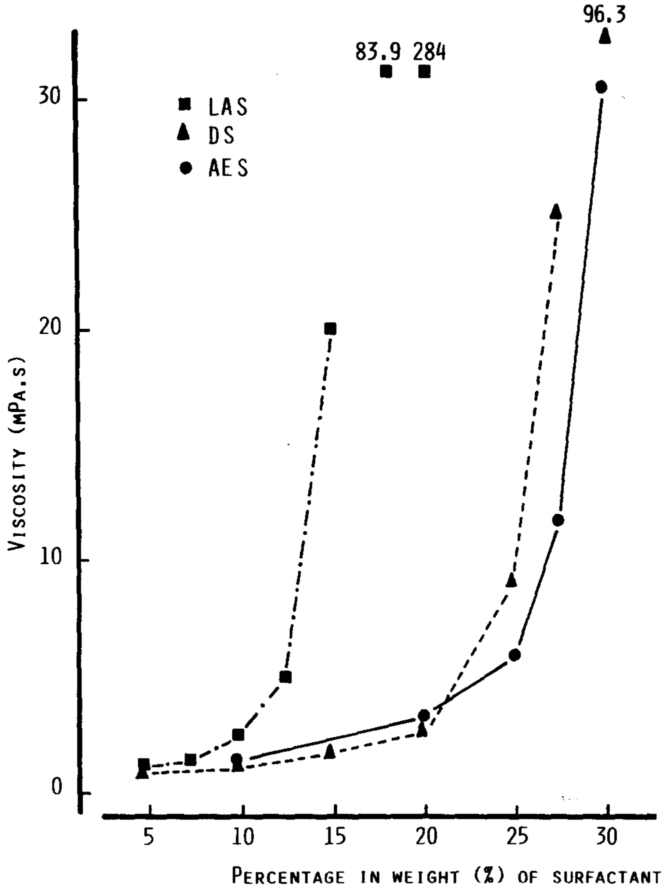

Fig. 4. Variation of the viscosity values, at 313 K, with the percentage in weight of surfactant.

aration due to the possibility of hydrogen bond formation between water and the ethoxy groups of the surfactant.

TABLE 1

Parameter values *w* (ml g^{-1}) of regression Eqn (1)

	278 K	283 K	288 K	293 K	298 K	303 K	308 K	313 K
AES	0.157	0.151	0.149	0.145	0.142	0.139	0.137	0.136
DS	S[a]	S	S-B	B	B	0.117	0.115	0.111
LAS	B-M[a]	B-M	B-M	0.168	0.164	0.163	0.162	0.160

[a] S, solid; B, biphasic; M, monophasic.

Effect of temperature and concentration on dynamic viscosity

The Newtonian rheological behavior of samples was determined using the rotational viscosimeter; the values of dynamic viscosity for each system and temperature were measured with the falling-ball viscosimeter.

Figures 1, 2 and 3 show the variations of dynamic viscosity with temperature, for systems with AES, DS and LAS, respectively. In all cases, an increase in the number of molecules of the surfactant results in an increased concentration of micelles in the system, and consequently, viscosity increases because of friction between micelles and the trapping of water by the micelles.

Systems with AES-10, AES-20 and AES-25 show "thermically normal Newtonian" rheological behavior, Figure 1, while systems AES-27.5 and AES-30 show a maximum viscosity value and therefore have a "thermically abnormal Newtonian" rheological behavior. This is explained by the action of counterposed effects dependent on temperature increases: (1) Hydrogen bonds between water and ethoxy groups are the first to break, which leads to an increase in micelle size and consequently viscosity increases. (2) Structured water around the micelles is released, causing the diminution of micellar size, and hence a decrease in viscosity. At temperatures below that for 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 a single value related to the minimum micellar size corresponding to a sphere of characteristic hydration radius for each type and concentration of surfactant [3].

Systems with LAS demonstrate the greatest viscosity values, due to the presence of a benzene ring in the structure of the surfactant which can form a structure based on cylindrical-shaped micelles [4,5] and not spherically-shaped micelles as in the case of the other two surfactants studied. A consequence of this fact is that the flow resistance of systems with LAS is greater in comparison with the other systems. On the other hand, in systems with LAS, an increase in temperature produces a reduction in viscosity, which indicates a more perfect arrangement of the surfactant micelles, and consequently less resistance to flow.

Differences in the viscosity values demonstrated by the systems at equal concentration and temperature can be explained when considering the differences in the micellar volume of the surfactants due to the very different structures of the latter. These differences are apparent in Fig. 4. For concentrations equal to or less than 20% w/w of surfactant, the viscosity values at each temperature corresponding to systems with DS are lower than those corresponding to systems with AES. This tendency is reversed at concentrations above 20% w/w (Fig. 4). This is due to the different solubility of two surfactants in water. The different solubility of DS and AES is due, no doubt, to the formation of hydrogen bonds between water and the ethoxy groups of AES.

CONCLUSIONS

(1) Specific refractive index values do not vary significantly with temperature, in the temperature range studied.

(2) For the three surfactants, linear variation is observed for the specific volume and specific refractive index with variation in the weight fraction of the surfactant in the systems.

(3) All the systems studied show Newtonian rheological behavior.

(4) The ethoxylation of the hydrocarbonate chain increases the solubility of the surfactant in water, and those systems with AES can be examined over the whole temperature range studied, unlike the DS and AES systems, in which solid and biphasic systems occur.

(5) Systems AES-27.5 and AES-30 demonstrate "thermically abnormal Newtonian" rheological behavior.

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