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Specific Viscosity of Newtonian Aqueous Solutions Containing an Anionic Surfactant and an Alkaline Pyrophosphate

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The effects that both temperature and solute concentrations exert on specific viscosity are studied in this paper. The products used were sodium or triethanolammonium dodecylsulfates or dodecylbenzenesulfonates, as surfactants, and tetrasodium or tetrapotassium pyrophosphates, as electrolytes. All are of technical quality. As temperature decreases, within the temperature range studied, a phase separation or an appearance of non-Newtonian behavior is noted in many solutions. The solutions studied fit, within the accuracy range for experimental measurements, an empirical equation that agrees with what is called the activated diffusive relaxation model. For this model, the relative viscosity is a linear superposition of stresses coming from hydrodynamic interactions and from activation energy due to structural relaxation of the uniform distribution of micelles in the quiescent micellar solution. Solutions containing a dodecylsulfate show very slight hydrodynamic effects. Their activation energy, which is independent of temperature, becomes greater by increasing the concentrations of surfactant and pyrophosphate. The specific viscosities of these solutions also increase by replacing the triethanolammonium counter-ion with sodium. Solutions containing sodium dodecylbenzenesulfonate show considerable hydrodynamic effects, which increase with the addition of tetrasodium pyrophosphate. The activation energy is independent of temperature. Solutions containing triethanolammonium dodecylbenzenesulfonate show decreasing activation energy values when temperature is increased. Consequently, a maximum for specific viscosity appears at a certain temperature. This maximum diminishes progressively with the addition of pyrophosphate, while the corresponding temperature becomes higher. From the investigation carried out, the necessity for further basic studies remains clear. Research should be done on concentrated aqueous solutions containing surfactants and electrolytes, taking into consideration the variations that their dynamic viscosities present along with composition and temperature. All of this, naturally, must be carried out before developmental research on manufacturing, commercialization and usage of such solutions proceeds.

The rheology of highly concentrated aqueous solutions containing an anionic surfactant and a strong electrolyte as solutes is very complicated and has not yet been studied systematically (1).

For spherical micelles of similar sizes in quite diluted aqueous solutions, if they are considered comparable to dispersed solid particles, the equation for specific viscosity η^{sp} is:

$$\eta^{sp} = {}^{1}\eta^{1}\ \phi \qquad [1]$$

where ϕ is the volume fraction of the micelles. The intrinsic viscosity ${}^{1}\eta^{1}$ depends on several factors, such as the mean radius of hydrated micelles, the thickness of the diffuse electrical double layer which surrounds the micelle, the electrokinetic potential and temperature, as well as the dynamic viscosity, the permittivity and the specific electrolytical conductivity of the continuous aqueous phase (2–7).

As the concentration of micelles increases above the critical micellar concentration, the equation which relates η^{sp} to the characteristics of micellar dispersion becomes more complicated (8–12).

At high concentrations, hydrodynamic interactions and collisions between micelles have to be taken into account. This being the case, the specific viscosity is usually represented by the equation:

$$\eta^{sp} = {}^{1}\eta^{1}\ \phi + k_2\ \phi^2 + k_3\ \phi^3 + \ldots \qquad [2]$$

Subsequently, at very high concentrations, intermicellar interactions can give rise to the formation of nonspherical-shaped micelles.

The activated diffusive relaxation model, described by Goodwin (13), establishes that in disperse systems at a very low gradient of shear rate the relative viscosity, $\eta^{rel} = \eta^{sp} + 1$, is a linear superposition of stresses, some due to hydrodynamic interactions and others to the structural relaxation of the uniform distribution of micelles in the quiescent micellar dispersion.

When the volume fraction is high, the disturbance in the fluid as it flows around each micelle interacts with the flow around neighboring micelles. As a result, a hydrodynamic increase in viscosity takes place. The contribution of these hydrodynamic interactions, q^{rel}, to the relative viscosity of an aqueous system is expressed as follows:

$$q^{rel} = (1 - k_p\ \phi)^{-{}^{1}\eta^{1}k_p} \qquad [3]$$

where k_p is the so-called "crowding factor," which is a function of the coordination number of the ordered, liquid-like, micellar structure (14).

When an ordered, liquid-like, micellar structure is subjected to shear flow and is strained, then a nonuniform distribution is produced. Structural relaxation is caused by a long-range diffusive motion in the dispersed phase. This is restricted by the repulsive forces of neighboring micelles, which produce an activation energy barrier in opposition to this process. Assuming that there is no cooperative motion, the activation energy is easily calculated from the structure and the sum of the pair interaction energies.

The stresses due to structural relaxation contribute to the relative viscosity of a system in this way:

$$J \exp(E/kT) = [\hbar/(16\,\pi\,\eta_w\,a^3)]\exp(E/kT) \qquad [4]$$

where $\hbar$ is Planck's constant divided by 2 π, η_w is the dynamic viscosity of the continuous aqueous phase, a is the mean radius of micelles having similar sizes, E is the activation energy for long-range diffusive motion, k is Boltzmann's constant and T is the absolute temperature.

The complete equation for the activated diffusive relaxation model is:

$$\eta^{rel} = q^{rel} + J \exp(E/kT) \qquad [5]$$

At very high concentrations, cooperative motion acquires an increasing importance, which leads to a rise in relative viscosity at a slower rate than that predicted by the preceding equation (15).

This model is a micellar close association model (16) which is acceptable only for micelles with a narrow size range and with very lengthy residence times for each monomer in each micelle.

In this paper, the effects of both temperature and the concentrations of solutes (an anionic surfactant and a strong electrolyte) on the specific viscosity of aqueous solutions showing a Newtonian rheological behavior are studied. The anionic surfactants used were sodium or triethanolammonium dodecylsulfate and dodecylbenzenesulfonate, while the strong electrolytes were tetrasodium or tetrapotassium pyrophosphate.

The interpretation of the results obtained for these solutions has been based on Goodwin's activated diffusive relaxation model.

EXPERIMENTAL

Products. The technical anionic surfactants used at concentrations of 0.25 and 0.50 mol/l were the following: sodium dodecylsulfate, Na-DS; triethanolammonium dodecylsulfate, TEA-DS; sodium dodecylbenzenesulfonate, Na-LAS, and triethanolammonium dodecylbenzenesulfonate, TEA-LAS. Their mean molecular weights are 299, 427, 344 and 471, respectively. A complete description of these surfactants was presented in a previous paper (17).

A tetrasodium pyrophosphate, Na-PF, and a tetrapotassium pyrophosphate, K-PF, were used. Both were of technical quality. They were used at concentrations of 0.25, 0.50, 0.75, 1.00 and 1.25 eq/l.

Equipment. Experimental measurements of dynamic viscosity were taken at temperature between 5 and 60°C, according to Scheme 1. The equipment required, at each temperature, was the following:

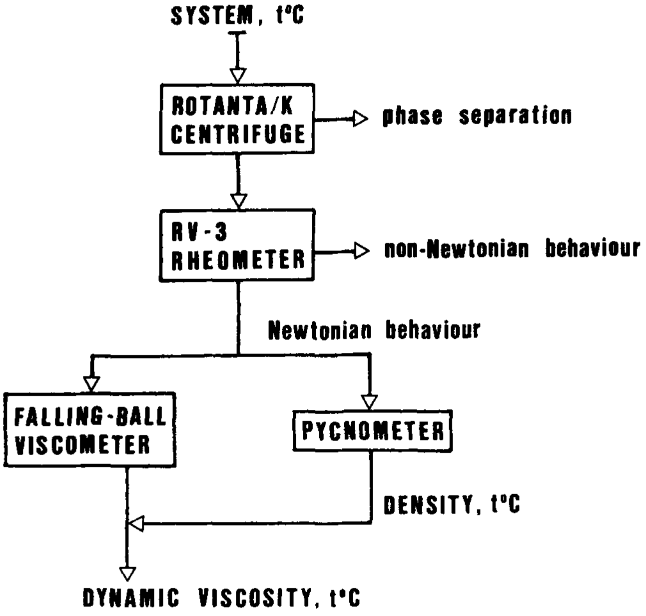
- A Hettich, model Rotanta/K, thermostatic centrifuge was used in order to exclude samples that separate into phases after being subjected to an acceleration of 25,000 m/s^2 for 30 min.
- A rotational rheometer Haake, model RV-3, was required in order to select those samples that show Newtonian rheological behavior.
- A Hoepler falling-ball viscometer was used for Newtonian solutions to obtain their dynamic viscosities. The density values required for these calculations were done by pycnometry.

RESULTS AND DISCUSSION

First, it is necessary to take into account that, as temperature decreases, within the temperature range studied, a phase separation or an appearance of non-Newtonian behavior is produced in many solutions. Due to this, the minimum temperature at which dynamic viscosity was measured (denoted by t_{inf}) is included for each system in every table.

Solutions containing only an alkaline pyrophosphate. The specific viscosity values do not change significantly with temperature within the range studied. These values are shown in Table 1. The 95% confidence limits diverge from these values only in the last digit.

The plots of specific viscosity versus concentration adequately fit linear regressions in which the intercept does not differ significantly from zero. The slopes of these regressions may be estimated as 2.11 l/mol for Na-PF and 0.88 l/mol for K-PF. This difference is explained by the greater hydration of the sodium cations. To deliberate further, it is necessary to bear in mind



SCHEME 1

TABLE 1

Specific Viscosity Values for Solutions Containing Pyrophosphate as the Only Solute

	Tetrasodium pyrophosphate		Tetrapotassium pyrophosphate	
Concentration	t_{inf}	η^{sp}	t_{inf}	η^{sp}
0.25 eq/l	5°C	0.172	5°C	0.039
0.50 eq/l	5°C	0.282	5°C	0.091
0.75 eq/l	20°C	0.552	5°C	0.151
1.00 eq/l	30°C	0.632	5°C	0.211
1.25 eq/l	35°C	0.687	5°C	0.247

These values remain unchanged within the range of temperature studied.

TABLE 2

Parameters for the Equations Relating Specific Viscosity to Absolute Temperature in Solutions Containing Dodecylsulfate

Pyrophosphate concentration	t_{inf}	$\eta^{sp}(40)$	B	VNJ
Sodium dodecylsulfate at 0.25 mol/l				
None	25°C	0.674	0	-
0.25 eq/l Na-PF	25°C	0.711	0	-
0.50 eq/l Na-PF	25°C	1.26	1.75	1.95
0.75 eq/l Na-PF	25°C	3.13	3.70	0.53
1.00 eq/l Na-PF	25°C	8.78	5.52	1.17
1.25 eq/l Na-PF	40°C	34.4	8.71	0.04
0.25 eq/l k-PF	40°C	2.04	5.09	5.32
Sodium dodecylsulfate at 0.50 mol/l				
None	25°C	2.04	0	-
0.25 eq/l Na-PF	25°C	3.13	1.71	0.84
0.50 eq/l Na-PF	25°C	12.5	5.22	0.24
0.75 eq/l Na-PF	30°C	74.7	8.43	0.23
0.25 eq/l K-PF	40°C	16.4	7.54	1.73
Triethanolammonium dodecylsulfate at 0.25 mol/l				
None	5°C	0.376	0	-
0.25 eq/l Na-PF	20°C	0.852	0	-
0.50 eq/l Na-PF	25°C	1.06	0.440	6.35
0.75 eq/l Na-PF	25°C	1.68	1.86	4.33
1.00 eq/l Na-PF	25°C	3.04	3.18	0.17
1.25 eq/l Na-PF	30°C	6.00	4.70	0.70
0.25 eq/l K-PF	40°C	0.719	0	-
0.50 eq/l K-PF	40°C	3.85	5.93	1.74
0.75 eq/l K-PF	40°C	34.1	11.5	0.12
Triethanolammonium dodecylsulfate at 0.50 mol/l				
None	5°C	0.834	0	-
0.25 eq/l Na-PF	20°C	2.43	0	-
0.50 eq/l Na-PF	25°C	3.05	0.626	1.94
0.75 eq/l Na-PF	25°C	6.74	2.98	1.32
1.00 eq/l Na-PF	25°C	17.8	5.24	0.34
1.25 eq/l Na-PF	30°C	38.9	5.45	0.04
0.25 eq/l K-PF	30°C	2.48	0.517	2.19
0.50 eq/l K-PF	40°C	8.35	4.58	2.50
0.75 eq/l K-PF	40°C	68.0	9.82	0.10
1.00 eq/l K-PF	40°C	175.0	12.1	0.86

the fact that the specific viscosities of these pyrophosphate solutions do not exceed a value of 0.7.

Solutions containing a surfactant. Because of the different behaviors shown by solutions containing a dodecylsulfate, sodium dodecylbenzenesulfonate or triethanolammonium dodecylbenzenesulfonate, their results are presented and discussed separately.

Solutions containing a dodecylsulfate. These solutions fit the equation given below:

$$\ln\left[\eta^{sp}/\eta^{sp}(40)\right] = 10^3\, B(1/T - 1/313.2) \qquad [6]$$

The values for parameters $\eta^{sp}(40)$, specific viscosity at 40°C, and B in equation [6], as well as the percentages of the residual variance for the linear regressions VNJ, are presented in Table 2. [VNJ = 100 $(1 - r^2)(N - 1)/(N - 2)$, where r is the linear regression coefficient and N is the number of the pairs of data.]

As this table shows, parameter B does not differ significantly from zero in solutions without pyrophosphate. The same occurs in some solutions containing 0.25 eq/l of pyrophosphate. In these cases, the 95% confidence limits for each $\eta^{sp}(40)$ value diverge from this in the last digit appearing in Table 2. The rest of the solutions present clearly positive values for parameter B.

If the dodecylsulfate concentration remains constant, parameters $\eta^{sp}(40)$ and B become greater by increasing the pyrophosphate concentration. If, on the contrary, it is the pyrophosphate concentration that remains constant, both parameters increase by duplicating the dodecylsulfate concentration or by replacing the triethanolammonium counter-ion with sodium.

The replacement of Na-PF by K-PF produces a pronounced increase in the parameters $\eta^{sp}(40)$ and B, except for those solutions containing 0.25 eq/l of pyrophosphate and 0.25 or 0.50 mol/l of TEA-DS.

Solutions containing sodium dodecylbenzenesulfonate. These solutions fit the following equation:

$$\ln\left[(\eta^{sp} - Q)/(\eta^{sp}(40) - Q)\right] = 10^3\, B(1/T - 1/313.2) \qquad [7]$$

The values for the three parameters in equation [7], as well as their corresponding values for VNJ, are presented in Table 3. [VNJ = 100 $(1 - r^2)(N - 1)/(N - 2)$, where r is the linear regression coefficient and N is the number of the pairs of data.]

TABLE 3

Parameters for the Equations Relating Specific Viscosity to Absolute Temperature in Solutions Containing Sodium Dodecylbenzenesulfonate

Concentration of surfactant	Pyrophosphate concentration	t_{inf}	Q	$\eta^{sp}(40)$	B	VNJ
0.25 mol/l	None	5°C	0.7	1.99	5.08	0.22
0.25 mol/l	0.25 eq/l	20°C	1.6	7.27	10.4	0.40
0.50 mol/l	None	15°C	9.0	66.0	9.74	0.08
0.50 mol/l	0.25 eq/l	40°C	16.0	247.	3.65	1.24

The addition of 0.25 eq/l of Na-PF to the solution containing only 0.25 mol/l of Na-LAS increases the values for the three parameters. However, if this addition is carried out in the solution containing 0.50 mol/l of Na-LAS, parameters $\eta^{sp}(40)$ and Q increase, but B decreases to less than half its initial value.

By increasing the Na-LAS concentration from 0.25 to 0.50 mol/l, in systems without Na-PF, the values for the three parameters increase. However, if the systems contain 0.25 eq/l of Na-PF, the increase in Na-LAS concentration from 0.25 to 0.50 mol/l raises the values of the parameters $\eta^{sp}(40)$ and Q, but it decreases B to less than half its initial value.

Solutions containing triethanolammonium dodecylbenzenesulfonate. The solutions without pyrophosphate fit equation [6]. The values for parameters $\eta^{sp}(40)$ and B, as well as the VNJ values, are presented in Table 4.

The solutions with a pyrophosphate fit this equation:

$$\ln[(\eta^{sp} - Q)/(\eta^{sp}(40) - Q)] = 10^3 B(1/T - 1/313.2) - 10^6 C(1/T^2 - 1/313.2^2) \qquad [8]$$

The values for the four parameters in equation [8], as well as the values for the multiple regression coefficient R, are presented in Table 4.

Parameters Q and C become clearly superior to zero by adding pyrophosphate up to 0.25 eq/l to solutions with TEA-LAS at 0.25 or 0.50 mol/l. Moreover, high increases in parameters $\eta^{sp}(40)$ and B also are produced.

The solution containing 0.25 mol/l TEA-LAS exhibits a relevant increase in the four parameter values when the Na-PF concentration is raised from 0.25 to 0.50 eq/l. If this concentration ascends to 0.75 eq/l, $\eta^{sp}(40)$ keeps on increasing and Q becomes null, while B and C decrease significantly. A further addition of Na-PF up to 1.00 eq/l produces a reduction in the values for $\eta^{sp}(40)$, B and C, while Q remains null.

In reference to the solution containing 0.50 mol/l TEA-LAS, the increase in the Na-PF concentration from 0.25 to 0.50 eq/l gives a null value for Q and produces a decrease in the other three parameters. Furthermore, parameter Q remains null and $\eta^{sp}(40)$, B and C diminish by increasing the Na-PF concentration from 0.50 eq/l to 1.00 eq/l.

Because in each of these systems specific viscosity fits equation [8], it passes through a maximum when the temperature has a value of

$$t_{max} + 273.2 = 2 \bullet 10^3 \, C/B$$

Both sets of values, t_{max} and their corresponding maximum specific viscosity, η^{sp}_{max}, are included in Table 4.

The influence that the addition of a pyrophosphate exerts on η^{sp}_{max} and t_{max} in a solution already containing 0.25 eq/l should be emphasized. Thus, η^{sp}_{max} diminishes progressively, and t_{max} becomes higher.

In order to facilitate the study of the relationship between the values for $\ln\eta^{sp}$ and 1/T for each of the pyrophosphate concentrations, their corresponding graphs have been plotted in Figures 1 through 4.

From the analysis of these curves it can be inferred that the addition of pyrophosphate to a solution containing 0.25 mol/l of TEA-LAS always leads to an increase in specific viscosity. On the contrary, if the concentration of surfactant is 0.50 mol/l, the solution without pyrophosphate presents, below 25°C, a higher specific viscosity than the solutions containing a pyrophosphate. It also can be deduced that, at low enough temperatures, the specific viscosity of a solution containing

TABLE 4

Parameters for Equations Relating Specific Viscosity to Absolute Temperature in Solutions Containing Triethanolammonium Dodecylbenzenesulfonate

Pyrophosphate concentration	t_{inf}	Q	$\eta^{sp}(40)$	B	C	t_{maz}	η^{sp}_{max}	Adjustment
Triethanolammonium dodecylbenzenesulfonate at 0.25 mol/l								
None	15°C	0	5.71	6.59	0	-	-	VNJ=0.38
0.25 eq/l Na-PF	20°C	4	40.2	56.78	7.142	-22°C	2840	R=0.9995
0.50 eq/l Na-PF	5°C	7	76.1	123.2	17.62	13°C	358	R=0.9998
0.75 eq/l Na-PF	20°C	0	94.3	100.5	15.05	26°C	130	R=0.9995
1.00 eq/l Na-PF	30°C	0	72.4	82.45	12.76	36°C	74	R=0.9993
0.25 eq/l K-PF	5°C	6	52.0	199.8	28.84	15°C	397	R=0.9984
Triethanolammonium dodecylbenzenesulfonate at 0.50 mol/l								
None	15°C	0	292.	8.28	0	-	-	VNJ=0.08
0.25 eq/l Na-PF	5°C	25	361.	57.0	7.86	2°C	1520	R=0.9999
0.50 eq/l Na-PF	5°C	0	256.	41.9	5.96	12°C	466	R=0.9989
0.75 eq/l Na-PF	15°C	0	152.	26.6	3.84	15°C	204	R=0.9944
1.00 eq/l Na-PF	25°C	0	110.	20.5	3.00	19°C	129	R=0.9908
0.25 eq/l K-PF	5°C	38	311.	83.0	11.9	15°C	745	R=0.9998
0.50 eq/l K-PF	25°C	0	154.	58.0	8.92	34°C	159	R=0.9972

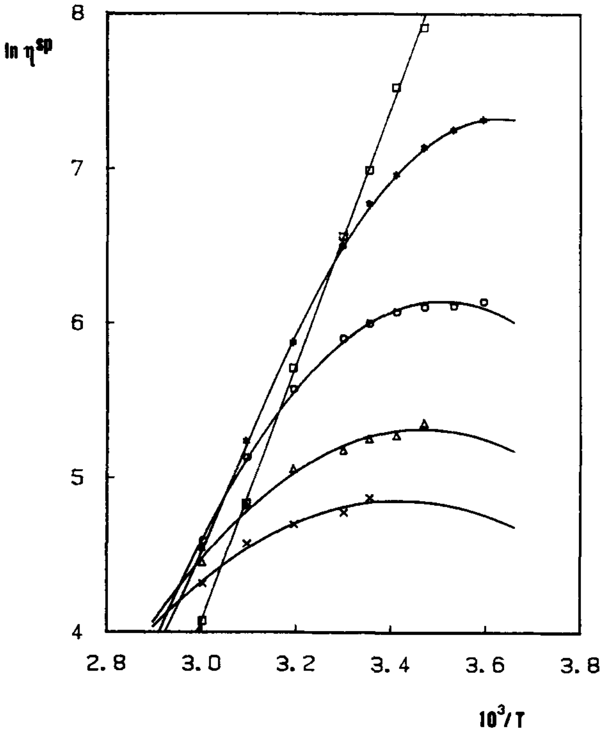


FIG. 1. Relationship between ln η^{sp} and 1000/T for solutions containing 0.25 mol/l of triethanolammonium dodecylbenzenesulfonate and tetrasodium pyrophosphate. (□, 0.00; *, 0.25; O, 0.50; △, 0.75; x, 1.00 eq/l).

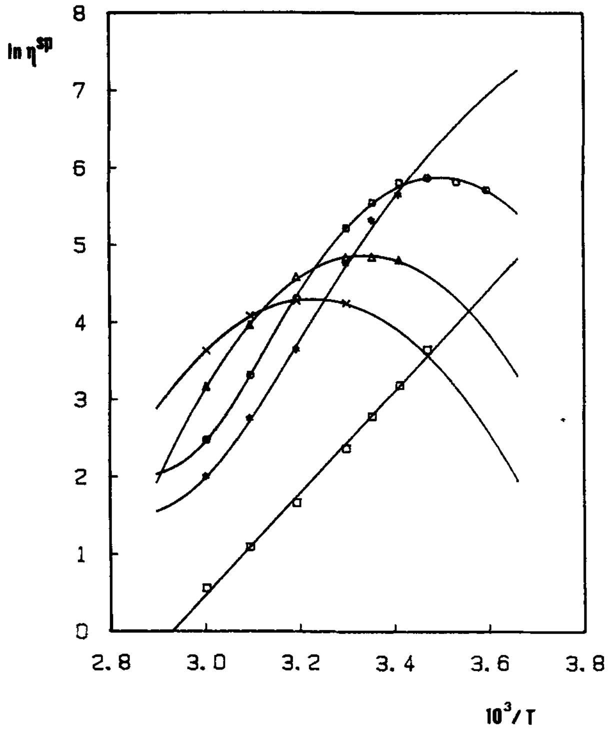


FIG. 2. Relationship between ln η^{sp} and 1000/T for solutions containing 0.50 mol/l of triethanolammonium dodecylbenzenesulfonate and tetrasodium pyrophosphate. (□, 0.00; *, 0.25; O, 0.50; △, 0.75; x, 1.00 eq/l).

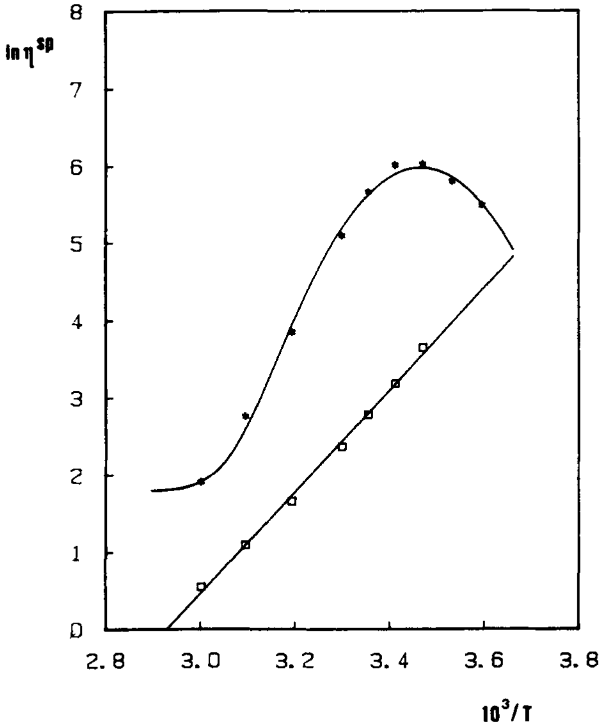


FIG. 3. Relationship between ln η^{sp} and 1000/T for solutions containing 0.25 mol/l of triethanolammonium dodecylbenzenesulfonate and tetrapotassium pyrophosphate. (□, 0.00; *, 0.25 eq/l).

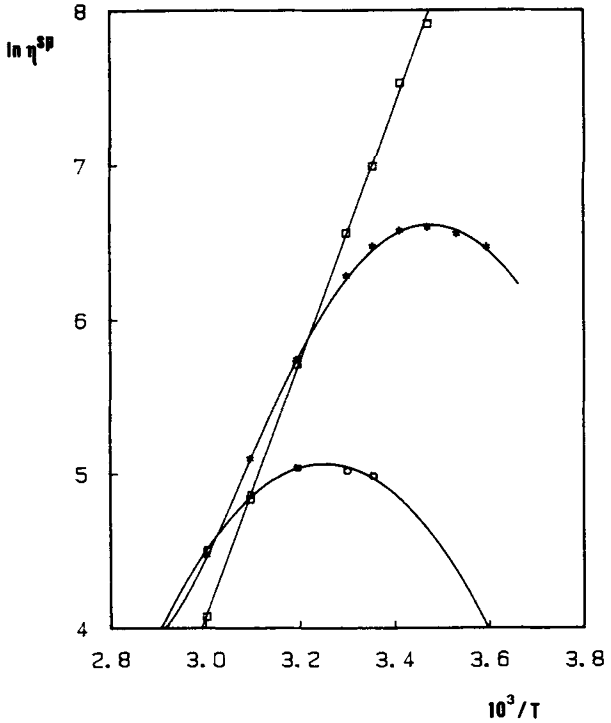


FIG. 4. Relationship between ln η^{sp} and 1000/T for solutions containing 0.50 mol/l of triethanolammonium dodecylbenzenesulfonate and tetrapotassium pyrophosphate. (□, 0.00; *, 0.25; O, 0.50 eq/l).

TEA-LAS may diminish when the pyrophosphate concentration is raised. The following case may be mentioned as a typical example: The addition of Na-PF up to 0.50 eq/l to a solution containing 0.50 mol/l of TEA-LAS reduces, at 15°C, the specific viscosity from 2730 to 449; whereas at 60°C this addition provokes an increase in specific viscosity from 59 to 99. That is to say, at 15°C, at which many hydrogen bonds are present, specific viscosity suffers a decrease of 84%; at 60°C, a temperature at which there are only a few hydrogen bonds left, the specific viscosity increases to 68%.

INTERPRETATION OF RESULTS

With respect to the explanation of the behaviors found in the solutions studied, the two following hypotheses may be assumed.

(i) If the parameters q^{rel} and J in equation [5] do not change significantly with temperature within the range studied, then that equation can be transformed into the following one:

$$\ln\left[(\eta^{rel} - q^{rel})/(\eta^{rel}(40) - q^{rel})\right] = (E/k)\,(1/T - 1/313.2) \qquad [9]$$

where $\eta^{rel}(40)$ is the relative viscosity at 40°C.

(ii) If the activation energy for long-range diffusive motion may be expressed by the following function of temperature:

$$E = E_o - A/T \qquad [10]$$

where E_o and A do not change significantly with temperature within the range studied, then Equation [9] can be converted into the one below:

$$\ln\left[\,(\eta^{rel} - q^{rel})/(\eta^{rel}(40) - q^{rel})\right] = (E_o/k)\,(1/T - 1/313.2) - (A/k)\,(1/T^2 - 1/313.2^2) \qquad [11]$$

If it is assumed that the parameter q^{rel} does not significantly differ from unity, then Equation [9] is equal to Equation [6], which was found to be valid for those solutions containing Na-DS or TEA-DS, and for those containing TEA-LAS as the only solute. The parameter 10^3 B in Equation [6] corresponds to the parameter E/k in Equation [9].

Unity values for q^{rel} may be due to the fact that intrinsic viscosity, $[\eta]$, for micelles is very low. Thus, Equation [3] results as follows:

$$q^{rel} = (1 - k_p\,\phi)^{-[\eta]k_p} \cong (1 - k_p\,\phi)^0 = 1 \qquad [12]$$

Equation [9] is equal to Equation [7], which was found to be valid for those solutions containing Na-LAS, and where $Q = q^{rel} - 1$ and 10^3 B = E/k.

Finally, Equation [11] is equal to Equation [8], which is valid for those solutions containing TEA-LAS and pyrophosphate, where $Q = q^{rel} - 1$; 10^3 B = E_o/k, and 10^6 C = A/k.

Consequently, all the experimental results can be explained if the equation for the activated diffusive relaxation model, modified according to the hypotheses proposed above, is acccepted.

With respect to the explanation of the behavior found in solutions containing TEA-LAS and a pyrophosphate, with an activation energy for long-range diffusive motion, E, which increases when temperature is raised, the following can be assumed:

(a) The large micelles formed in these solutions are surrounded by a layer of water molecules. These molecules are joined by hydrogen bonds to the hydroxyl groups of the triethanolammonium cations situated in the Gouy-Chapman and Stern layers of the micelles.

(b) This aqueous layer, because it contains alkaline pyrophosphate ions, helps to "screen" the electrostatic repulsion forces between micelles. Thus, the higher the pyrophosphate concentration is, the greater the "screening" effect.

(c) An increase in the "screening" effect produces a decrease in the activation energy for long-range diffusive motion.

(d) As temperature becomes higher, a breakdown of hydrogen bonds take place. Consequently, the efficiency of the "screening" process goes down as temperature increases.

(e) The rise in the "screening" process, caused by an increase in the concentration of pyrophosphate, leads to a drop in the $\eta^{sp}{}_{max}$ value, as well as to an increase in the t_{max} value.

(f) The addition of pyrophosphate to a solution containing 0.25 mol/l TEA-LAS provokes, within the range of temperature studied, an increase in viscosity as may be observed in Figures 1 and 3. Nevertheless, as can be deduced from inspection of Figures 2 and 4, if the concentration of TEA-LAS is 0.50 mol/l and temperature stays below 30°C, the opposite effect takes place when pyrophosphate is added. These contrasting effects may be attributed to the difference in magnitude of the intermicellar repulsions in each solution, because they are obviously higher at a double concentration of TEA-LAS.

The influence of the changes in the surfactant anion, in its counter-ion and in the cation of pyrophosphate will be analyzed extensively in a subsequent paper.

To sum up, interactions among water, surfactants and alkaline pyrophosphates are very complex, and a satisfactory explanation of rheological behaviors of aqueous media containing them requires additional studies.

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