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Effect of Temperature on Viscosity of Aqueous Triton X-114 Solution

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ABSTRACT: Nonionic surfactant solution is often used to separate and purify biomaterials, and the viscosity of nonionic surfactant solution plays an essential role in the design of separation process. In this study, the viscosity data are obtained for aqueous Triton X-114 ((1,1,3,3-tetramethylbutyl)phenyl−polyethylene glycol) solutions of three mass fractions of 0.01, 0.02, and 0.05 at temperatures from 293.15 to 313.15 K, and an empirical correlation describing the effect of temperature on the viscosity is derived. The predicted values by the correlation are in good agreement with the experimental data.

INTRODUCTION

A nonionic surfactant aqueous solution usually becomes turbid when heated to a certain temperature known as the cloud point. This cloudiness is related to a phase separation process driven by noncovalent interactions between the hydrophilic and hydrophobic parts of the surfactant and the surrounding water. Cloud point extraction (CPE) has been used as an important separation and purification technique of biomaterials while keeping their activities.[1−5] As CPE is formed generally at low surfactant concentration and can be recycled, it is considered as an economical extraction system.[6,7]

To understand the cloud point phenomenon of nonionic surfactant solutions, a variety of techniques, including fluorescence spectroscopy,[8] turbidimetry,[9−11] small-angle neutron scattering,[12] static and dynamic light scattering,[13] and viscosimetry,[13] have been used. The viscosities of nonionic surfactant solutions and their dependence on temperature are important from the technical and engineering points of view. Surfactant solutions are usually classified based on their behavior between shear stress and shear rate into Newtonian and non-Newtonian. Newtonian fluids are defined as those exhibiting a direct proportionality relationship between shear stress and shear rate, whereas for non-Newtonian fluids, the relationship between shear stress and shear rate is not linear.

The objectives of the present work are to measure the temperature-dependent viscosity in aqueous nonionic surfactant solutions that undergo phase separation and to develop an empirical correlation to predict the experimental data. These can provide us with new information to evaluate the possible changes in the rheological properties of aqueous surfactant solutions after phase separation.

EXPERIMENTAL SECTION

Triton X-114 ((1,1,3,3-tetramethylbutyl)phenyl−polyethylene glycol) was purchased from Aladdin, and used without further purification. Three different mass fractions of 0.01, 0.02, and 0.05 of aqueous Triton X-114 solution were prepared. Each solution was mixed for 24 h using a magnetic stirrer to ensure the solutions homogeneous and perfectly mixed. An AR-G2 rheometer (TA Instruments, New Castle, DE) was used to measure the viscosity and flow characteristics of solutions. A transparent parallel plate configuration (50 mm diameter) with a 1 mm gap was used for all tests. The measurements were made at shear rates from 1 s^{-1} to 100 s^{-1}, and temperatures from 293.15 to 313.15 K, the same as used in the CPE techniques, and the temperature was controlled within 0.1 K. Measurements were repeated at least three times for each solution. The accuracy of the viscosity determination is within 1%.

RESULTS AND DISCUSSION

Figure 1 shows a log−log plot of the viscosity vs the shear rate for the surfactant solutions of different mass percentages. In the available range of the shear rates (1 s^{-1} to 100 s^{-1}), a shear thinning region at low shear rates followed by an plateau (Newtonian behavior) is observed for the cures of all the solutions, and by a final shear thickening part at the highest shears for 0.05 mass fraction of the solution. It is expected surfactant concentration dependence is observed, i.e., at all shear rates the viscosity is an increasing function of concentration.

Table 1 shows the influences of temperature (from 293.15 K to 313.15 K) on the viscosity measured at a shear rate of 10 s^{-1}. At a specific temperature, the viscosity increases with increasing surfactant concentration, as a consequence of the existence of more surfactant molecules available for the growth of micelles. With the increase of temperature of the solution, the viscosity first increases and after passing through a maximum value begins to decrease. The value of the maximum viscosity and the temperature at which the maximum viscosity (T_{max}) appeared are dependent on the surfactant concentration. It is revealed that the T_{max} is 295.15 K, 297.15 K, and 298.15 K for 0.01, 0.02, and 0.05 mass fraction of the solution, respectively. This phenomenon can be explained by the fact that the water molecule movement at temperatures near the cloud point is sufficient to reduce hydration of surfactant and to cause the formation of large molecular assemblies of the surfactant, and the increase of the assemblies number induces an increase in the viscosity. However,

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at higher temperature the molecular motions overcome the molecular interactions, and then the viscosity decreases.

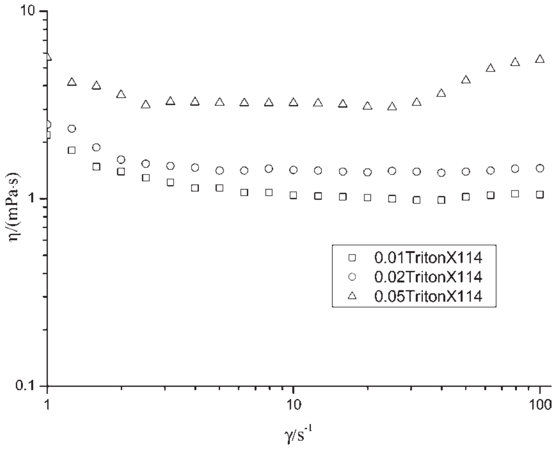

Figure 1. Viscosity, η, of aqueous TX-114 solutions as a function of shear rate, γ, at 303.15 K.

Table 1. Viscosity, η, of Aqueous Triton X-114 Solutions of Three Mass Fractions, f, at Different Temperatures from 293.15 to 313.15 K

T/K	η/mPa·s	T/K	η/mPa·s	T/K	η/mPa·s
		$f = 0.01$			
293.15	1.64	300.15	1.28	307.15	0.87
294.15	1.73	301.15	1.26	308.15	0.81
295.15	1.87	302.15	1.23	309.15	0.77
296.15	1.72	303.15	1.16	310.15	0.68
297.15	1.66	304.15	1.06	311.15	0.62
298.15	1.52	305.15	0.99	312.15	0.53
299.15	1.46	306.15	0.95	313.15	0.53
		$f = 0.02$			
293.15	3.31	300.15	2.36	307.15	1.23
294.15	3.52	301.15	2.15	308.15	1.16
295.15	3.75	302.15	1.83	309.15	1.01
296.15	3.93	303.15	1.62	310.15	0.97
297.15	4.05	304.15	1.54	311.15	0.81
298.15	3.35	305.15	1.37	312.15	0.76
299.15	2.96	306.15	1.25	313.15	0.69
		$f = 0.05$			
293.15	4.66	300.15	5.62	307.15	2.17
294.15	5.14	301.15	4.86	308.15	1.95
295.15	6.36	302.15	3.90	309.15	1.86
296.15	7.75	303.15	3.37	310.15	1.72
297.15	8.34	304.15	2.97	311.15	1.45
298.15	9.72	305.15	2.65	312.15	1.39
299.15	6.81	306.15	2.40	313.15	1.35

Numerous empirical and theoretical equations have been formulated to relate the variations of viscosity with temperature for the surfactant solutions. The most notable empirical equation used is the Andrade equation,[14−18] which relates viscosity, η, and absolute temperature, T, by an Arrhenius type of exponential function as follows:

$$\eta = A \exp\left(\frac{E}{RT}\right) \tag{1}$$

According to the Andrade equation, we divide the viscosity data into two parts:

$$\eta = \begin{cases} A_1 \exp\left(\dfrac{E_1}{RT}\right) & T \leq T_{\max} \\ A_2 \exp\left(\dfrac{E_2}{RT}\right) & T > T_{\max} \end{cases} \tag{2}$$

where A_1 and A_2 are constants, E_1 and E_2 are the activation energies for viscous flow, R is the gas constant, and $T_{\max}$ is the temperature for the maximum viscosity.

The correlation has been performed with experimental data by minimizing the following objective function

$$\text{AAD} = \frac{100\%}{N} \sum_{i=1}^{N} \frac{|\eta_{i,\text{exp}} - \eta_{i,\text{calc}}|}{\eta_{i,\text{exp}}} \tag{3}$$

where AAD is the average absolute deviation, N is the number of experimental data points, and $\eta_{i,\text{exp}}$ and $\eta_{i,\text{calc}}$ are the experimental and calculated viscosity, respectively. The fitting parameters, the average absolute deviation (ADD), and the maximum absolute deviation (MAD) at different temperatures are reported in Table 2. It is seen that the calculated viscosity values show good agreement with the experimental values.

CONCLUSIONS

The viscosity of aqueous Triton X-114 solution increases with the increasing surfactant mass fraction from 0.01 to 0.05. The temperature dependence of the viscosity exhibites a peculiar behavior, showing a maximum at one critical temperature, and an empirical correlation is found to successfully correlate the viscosity of the surfactant solutions for the temperature range 293.15 K to 313.15 K.

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Table 2. Adjustable Parameters of eq 2 and Standard Deviations for Aqueous TX-114 Solutions of Three Mass Fractions, f

f	A_1	E_1/J·mol^{-1}	A_2	E_2/J·mol^{-1}	$T_{\max}$ /K	ADD/%	MAD/%
0.01	4.19×10^{8}	−47228.48	6.77×10^{-10}	53490.11	295.15	3.56	12.53
0.02	1.43×10^{7}	−37251.14	1.19×10^{-13}	76521.54	297.15	4.16	11.14
0.05	2.35×10^{20}	−110672.64	1.83×10^{-15}	88857.60	298.15	5.68	14.03

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