Viscosity vs. Pour Point Relationships for Alcohol Nonionic Surfactants

GARLAND D. SMITH, Chemicals Research Division,
Continental Oil Company, Ponca City, Oklahoma 74601

ABSTRACT

A relationship between the room temperature viscosity of neat nonionic surfactants and the pour point has been discovered which has considerable practical value and useful theoretical implications. The pour points of nonionic surfactants are a semiquantitative indication of liquidity, which is an important property for storage and handling. The relationship between viscosities measured at room temperature and pour points follows an Arrhenius function, which is a commonly encountered mathematical form in nonturbulent flow. The phenomena are evaluated using a model based on Eyring's kinetic approach to the Stokes-Einstein relationship. An obvious practical feature of this work is that instead of the tedious, relatively inexact practice of measuring pour points, it is apparent that one can obtain the same information from the more accurate and convenient measurement of viscosity. Useful inferences are also made which provide insight into the mechanisms which give rise to the pour point, the molecular structure of neat nonionics, and the nature of homolog mixing. Data for both primary and secondary alcohol ethoxylates have been investigated.

INTRODUCTION

Liquids are more readily manageable materials than solids from the viewpoint of commercial processing and handling. Consequently, liquid nonionic surfactant chemicals are generally preferred over the more waxy materials. In spite of the industrial importance of liquidity, very little information exists concerning the nature of the factors which lead to the rheological properties of nonionic surfactants. The majority of the work reported is related to aqueous solutions (1).

Among the most important measurements made to quantify the liquidity of surfactants is the "pour point" (2). While pour points have an accuracy of ± 5F (±3C), by the definition of the test and anomalies in the fluidity of samples can be misleading; these data are widely used in the industry as an indication of the liquidity of nonionic surfactants. Further, for these chemicals pour point data appear to be reliable information for most applications. The test still has the disadvantage, however, of being somewhat tedious.

In the work described here, a relationship between the flow properties of the liquid phase and pour point data is discussed. Given the proper data, an empirical relationship can be found which can be explained based on models of viscous flow. Once the relationship is found, pour points can be predicted with reasonable accuracy from relatively simple viscosity measurements.

EXPERIMENTAL

Materials

All of the measurements reported herein were made on neat surfactants. The surfactants were polyoxyethylene adducts of straight chain primary and secondary alcohols. Some of the samples were commercially available products, while others were experimental samples synthesized in the laboratory. All of the primary alcohol adducts were prepared by the same single step, base-catalyzed process. All of the seconday alcohol adducts were prepared by the same two step process involving an acid-catalyzed reaction followed by a base-catalyzed reaction.

Methods

Viscosities were measured at room temperature (75 F or 24 C) using a Brookfield model LVT viscometer. Pour points were measured with the standard ASTM method (2).

TABLE I

Properties of Primary (Ziegler) Alcohol Ethoxylates

Chain lengths in blend (No. of C Atoms)	Average chain length (No. of C Atoms)	Average moles of ethylene Oxide	Viscosity cP @75F (24C)	Pour point (F/K)
6	6	2.8	16.1	10/260.8
6	6	3.5	15.6	15/263.6
6	6	4.3	20.7	30/271.9
6	6	5.4	24.3	40/277.4
8	8	3.6	18.8	25/269.1
8	8	4.4	22.0	30/271.9
8	8	5.5	25.0	45/280.2
8	8	6.9	33.3	50/283.0
10	10	4.4	24.3	40/277.4
10	10	5.4	26.0	45/280.2
10	10	8.3	40.4	65/291.3
4,6,8,10	8.2	2.0	12.5	-5/252.4
4,6,8,10	8.2	3.0	16.1	10/260.8
4,6,8,10	8.2	4.5	22.7	30/271.9
4,6	5.5	2.2	9.0	-15/246.9
4,6	5.5	3.2	13.1	5/258.0
6,8,10,12,14,16,18	13.3	4.6	31.7	45/280.2
6,8,10,12,14,16,18	9.4	4.0	21.0	35/274.7
6,8,10,12,14,16,18	9.7	4.6	26.3	40/277.4
6,8,10,12,14,16,18	10.0	4.2	26.5	45/280.2

TABLE II

Properties of Secondary Alcohol Ethoxylates

Chain lengths in blend (No. of C Atoms)	Average chain length (No. of C Atoms)	Average moles of ethylene Oxide	Viscosity cP @75F (24C)	Pour point (F/K)
11,12,13	11.2	7	52.8	25/269.1
11,12,13,14,15	13.4	3	24.2	-60/221.9
13,14,15	14.0	7	52.2	25/269.1
13,14,15	14.0	10	79.4	55/285.8
13,14,15	14.0	3	24.4	-50/227.4
11,12,13	11.2	7.7	51.2	25/269.1
11,12,13	11.2	9	57.0	40/277.4
13,14,15	14.0	6	47.1	10/260.8
11,12,13,14,15	13.4	9	65.6	45/280.2
13,14,15	14.0	8	61.9	40/277.4
11,12,13	11.2	5	30.8	-25/241.3

RESULTS

Tables I and II contain the data used for the evaluations in this paper. The tabulation of these data assists one in visualizing the types of materials studied and the nature and size of the errors involved in this treatment. It is of interest to see the rather wide range of homolog blends which give similar pour points with only nominal variations in viscosity. Indeed, the relatively small range of viscosities in these tables tend to magnify the experimental error. Also apparent in these tables is the five Fahrenheit degree increment between pour points which itself introduces a range of uncertainty.

The substance of the work described here rests on the discovery that the data in Tables I and II obey an exponential relationship of the type

$$\eta = Be^{bT_p} \quad 1$$

where η is the room temperature viscosity, B and b are constants, and T_p is the pour point. This is in the form of an Arrhenius function and can also be written as a natural log expression.

$$\ln\eta = \ln B + bT_p \quad 2$$

The suggested semilog plots for Tables I and II are presented in Figures 1 and 2, respectively. By fitting the best lines to these data, one obtains the folowing equations:

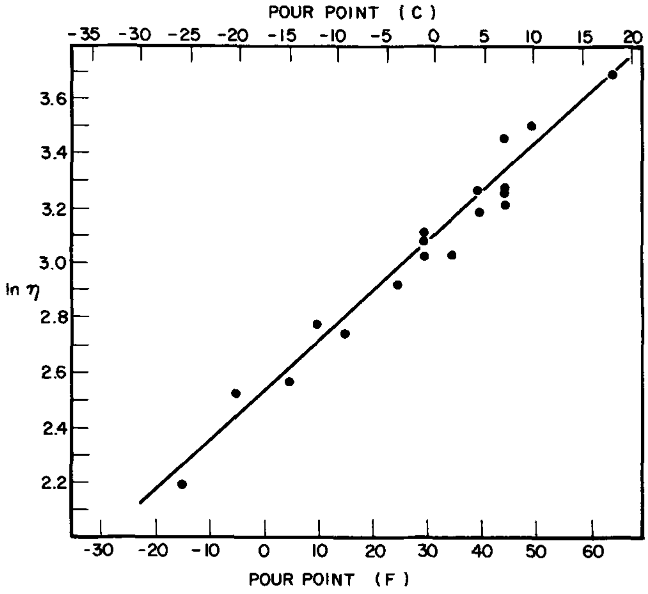

FIG. 1. Natural logrithm of room temperature viscosity (in centipoise) vs. pour point for primary alcohol ethoxylates.

Primary Alcohol:

$$\eta = 12.6e^{0.018T_P(F)} \quad 3$$

$$\eta = 0.0039e^{0.032T_P}\ (K) \quad 4$$

Secondary Alcohol:

$$\eta = 41.6e^{0.0098T_P}\ (F) \quad 5$$

$$\eta = 0.46e^{0.018T_P}\ (K) \quad 6$$

By employing models which appear in the literature to explain viscous flow, one can derive an expression similar to that shown in equation 1 and thereby provide some sorely needed insight into the rheology of neat nonionic surfactants (3).

By the "hole" theory of nonturbulent flow, viscosity is a function of temperature and also obeys an Arrhenius function

$$\eta = A_\eta\, e^{E_\eta/RT_\eta} \quad 7$$

where A_η is the Arrhenius constant, R is the molar gas constant, T_η is the temperature at which η was measured, and E_η is the activation energy required for a "particle" of the liquid to move from one "hole" to the next (4).

The phenomenon of a pour point also involves a viscous flow which is best treated by a diffusion like process such as that described by the Stokes-Einstein relation (4). In this treatment one defines a pourable mass, Mp, such that at the

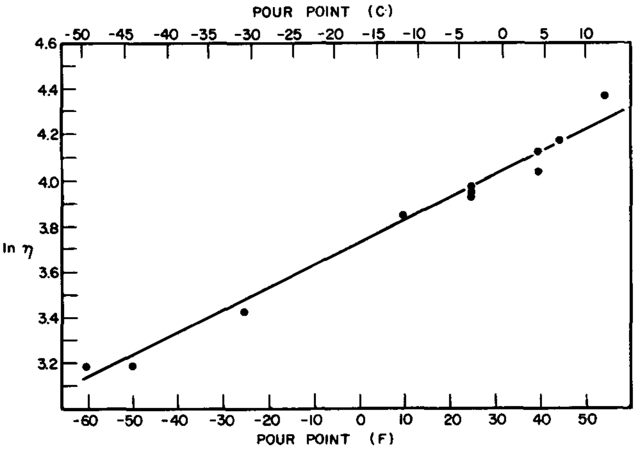

FIG. 2. Natural logrithm of room temperature viscosity (in centipoise) vs. pour point for secondary alcohol ethoxylates.

pour point one has

$$M_p = \frac{C}{\eta_p} \qquad 8$$

in which η_p is the viscosity at the pour point and C is a constant which is independent of molecular homolog effects (cf Appendix I). Since viscosity is described by equation 7, equation 8 becomes

$$M_p = \frac{C}{A_p} e^{-E_p/RT_p} \qquad 9$$

or

$$\ln \frac{M_p A_p}{C} = -\frac{E_p}{RT_p} \qquad 10$$

The subscript "p" indicates values which are applicable at the pour point, T_p. Rearranging,

$$E_p = RT_p \ln \frac{C}{M_p A_p} \qquad 11$$

In the present treatment, E_η, from equation 7 is a molecular fluidity problem and is, therefore, different from E_p which is at least partially a melting process. In any case both terms are activation energies and are somewhat temperature dependent. The two values can, therefore, be related to each other by

$$E_\eta = \alpha E_p \qquad 12$$

where α is a proportionality constant which cannot be unity for the reasons just stated. Equation 11 now becomes

$$E_\eta = \alpha RT_p \ln \frac{C}{M_p A_p} \qquad 13$$

Substituting this result into equation 7, one has

$$\eta = A_\eta \exp \left[\left(\alpha RT_p \ln \frac{C}{M_p A_p}\right) \frac{1}{RT_\eta}\right]$$

$$\eta = A_\eta \frac{C}{M_p A_p} \exp \left[\left(\frac{\alpha}{T_\eta}\right) T_p\right]$$

$$= \frac{c}{M_p} \exp\left(\frac{\alpha}{T_\eta}\right) T_p \qquad 14$$

where $c = A_\eta \frac{C}{A_p}$

Since the experimental measurements in this work were at constant T_η and M_p, we can define $a = c/M_p$ and $b = \alpha/T_\eta$ which modifies equation 14 to give

$$\eta = ae^{bT_p} \qquad 15$$

This relation, which one might reasonably anticipate for the behavior of room temperature viscosities with respect to pour points, is, in fact, the form of equation 1, which was determined experimentally.

This theoretical treatment suggests that the slopes of the lines in Figures 1 and 2 should allow one to measure the ratio $E_\eta/E_p = \alpha$. This ratio is 9.5 for primary alcohols and 5.1 for secondary alcohols. These values indicate that the viscosity process involves substantially more energy than that which gives rise to pour points according to this model.

DISCUSSION

The practicable accuracy of a pour point test depends on the ability to determine M_p in equation 8. Herein lies the value of equations 3 through 6. Nonionics can be screened for pour points with relatively simple viscosity measurements which are also more accurate than pour point tests.

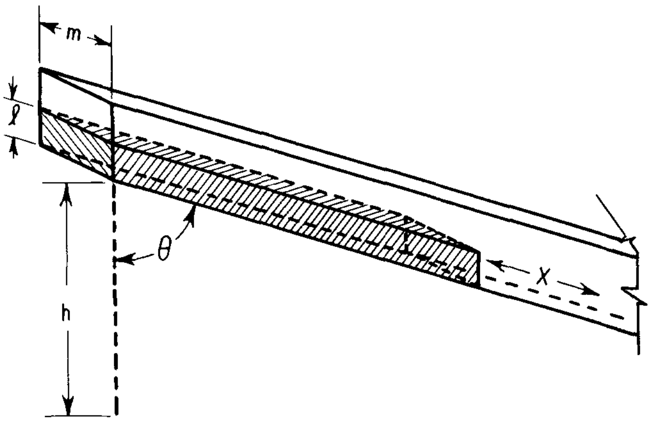

FIG. I-1. Flow of a fluid material (shaded) down an incline which is tilted from the vertical by an angle θ.

When using this technique, however, one must be careful when using viscosity data which are measured at a temperature near the pour point. Obviously, partial solidification results in substantial deviations from a linear behavior for such data.

Implicit in the obedience of a regular function for a wide range of blends and the relative magnitudes of E_η and E_p are that mixing is nearly ideal as suggested by Becher (5). Further, it indicates that liquid nonionic surfactants are molecularly dispersed. Apparently mathematically similar processes apply to both the liquid phase and the solidification process, and changes in E_η are accompanied by similar changes in E_p from sample to sample. Equation 15 describes, if only qualitatively, how the solid and liquid phases of these materials depend on the same types of molecular interactions. The differences in the magnitude of the constants between the primary and secondary alcohol derivatives indicate an obvious difference in molecular interactions

The different α values for primary and secondary alcohol ethoxylates is of some interest but is not readily decipherable from these data. It would be instructive to know whether E_η or E_p made the greater contribution to the change, but, again, one would require more direct information on E_η and E_p. At first glance it would appear that the difference in the hydrophobe would be the primary source of difference, and this is certainly an important factor. On the other hand, there is a different distribution of ethylene oxide homologs on the primary and secondary ethoxylates used here because of the different methods of preparation. And, as Tanford points out (6), the polar portions of surfactant molecules give rise to the majority of the intermolecular interactions.

APPENDIX I

To show that the constant "C" which relates the pourable mass M_p to the pour point viscosity η_p is not a function of molecular structure, consider the relations depicted in Figure I-1. The force, f, causing the fluid to flow a distance x down the incline is

$$f = \rho gh \cos\theta \qquad \text{I-a}$$

where ρ is the fluid density and g is the gravitational constant. If we define

$$u = \frac{x\rho gh \cos\theta}{\eta_p} \qquad \text{I-b}$$

where η_p is the viscosity at the pour point, then

$$f = \left(\frac{u}{x}\right)\eta_p \qquad \text{I-c}$$

The volume flow rate, M_p, (cm^3/sec) is

$$\begin{aligned} M_p &= \int_0^{\ell} u m dx \\ &= m\left[\frac{\rho g h \cos\theta}{\eta_p}\right] \int_0^{\ell} x dx \\ &= \left[\frac{\ell^2}{2}\, m\, g h \cos\theta\right] \eta_p^{-1} \qquad \text{I-d} \end{aligned}$$

where m is the mass of the fluid.

This is of the same form as equation 8 in the preceding text; therefore,

$$C = \frac{\ell^2}{2}\, m\, g h \cos\theta \qquad \text{I-e}$$

If ρ is invariant, as it is within the limit of the experimental conditions here, then c is a constant.

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