Viscosity, Pour Point, and Chain Length Relations for the Alcohol Ethoxylates

C.H. FISHER, Chemistry Department,
Roanoke College, Salem, VA 24153

ABSTRACT

Because pour points of surfactant alcohol ethoxylates are important and tedious to determine experimentally, it is desirable to have methods for calculating pour points from other properties, e.g., viscosities (1). To facilitate calculating pour points, several types of equation were developed that relate (a) chain lengths of the alcohol ethoxylates to pour points, (b) chain lengths to viscosities, and (c) viscosities to pour points.

INTRODUCTION

Smith recently published viscosity and pour point data for neat alcohol ethoxylates (monoalkyl ethers of poly (ethylene oxides)) and pointed out that, because the determination of pour points is experimentally tedious, methods are needed for calculating pour points from easily determined viscosities. He provided equations for calculating pour points based on the linear relation between pour points (p) and viscosity (v) logarithms:

$$p = b + m \log v \tag{1}$$

As reported below, the present author used Smith's data (1) to calculate the average chain lengths (total number of carbons and oxygens) of the primary and secondary alcohol ethoxylates and to develop equations relating: chain lengths (y) to pour points (p, °F); chain lengths (y) to viscosities (v); and pour points to viscosities.

EXPERIMENTAL

Average chain lengths (Tables I and II) were calculated by adding the number of carbons (x) in the alcohol or alkyl groups (R) to three times the number of ethoxyl units (n):

$$R(OCH_2CH_2)_nOH$$

The average number of carbons in R ranged from 5.5 to 13.3 for the primary alcohol ethoxylates and from 11.2 to 14 for the secondary alcohol ethoxylates. The number of ethoxyl units ranged from 2 to 8.3 for the primary alcohol ethoxylates and from 3 to 10 for the secondary alcohol ethoxylates (1). A Hewlett-Packard HP27 instrument was used to calculate least squares equations and correlation coefficients. Although the pour points reported by Smith (1) have an accuracy of only ± 5°F, the agreement between the experimental and calculated pour points of the present paper is reasonably good. Smooth curves (Figures 1 and 2) resulted when chain lengths were plotted against pour points and viscosities.

RESULTS

Confirming the work of Smith (1), it was found that logarithmic equations are suitable for calculating pour points from viscosities. Three-parameter equations (Eq. 2), however, are preferable in at least some instances to two-parameter equations (Eq. 1):

$$p = b + m \log(y + k) \tag{2}$$

Reciprocal equations also were found useful for relating pour points to viscosities:

$$p = b + m/(v + k) \tag{3}$$

Several equations were developed for relating chain lengths to pour points and viscosities. These should be very useful when the chain lengths or molecular weights are known. Such equations might be found useful also on some occasions for estimating the chain lengths of alcohol ethoxylates. Presumably the methods described herein can be employed to relate either chain lengths or molecular weights of alcohol ethoxylates to pour points, viscosities, and various other properties.

Some of the functions described below ($p(y + 4)$ of Eq. 4, y/P of Eq. 6, and $v^{.7}$ of Eq. 23) are linear with chain length. It may be expected that these particular functions are linear also with other functions that are linear with homolog chain length, including M/d, M/n, and T_b^2, °K (M, molecular weight; d, density; n, refractive index; and T_b, boiling point, °K).

The equations of the present work are discussed further below in separate sections concerned with primary or secondary alcohol ethoxylates.

Primary Alcohol Ethoxylates

Two types of equation previously used with melting points were found suitable for relating pour points (p, °F,

TABLE I

Chain Lengths (y), Pour Points (p, °F and P, °K), and Viscosities (v) of the Primary Alcohol Ethoxylates[a]

No.	Chain lengths	Pour points		Viscosities cP, 24°C	Calculated pour points[b]						Calculated viscosities				
		°F	°K		Eq. 4	Eq. 5	Eq. 6	Eq. 8	Eq. 14	Eq. 15	Eq. 9	Eq. 10	Eq. 11	Eq.12	Eq. 13
1	12.1	-15	246.9	9	-16.4	-16.6	246	246	-16.9	-17.3	9.6	9.3	9.1	9.0	9.4
2	14.2	-5	252.4	12.5	-.55	-.05	255	255	.96	.51	12.5	12.4	12.3	12.2	12.4
3	15.1	5	258	13.1	5.2	5.6	258	258	3.5	3.1	13.7	13.7	13.7	13.6	13.7
4	15.8	10	260.8	16.1	9.2	9.6	260	261	14.7	14.8	14.7	14.7	14.7	14.6	14.7
5	16.5	15	263.6	15.6	13.0	13.2	262	263	13.0	13.0	15.6	15.7	15.7	15.7	15.7
6	18.18	25	269.1	18.8	23.9	23.7	269	269	23.2	23.5	18.8	18.9	19.0	19.0	18.9
7	20.6	30	271.9	21.8	31.0	30.5	272	273	31.2	31.8	21.3	21.4	21.6	21.6	21.4
8	21.4	35	274.7	21.0	33.8	33.3	274	274	29.2	29.7	22.4	22.5	22.7	22.7	22.5
9	23.0	40	277.4	25.0	38.9	38.3	277	277	38.7	39.3	24.6	24.7	24.8	24.9	24.7
10	25.1	45	280.2	27.3	44.8	44.3	280	280	43.5	44.0	27.5	27.6	27.6	27.8	27.6
11	28.7	50	283.0	33.3	53.2	53.0	285	285	54.3	54.2	32.4	32.4	32.3	32.5	32.5
12	34.9	65	291.3	40.4	63.9	65.1	291	290	64.8	63.4	40.9	40.7	39.9	40.2	40.7

[a] Pour points and viscosities from Smith (1); chain lengths and viscosities were averaged for each pour point.
[b] Pour points in °K for Eqs. 6 and 8, in °F for the other equations.

TABLE II

Chain Lengths (y), Pour Points (p), and Viscosities (v) of Secondary Alcohol Ethoxylates[a]

No.	Chain length	Pour points °F	Pour points °K	Viscosities cP, 24°C	Calculated pour points Eq. 18	Eq. 20	Eq. 21	Eq. 24	Eq. 25	Eq. 26	Calculated viscosities Eq. 22	Eq. 23
1	22.4	-60	224.9	24.2	-58.6	-59.2	226.1	-55.5	-55.1	-56.1	23.7	23.7
2	23.0	-50	227.4	24.4	-52.2	-52.1	228.7	-54.4	-54.1	-53.7	25.0	25.0
3	26.2	-25	241.3	30.8	-23.6	-22.6	241.4	-26.0	-27.4	-26.4	31.9	31.9
4	32.0	10	260.8	47.1	12.8	12.7	260.3	15.5	15.7	16.2	45.6	45.5
5	33.8	25	269.1	52.1	21.3	21.0	265.3	24.2	24.7	25.4	50.1	50.0
6	38.1	40	277.4	59.5	38.4	38.0	275.9	35.2	35.8	35.1	61.4	61.4
7	40.4	45	280.2	65.6	45.9	45.7	281.0	43.1	43.4	42.5	67.7	67.7
8	44.0	55	285.8	79.4	56.1	56.5	288.1	57.9	57.1	57.6	77.9	78.0

[a] Pour points and viscosities are from Smith (1); chain lengths and viscosities averaged for each pour point.

and P, °K) to chain length (y). These are the reciprocal (2-4) and logarithmic (5) equations:

$$p = 120.59 - 2204.99/(y + 4) \tag{4}$$

(Correl. coeff., .996601

$$p = -94.9758 + 110.719\log(y-7) \tag{5}$$

(Correl. coeff., .996135)

The "molar volume" type of equation also is useful for calculating pour points (P, °K) from chain lengths:

$$y/P = .0115465 + .00310989y \tag{6}$$

(Correl. coeff., .999896)

The pour points of the primary alcohol ethoxylates were compared with the melting points, T, °K, of the corresponding n-alkanols (i.e., having the same chain lengths). The n-alkanol melting points were calculated by the previously published (4) Eq. 7 (x, number of carbons):

$$T = 408.096 - 1545.17/(x + 1.98) \tag{7}$$

The pour points (P, °K) were found to be lower than and linear with the calculated n-alkanol melting points:

$$P = 50.8539 + .653384T \tag{8}$$

(Correl. coeff., .997119)

The differences between the pour points and n-alkanol melting points ranged from about 60° for the lower members to 75° for the higher members. On the assumption the limiting melting point (T_∞ for n-alkane of infinite molecular weight) is 408.1°K, the limiting pour point was calculated by Eq. 8 to be 318°K or 112°F. The value of 112°F may be compared with the limiting pour points (p_∞) of 121°F and 119°F indicated by Equations 4 and 6, respectively. These limiting pour points of approximately 117°F are about 35° lower than the melting temperature (144-162°F) of poly(ethylene oxide) (6).

The viscosities (v) of the primary alcohol ethoxylates were found to be approximately linear with chain length:

$$v = -7.06081 + 1.37543y \tag{9}$$

(Correl. coeff., .996625)

The use of $y^{.9}$ instead of y, however, gave an equation having a slightly higher correlation coefficient (r):

$$v = -10.3273 + 2.08448y^{.9} \tag{10}$$

(Correl. coeff., .996771)

The following three additional equations were developed for elating chain length to viscosity:

$$y/(v + 11) = .556328 + .00371283y \tag{11}$$

(Correl. coeff., .995312

$$v = 262.053 - 41021.3/(y + 150) \tag{12}$$

(Correl. coeff., .996498)

$$v = -1633.18 + 705.998\log(y + 200) \tag{13}$$

(Correl. coeff., .996779)

In agreement with Smith (1), a logarithmic equation was found useful for calculating pour points (p) from viscosities:

$$p = -136.447 + 125.265\log v \tag{14}$$

(Correl. coeff., .989560)

The simple reciprocal equation also is suitable:

$$p = 127.701 - 3625.08/(v + 16) \tag{15}$$

(Correl. coeff., -.990230)

The following two equations employ chain lengths (y) as well as pour points (p, °F, and P, °K) and viscosities (v):

$$v = -12.1757 + 442.383\,y/P \tag{16}$$

(Correl. coeff., .996974)

$$p(y + 4) = -1085.96 + 86.8454\,v \tag{17}$$

(Correl. coeff., .993021)

Secondary Alcohol Ethoxylates

The secondary alcohol ethoxylates were found amenable to the techniques described above for the primary alcohol ethoxylates. Given below are equations relating chain lengths (y) to pour points (p, °F and P, °K):

$$p = 164.397 - 4549.44/(y - 2) \tag{18}$$

(Correl. coeff., -.998755)

$$p(y - 2) = -4878.23 + 164.397\,y \tag{19}$$

(derived from Eq. 18 above)

$$p = -204.644 + 180.467\log(y - 16) \tag{20}$$

(Correl. coeff., .998531)

$$y/P = .0434590 + .00248340\,y \tag{21}$$

(Correl. coeff., .998936)

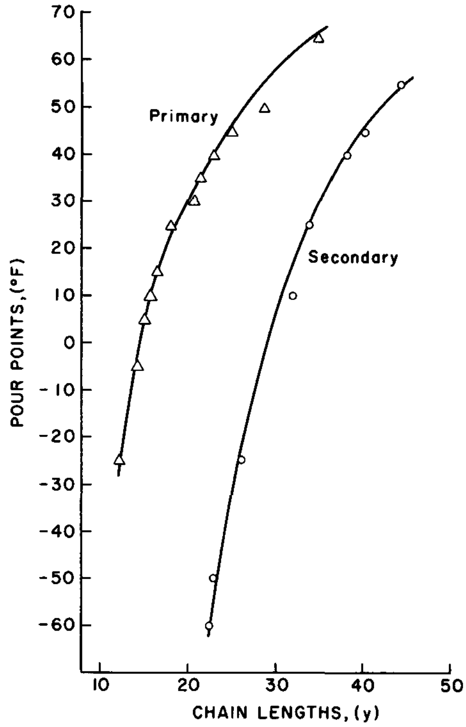

FIG. 1. Primary and secondary alcohol ethoxylates: relation of pour points, °F, to chain length, y.

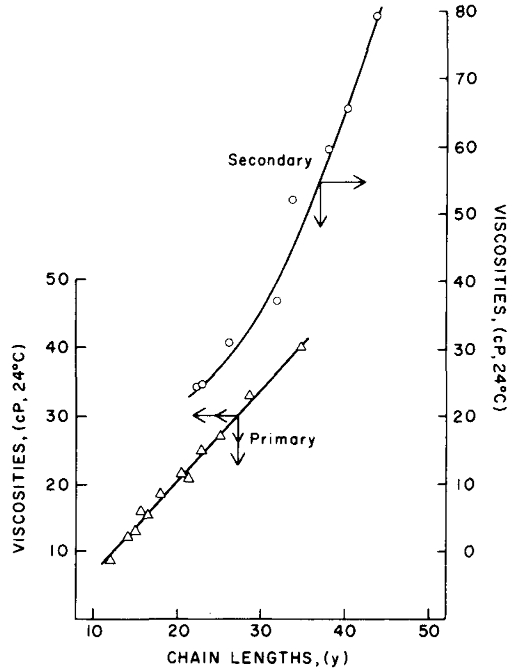

FIG. 2. Primary and secondary alcohol ethoxylates: relation of viscosities, cP, 24°C, to chain length, y.

The following equations may be used to relate viscosities (v) of the secondary alcohol ethoxylates to chain lengths (y):

$$v = -7.19485 + .291551\, y^{1.5} \tag{22}$$

(Correl. coeff., .996896)

$$v^{.7} = -3.18402 + .551866\, y \tag{23}$$

(Correl. coeff., .997096)

The following three equations relate pour points (p,°F) to viscosities (v):

$$p = -209.530 + 146.786 \log (v - 13) \tag{24}$$

(Correl. coeff., .996185)

$$p = 136.734 - 7519.35/(v + 15) \tag{25}$$

(Correl. coeff., .996273)

$$p(y - 2) = -3891.68 + 295.287\, v^{.7} \tag{26}$$

(Correl. coeff., .995864)

Eq. 26 is based on the fact that both p(y - 2) and $v^{.7}$ are linear with chain length (y).

By excluding the data for ethoxylates 1 and 8 (Table II), it was possible to derive a satisfactory two-parameter equation:

$$p = -358.544 + 222.808 \log v \tag{27}$$

(Correl. coeff., .997589)

When ethoxylates 1 and 8 were included, however, the correlation coefficient dropped from .997589 to .993587:

$$p = -361.123 + 222.892 \log v \tag{28}$$

(Correl. coeff., .993597)

As already indicated, the three parameter Eq. 24 is preferable to the two parameter Eq. 28 when all eight sets of data in Table II are included.

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