[CONTRIBUTION FROM EASTERN REGIONAL RESEARCH LABORATORY[1] AND TEMPLE UNIVERSITY]

Higher Alkyl Monoethers of Mono- to Tetraethylene Glycol[2a,b]

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The mono-*n*-dodecyl, tetradecyl, hexadecyl, and octadecyl ethers of mono- to tetraethylene glycol, $R(OCH_2CH_2)_iOH$, were synthesized from alkyl halides or tosylates or by alkali-catalyzed reaction of alcohols with ethylene oxide. In the dodecyl, tetradecyl, and hexadecyl series, freezing-point minima occurred at i = 3. The distribution of products in oxyethylation of tetradecanol followed the equations of Weibull and Nycander, with a distribution constant of 3.0.

In view of the industrial importance of mixtures of monoalkyl ethers of polyethylene glycol, it would be useful to have available individual members of this class. One objective of this investigation was therefore to synthesize the mono-*n*-dodecyl, tetradecyl, hexadecyl, and octadecyl ethers of mono- to tetraethylene glycol and to report their characterizing constants.

Some of the members of this group of sixteen compounds have been previously reported. The Williamson reaction has been used to prepare glycol ethers for nicotine synergism studies.[4] Ethylene glycol mono-*n*-dodecyl ether was synthesized from the alkyl bromide and glycol[5] and ethylene glycol mono-*n*-octadecyl ether from the alkyl tosylate.[6] More recently the stepwise synthesis of mono- to tetraethylene glycol mono-*n*-dodecyl ethers by the acid-catalyzed addition of ethylene oxide to the next lower homolog was reported.[7] Alkali-induced oxyethylation,[8,9,10] common for the preparation of adducts having various average degrees of polymerization, has been seldom employed for the preparation of individual glycol ethers.[11]

Three methods of synthesis were used in the present work: the alkyl halide and alkyl tosylate methods and the alkali-catalyzed oxyethylation of alcohols.

Distribution of Products. The distribution of products is a point of interest in reactions like oxyethylation. When polymer chains are built up ideally from a fixed number of propagating units by a sequence of kinetically identical additions of monomer, size distribution has been shown by Flory[12] to be described by Poisson's formula:[13]

$$\frac{n_i}{n_\infty} = e^{-\nu}\frac{\nu^i}{i!} \qquad (1)$$

Although the conditions producing Poisson distribution are indeed found in the reaction of ethylene glycol with ethylene oxide,[14] reactions in which all steps are kinetically different, as in the ammonia-ethylene oxide reaction and the chlorination of methane, require much more complicated mathematics, as shown by Natta and Mantica.[15]

Regarding the assumption of kinetic identity of all steps as an oversimplification and the formulas of Natta as very cumbersome, Weibull and Nycander[14] suggested a compromise treatment for the reaction of an alcohol with ethylene oxide. They proposed that all hydroxyl groups bound to an oxy-

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TABLE I

HIGHER *n*-ALKYL MONOETHERS OF MONO- TO TETRAETHYLENE GLYCOL

Glycol monoether	Method of preparation[a]	Yield %	B.P.	Mm.	F.P.	n^t_D	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
$C_{12}H_{25}OC_2H_4OH$[c]	C	18	137	2.2	20.3	1.4435^{25}	72.98	72.93	13.13	13.29
$C_{12}H_{25}O(C_2H_4O)_2H$[d]	B	80	127	0.010	19.0	1.4462^{25}	70.02	69.58	12.49	12.54
$C_{12}H_{25}O(C_2H_4O)_3H$[e]	B	62	153	0.035	17.2	1.4487^{25}	67.88	67.91	12.03	12.21
$C_{12}H_{25}O(C_2H_4O)_4H$[d]	B	78	166	0.02	20.5	1.4507^{25}	66.25	66.13	11.68	11.82
$C_{14}H_{29}OC_2H_4OH$	C	16	132	0.020	31.7	1.4330^{60}	74.36	74.49	13.26	13.22
$C_{14}H_{29}O(C_2H_4O)_2H$	B	80	146	0.02	28.5	1.4352^{60}	71.47	71.66	12.66	12.92
$C_{14}H_{29}O(C_2H_4O)_3H$	B	61	156	0.018	25.2	1.4373^{60}	69.31	69.11	12.22	12.15
$C_{14}H_{29}O(C_2H_4O)_4H$	B	70	183	0.018	28.5	1.4390^{60}	67.65	67.39	11.87	11.67
$C_{16}H_{33}OC_2H_4OH$	A	18	151	1.0	42.4–43.5[b]	1.4355^{60}	75.46	75.03	13.37	13.13
$C_{16}H_{33}O(C_2H_4O)_2H$	B	58	154	0.02	37.0	1.4373^{60}	72.67	72.86	12.81	12.74
$C_{16}H_{33}O(C_2H_4O)_3H$	B	63	172	0.013	30.5	1.4390^{60}	70.54	70.53	12.38	12.34
$C_{16}H_{33}O(C_2H_4O)_4H$	B	57	193	0.010	35.2	1.4407^{60}	68.85	69.08	12.04	12.27
$C_{18}H_{37}OC_2H_4OH$[f]	A	16	—	—	51.5–52.5[b]	1.4381^{60}	76.37	76.16	13.46	13.65
$C_{18}H_{37}O(C_2H_4O)_2H$	A	32	175	0.1	44.8–45.3[b]	1.4393^{60}	73.68	74.13	12.93	13.21
$C_{18}H_{37}O(C_2H_4O)_3H$	A	50	187	0.018	42.0	1.4407^{60}	71.59	71.51	12.52	12.78
$C_{18}H_{37}O(C_2H_4O)_4H$	B	76	214	0.05	40.8	1.4416^{60}	69.90	70.09	12.19	12.13

[a] A: etherification by *n*-alkyl *p*-toluenesulfonates; B: by alkyl bromides, C: by reaction of alcohols with ethylene oxide. [b] Melting points. [c–f] Previously reported: [c] Ref. 5, 7, 10, [d] Ref. 7, [e] Ref. 7, 10, [f] Ref. 6.

ethyl group have an equal ability to add ethylene oxide, differing, however, from that of the parent alcohol. This led to the following equations:

$$v = c \ln \frac{n_\infty}{n_0} - (c - 1)\left(1 - \frac{n_0}{n_\infty}\right) \quad (2)$$

$$\frac{n_i}{n_\infty} = \frac{c^{i-1}}{(c-1)^i}\left\{\frac{n_0}{n_\infty} - \left(\frac{n_0}{n_\infty}\right)^c \sum_{j=0}^{i-1} \times \frac{1}{j!}\left[(c-1)\ln\frac{n_\infty}{n_0}\right]^j\right\} \quad (3)$$

where

N_i = molecule with i added ethylene oxide molecules
m = number of moles of ethylene oxide consumed
n_∞ = number of moles of starting alcohol
n_0 = number of moles of surviving starting alcohol
n_i = number of moles of N_i in reaction product
k_i = velocity constant for reaction of N_i with ethylene oxide
k_0 = velocity constant for reaction of starting alcohol with ethylene oxide
c = k_i/k_0 = distribution constant
v = m/n_∞ = average number of moles of ethylene oxide per mole of starting alcohol

For the alkali-catalyzed reactions of ethylene glycol and of ethanol with ethylene oxide they found distribution constants c of 1 and 2.2 respectively.

Fractional distillation performed in the present preparation of ethylene glycol monotetradecyl ether provided data on the distribution of products for comparison with those required by the Poisson and the Weibull-Nycander equations.

EXPERIMENTAL

Materials. Good commercial grades of 1-dodecanol, tetradecanol, hexadecanol, and octadecanol were purified by fractional distillation and crystallization. *n*-Octadecyl and *n*-hexadecyl *p*-toluenesulfonates were made by the tosyl chloride–pyridine method[16] from the alcohols. Eastman grade *n*-dodecyl, tetradecyl, hexadecyl, and octadecyl bromides were found to have satisfactory purities and were used without further purification. Mono- to tetraethylene glycols were fractionally redistilled, and middle fractions with satisfactory refractive indices were used in synthesis. Commercial ethylene oxide of stated 99.5% purity was used.

Etherification by means of tosylates. For four ether alcohols the method of Shirley, Zietz and Reedy[6] was employed except that a higher ratio of glycol to alkyl tosylate was used. For ethylene glycol mono-*n*-hexadecyl ether, di- and tri-ethylene glycol mono-*n*-octadecyl ether, 10 mol. of glycol were used per mole of tosylate; for ethylene glycol mono-*n*-octadecyl ether, 5 mol.

Etherification by means of alkyl bromides. The preparation of *tetraethylene glycol mono-n-octadecyl ether* will serve as an example. With stirring, under a blanket of nitrogen, 8.28 g. (0.36 g.-atom) of sodium was dissolved, one small piece at a time, in 583 g. (3 mol.) of tetraethylene glycol at about 100°. After immersion of the flask in a 140° bath, 100 g. (0.3 mol.) of *n*-octadecyl bromide was added during 40 min. with vigorous stirring. After 5.5 hr. at this temperature, the reaction mixture diluted with xylene was neutralized and washed five times with hot water. Vacuum distillation through a Vigreux column gave a 76% yield of tetraethylene glycol mono-*n*-octadecyl ether. As noted in Table I, ten ethers were prepared by this method. The method has since provided intermediates for the synthesis of individual ether alcohol sulfates.[17]

Etherification by reaction of alcohols with ethylene oxide. Ethylene glycol mono-n-tetradecyl ether. In a 1 l., three necked flask,[9] 1.06 g. of sodium was dissolved with heating at 80–185° under a nitrogen atmosphere in 428.76 g. (2 mol.) of *n*-tetradecanol. At a temperature of 170–175°, this solution was stirred in an atmosphere of ethylene oxide for 3 hr., when weight increase indicated the reaction of 92.9 g. of ethylene oxide, or 1.055 mol. of ethylene oxide per mole of tetradecanol.

The reaction mixture was neutralized with the calculated amount of concentrated hydrochloric acid, dried, and filtered to give a colorless liquid, 481.5 g. of which was vacuum distilled through a protruded packing column having about 35 theoretical plates.[18] Refractive indices at 60° were

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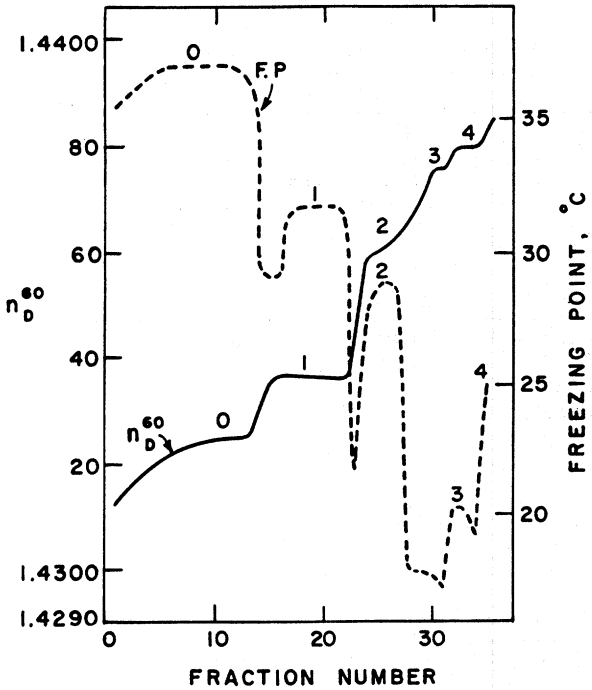

Fig. 1. Fractional distillation of oxyethylated tetradecanol (v = 1.055): refractive index and freezing point *vs* fraction number

measured on a refractometer having a precision of about 0.00003, and freezing points were measured in the cylindrical tubes used as fraction receivers.

From the curves of refractive index and freezing point plotted against fraction number (Fig. 1), fractions 16 to 22 were considered to be almost entirely ethylene glycol mono-*n*-tetradecyl ether, amounting to 74.7 g. (16% yield based on tetradecanol and adjusted for use of less than total reaction product in the distillation).

Distribution of products from oxyethylation. In order to examine the results of the reaction in the manner of Weibull and Nycander, it was first necessary to adjust the weights of reactants to reflect the fact that the fractional distillation was applied to 481.5 g. rather than to the entire reaction product, exclusive of sodium, of 521.7 g.

The weights (and number of moles) of the major components of the mixture resulting from oxyethylation of tetradecanol were estimated with the help of the plot of refractive index and freezing point *vs.* fraction number (Fig. 1). In general, the composition of intermediate fractions was estimated by interpolation of refractive indices; in a few cases assignments were somewhat arbitrary. The estimated amounts of uncombined tetradecanol and the mono-, di-, and triethylene glycol mono-*n*-tetradecyl ethers are collected in Table II.

The distribution constant c is calculated from both equation 2 (when it is designated c′) and from equation 3 (when designated c″). Thus, for v = 1.0549 and $n_0/n_\infty = 0.5183$, $c' = 3.2668 \simeq 3.27$.

For the calculation of c″, i is taken as having the value 1, and equation 3 reduces[19] to:

$$c'' = 1 + \frac{n_0}{n_1} - \frac{n_0}{n_1}\left(\frac{n_0}{n_\infty}\right)^{c''} - 1 \qquad (4)$$

which can be solved by successive approximations, as $c'' = 2.8186 \simeq 2.82$.

The values 3.27 for c′ and 2.82 for c″ suggest a mean value of about 3.0 for the distribution constant.

(19) B. Weibull, private communication.

TABLE II

COMPOSITION OF FRACTIONS: AMOUNT OF COMPONENTS, $RO(CH_2CH_2O)_iH$, INDICATED IN DISTILLATION OF TETRADECANOL–ETHYLENE OXIDE REACTION PRODUCT

	Fraction		Individual component, $RO(CH_2CH_2O)_iH$		
i	No.	Wt., g.	Wt., g.	n_i	n_i/n_∞
0	1–5	72.7	65.43		
	6–13	132.7	132.70		
	14	10.8	5.94		
	15	11.6	1.04		
				0.9568	0.5183
1	14	10.8	4.86		
	15	11.6	10.56		
	16–22	74.70	74.70		
	23	10.59	4.24		
	24	11.19	0.45		
				0.3669	0.1988
2	23	10.59	6.35		
	24	11.19	10.74		
	25–26	32.24	32.24		
	27	13.16	11.71		
	28	4.46	3.21		
	29	4.28	2.01		
	30	4.75	1.14		
	31	4.00	0.84		
				0.2256	0.1222
3	27	13.16	1.45		
	28	4.46	1.25		
	29	4.28	2.27		
	30	4.75	3.61		
	31	4.00	3.16		
	32–34	8.69	8.69		
	35	14.84	12.47		
				0.0949	0.0514
4	35	14.84	2.37		
	—	—	—		
				—	—

Using this value for c, a theoretical value of $\frac{n_0}{n_\infty} = 0.5062$ is found by successive approximation in equation 2, and is used in equation 3 to permit calculation of theoretical values of n_1/n_∞, n_2/n_∞, and n_3/n_∞ for inclusion in Table III.

DISCUSSION

Physical constants. The boiling points, freezing points, and refractive indices found for the sixteen ether alcohols synthesized in this study are collected in Table I.

In Fig. 2 the freezing points (in three cases the melting points) are plotted against the number of oxyethyl groups, i, added to a given alkyl group. In the dodecyl, tetradecyl, and hexadecyl series, minimum freezing points occur for the triethylene glycol derivative. The apparent leveling off in the plot of the octadecyl series suggests that a minimum freezing point in that series may occur at or shortly after the fourth member.

Solubility of the glycol monoethers. At the arbitrary ratio of 0.10 g. of glycol ether to 2.5 ml. of solvent, three typical products, glycol monooctadecyl, triglycol monotetradecyl, and tetraglycol monododecyl ether, were insoluble in water, both at room temperature and at 75°, but soluble in ben-

TABLE III

ALKALI-CATALYZED OXYETHYLATIONS OF FATTY ALCOHOLS, DISTRIBUTION OF COMPOUNDS IN REACTION PRODUCT

n-Fatty Alcohol:	Tetradecanol			Dodecanol	Hexadecanol
Wt., ROH, g.	395.72			369	112
Ethylene oxide, g.	85.74			101	60
Catalyst	0.978 g. Na			1.85 g. KOH	0.56 g. KOH
Temperature	170–175°			155–160°	130–150°
v	1.055			1.15	3.0
Experimental or Theoretical	Exptl.	Theoretical[a] WN	Theoretical[a] FP	Exptl.	Exptl.
n_0/n_∞	0.518	0.506	0.348	0.46	0.24
n_1/n_∞	0.199	0.188	0.367	0.21	
n_2/n_∞	0.122	0.150	0.194	—	
n_3/n_∞	0.051	0.090	0.068		
$\sum \frac{n_i}{n_\infty}$	0.890	0.934	0.977	0.67	0.24
$\sum \frac{in_i}{vn_\infty}$	0.566	0.717	0.909	0.18	0.000
c′	3.27			2.5	3.4
c″	2.82			2.5	
c		3.0	(1)	2.5	

[a] Theoretical distributions are calculated by Weibull-Nycander and by Flory-Poisson equations as indicated.

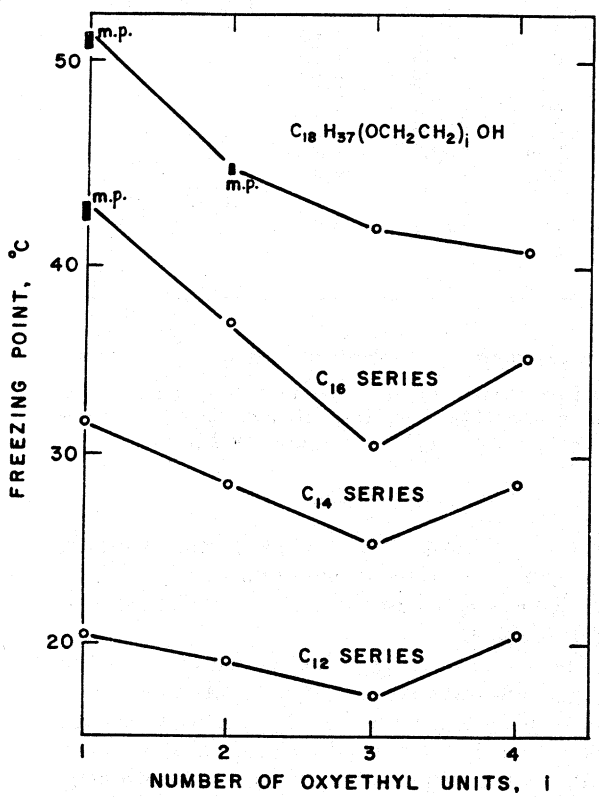

Fig. 2. Freezing points (or melting points, m.p.) of mono- to tetraethylene glycol mono-n-dodecyl, tetradecyl, hexadecyl, and octadecyl ethers

zene, carbon tetrachloride, and ethanol. In isooctane, clear solutions were obtained except for glycol monooctadecyl ether at room temperature and tetraglycol monododecyl ether at 75°.

Dilute mixtures (0.025 to 0.30%) of tetraethylene glycol monododecyl ether and water became clear when cooled to temperatures near 0°, and cloud points[20] of 9.5 to 5.2° were found. Clarification by cooling is probably related to the strengthening of hydrogen bonds between ether-alcohol and water.

Infrared spectra. Infrared spectra of the sixteen mono- to tetraethylene glycol monoethers synthesized in this study possessed major bands corresponding to the structures expected and found in related work.[7]

By dipole measurements evidence has been adduced for the coexistence of both *trans* and *gauche* forms of mono- to heptaethylene glycol,[21] and Kuroda and Kubo[22,23] have reported that certain infrared bands between 800 and 1000 cm.$^{-1}$ (measured on the pure liquids) reflect these *trans* and *gauche* conformations. A comparison made in Table IV of values from the work cited and appropriate spectra of the present glycol monododecyl ether series suggests that these ethers also exist in the liquid state in both *gauche* and *trans* conformations.

Distribution of products from oxyethylation. It is evident from Table III and Fig. 3, that there is disagreement between the experimental distribution of products from the alkali-catalyzed oxyethylation of tetradecanol to an average of 1.055 oxyethyl groups and the Flory-Poisson distribution calculated for the same degree of polymerization. Whereas the Poisson formula predicts slightly more

(20) J. M. Cross, *Proc. Chem. Specialties Mfrs. Assoc.*, 135 (June, 1950).

(21) T. Uchida, Y. Kurita, N. Koizumi, and M. Kubo, *J. Polymer Sci.*, 21, 313 (1956).

(22) Y. Kuroda and M. Kubo, *J. Polymer Sci.*, 26, 323 (1957).

(23) Y. Kuroda and M. Kubo, *J. Polymer Sci.*, 36, 453 (1959).

TABLE IV

COMPARISON OF SPECTRAL BANDS DUE TO CH_2 ROCKING FREQUENCIES OF MONO- TO TETRAETHYLENE GLYCOL[a] WITH BANDS FOUND IN INFRARED SPECTRA OF THE CORRESPONDING MONO-*n*-DODECYL ETHERS (LIQUID STATE)[b]

	Gauche Form		Trans Form	
i	A	B	A_u	B_g
$H(OCH_2CH_2)_iOH$[a]				
1	—	883	863	—
2	922	896	816	1000
3	934	888	830	1000
4	942	889	831	1000
(7)	(947)	(887)	(844)	(1000)
$n\text{-}C_{12}H_{25}(OCH_2CH_2)_iOH$				
1	920[c]	894	865[c]	—
2	935	890	830[d]	—
3	937	888	844[c]	(—)
4	940	885	841[d]	1000[c]

[a] Data of Kuroda and Kubo.[22] [b] Frequencies given in cm.$^{-1}$. [c] Shoulder. [d] Weak.

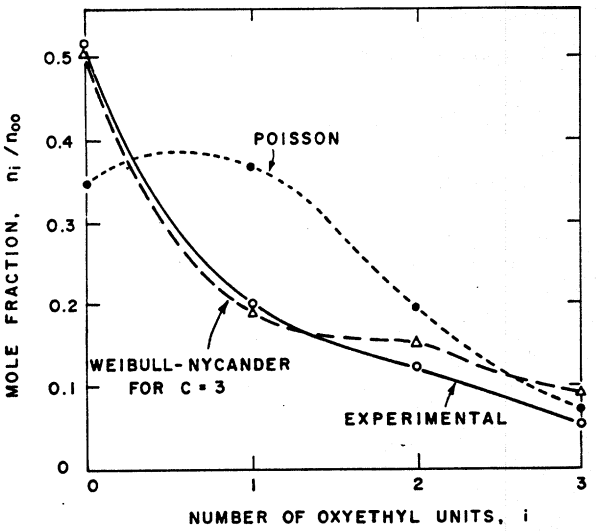

Fig. 3. Experimental distribution of products in oxyethylation of tetradecanol to v = 1.055 compared with theoretical Poisson distribution and with Weibull-Nycander distribution calculated for c = 3

ethylene glycol monotetradecyl ether than recovered parent alcohol, there was actually found over 50 mole per cent of the parent and only 20 mole per cent of the first glycol ether.

Treated in the Weibull-Nycander way, the experimental results suggest distribution constants c′ and c″ of 3.27 and 2.82. The experimental distribution agrees fairly well with a theoretical Weibull-Nycander distribution calculated for c = 3.0. The agreement is good for $i = 0$ and 1 and, though less close, still fairly satisfactory at $i = 2$ and 3. Excessive pot temperatures in the equipment employed prevented continuing the distillation much into the $i = 4$ region.

The sum of experimental values of n_i/n_∞ for $i =$ 0 to 3 amounts to 0.89, whereas theoretical recovery at the same stage would be 0.93 if calculated by the Weibull-Nycander equations and 0.98 by the Poisson formula. For the sum of values of in_i/vn_∞ the experimental is again closer to the Weibull-Nycander than to the Poisson total. Discrepancies, magnified in this second test, may reflect incomplete recovery of derivatives having $i = 2$ and 3. In spite of the imperfections noted, it seems reasonable to recognize a Weibull-Nycander distribution and to accept a distribution constant in the neighborhood of 3 for the alkoxide-catalyzed reaction of tetradecanol with ethylene oxide under the conditions employed.

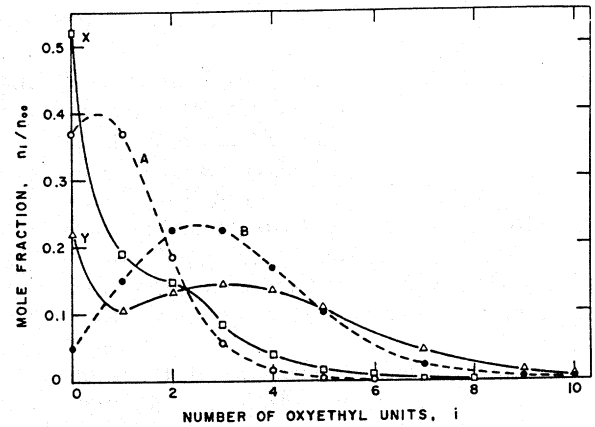

Fig. 4. Theoretical distribution of products of oxyethylation calculated by equations of Weibull and Nycander for c = 3, and v = 1 (solid curve X) or 3 (solid curve Y). Dotted curves A and B show distributions required by Flory-Poisson equation for v = 1 or 3

For comparative purposes the table lists some data available from distillations incidental to the preparation of ethylene glycol mono-*n*-dodecyl ether and of a parent-alcohol-free oxyethylate of *n*-hexadecanol. The indicated distribution constants of 2.5 and 3.4 support the order of magnitude found for the tetradecanol experiment.

Flory-Poisson distribution has been found valid for oxyethylation of ethylene glycol,[14] phenols,[24,25] and stearic acid,[26] in the last two cases because of the preferential combination of the parent compound with ethylene oxide before significant further reaction of the ether alcohols.[9,27] The present results indicate, however, that oxyethylation of long-chain primary alcohols results in Weibull-Nycander distribution as established for ethanol[14] rather than Poisson distribution as assumed for lauryl alcohol.[28]

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(28) J. V. Karabinos and E. J. Quinn, *J. Am. Oil Chemists' Soc.*, **33**, 223 (1956).

Comparison of theoretical Weibull-Nycander and Poisson distributions. It is of interest, therefore, to compare, in Fig. 4, theoretical distributions calculated by the two methods at degrees of oxyethylation of 1 and 3. In a Poisson distribution (c by definition equal to 1), even at v = 1 the predicted fraction of surviving parent compound (n_0/n_∞) is no higher than that of any oxyethylated derivative. In fact, on passing to v = 3, n_0/n_∞ is smaller than n_{1-5}/n_∞.

By contrast, Weibull-Nycander distribution (with c = 3, let us say) requires that the fraction of surviving alcohol in each case exceed that of any oxyethylated descendant. The maxima of the curves are broader and weaker than for the Poisson forula. There are minima, or a tendency toward a minimum, at $i = 1$, reflecting the preferential consumption of the oxyethylated derivatives compared to the parent alcohol.

Acidity and Nucleophilicity. In alkaline-catalyzed reactions the distribution constant has been regarded as the product of two factors, one measuring the acidity of the derivative hydroxyl groups compared to the parent, the other, the relative reactivity of derivative and parent anions toward ethylene oxide.[14] Ethoxyethanol has been shown to have a relative acidity of 12 compared to 0.95 for ethanol.[29] A reversal of the order of relative nucleophilic reactivities of derived and parent anions is to be expected, and initial rates of oxyethylation were indeed higher for ethanol than for ethoxyethanol.[14] Preliminary attempts by the present authors to measure the separate oxyethylation reactivities of dodecanol and diethylene glycol monododecyl ether, catalyzed by potassium alkoxide at 120°, suggest a ratio of 1.5 to 1 in favor of the former.

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