ANALYSIS AND MOLAR MASS DISTRIBUTION OF POLYOXYETHYLENE 4-ALKYLPHENYLAMINES

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(First received June 17th, 1988; revised manuscript received August 19th, 1988)

SUMMARY

Polyoxyethylene 4-alkylphenylamines having from 1 to 16 carbon atoms in their alkyl groups and average degrees of ethoxylation from 1 to 8 were analyzed by gas chromatography and distribution coefficients were computed. Successive homologues having different numbers of oxyethylene groups were separated according to their increasing molar masses. Arithmetic retention indices were determined for separated homologues and increments for characteristic molecular fragments were calculated. They are equal to 298 and 805 for the oxyethylene group and the benzene ring, respectively. Retention indices of polyoxyethylene 4-alkylphenylamines can be estimated from the appropriate increments with an error of about 10 units. The molar mass distribution for these compounds is between those obtained for polyoxyethylene alkylamines and polyoxyethylene alcohols.

INTRODUCTION

4-Alkylphenylamines are known as extractants for noble metals[1,2]. They were also used as intermediates to obtain quaternary ammonium salts[3] and polyoxyethylene 4-alkylphenylamines[4,5]. These last surfactants were obtained in the reaction of 4-alkylphenylamines with ethylene oxide:

$$R-\!\!\left\langle\!\bigcirc\!\right\rangle\!\!-NH_2 \ + \ (n+m)\,CH_2\!\!-\!\!CH_2 \longrightarrow R-\!\!\left\langle\!\bigcirc\!\right\rangle\!\!-N\!\!\begin{array}{c}(CH_2CH_2O)_nH \\ (CH_2CH_2O)_mH\end{array} \tag{1}$$

They are polydisperse mixtures and contain successive homologues having various numbers of oxyethylene groups.

The molar mass distribution of typical non-ionic surfactants, *i.e.*, polyoxyethylene alcohols and polyoxyethylene alkylphenols, was discussed in several independent

papers and different models were proposed to calculate the molar fractions of successive homologues[6-10]. Recently, a general and mathematically improved computing technique was used and molar mass distributions were computed for polyoxyethylene alcohols and polyoxyethylene alkylphenols and also for typical polyoxyethylene alkylamines[11].

The aim of this work is to determine the composition of polyoxyethylene 4-alkylphenylamines and the retention indices of their successive homologues having different numbers of oxyethylene groups and to use these data to calculate the increments of the retention indices for characteristic molecular fragments and to compute the so-called distribution coefficients.

EXPERIMENTAL

Polydisperse polyoxyethylene 4-alkylphenylamines having 1, 6, 8, 10, 12 and 16 carbon atoms in their alkyl groups and average degrees of ethoxylation equal to 1, 3, 5 and 8 were used.

A gas–liquid chromatograph (Perkin-Elmer Model 900) with a flame ionization detector was used. The separation was carried out in stainless-steel columns (0.4 m × 2.7 mm I.D., 0.9 m × 2.7 mm I.D. or 1.8 m × 2.7 mm I.D.), Chromosorb G AW DMCS (60–80) mesh was used as the support and silicone resin OV-17 (3%) as the liquid phase.

Nitrogen was used as the carrier gas and its flow-rate was 20 cm^3/min. The analyses were started with a column temperature, depending on the product composition, of 80–170°C, which after 1 min of separation was increased at 6°C/min to 320°C, where it was maintained.

Trimethylsilyl derivatives were prepared in a glass microreaction vessel (capacity 3 cm^3) having a PTFE-lined cap (Supelco, Bellefonte, PA, U.S.A.). A sample of about 0.05 g was weighed and 0.5 cm^3 of N,O-bis(trimethylsilyl)acetamide (Applied Science Labs., State College, PA, U.S.A.) were added. The sealed reaction vessel was maintained at 70°C for 1 h and shaken from time to time.

The arithmetic retention indices[12] were determined for the homologues separated. The percentages of the components were calculated from the areas of their peaks, assuming correction coefficients of 1. The values of the peak resolutions were calculated according to

$$R = \frac{2(t_{R1} - t_{R2})}{w_1 + w_2} \tag{2}$$

where t_{R1} and t_{R2} denote the retention times of successive peaks and w_1 and w_2 the widths of these peaks measured at their bases.

RESULTS AND DISCUSSION

The chromatographic conditions were similar to those reported previously for polyoxyethylene alkylamines[14-16]. Under these conditions, successive homologues having different numbers of oxyethylene groups are eluted according to their increasing molar masses, and they can easily be identified by their retention indices.
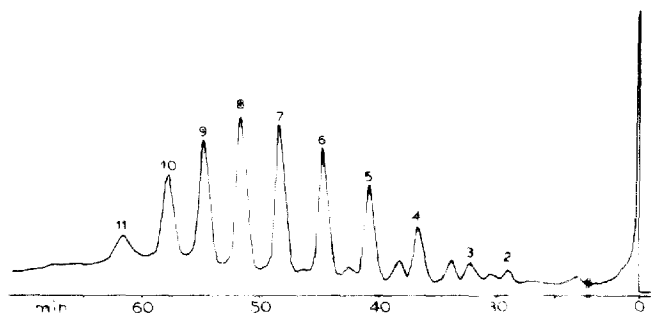
Fig 1 Chromatogram of polyoxyethylene 4-dodecylphenylamine Average degree of ethoxylation, 8; peak numbers denote oxyethylene groups present in the homologues separated.

Positional isomers having the same total number of oxyethylene groups but located in different ways in both the polyoxyethylene chains are not separated. An exemplary chromatogram of polyoxyethylene 4-dodecylphenylamine with an average degree of ethoxylation equal to 8 is shown in Fig. 1 The separation of polyoxyethylene 4-alkylphenylamines up to the homologues containing thirteen oxyethylene groups was achieved. Small peaks due to by-products. mainly polyoxyethylene glycols, are also observed between the main peaks of polyoxyethylene 4-alkylphenylamines.

The values of the arithmetic retention index for successive homologues of polyoxyethylene 4-alkylphenylamines and of the peak resolutions are given in Table I. The arithmetic retention index is linearly correlated with the number of oxyethylene groups. The slopes of such plots give the increments of the retention index per

TABLE I

ARITHMETIC RETENTION INDICES. I_A, AND PEAK RESOLUTIONS, R_s, FOR TRIMETHYL-SILYL DERIVATIVES

No of oxyethylene groups	Polyoxyethylene 4-alkylphenylamines					
	Methyl		Hexyl		Dodecyl	
	I_A	R_s	I_A	R_s	I_A	R_s
0	1390	—	1875		2480	—
1	1695	8.5	2170	5.6	2785	3.2
2	1955	6.7	2475	5.3	3080	3.6
3	2276	6.3	2780	5.0	3375	3.1
4	2584	5.2	3082	4.5	3670	2.6
5	2883	4.6	3380	3.6	3970	2.5
6	3180	4.2	3678	3.6	4265	2.4
7	3479	3.7	3975	2.1	4565	2.4
8	3770	3.4	4270	2.0	4860	1.7
9	4069	3.0	4565	2.0	5160	1.7
10	4366	2.6	4860	1.9	5455	1.5
11	4660	2.6	5155	1.7	5755	1.2
12	4960	2.4	5430	1.8	6050	1.3
13	5260	2.5	5750	1.7	6350	1.2

TABLE II

COMPOSITION OF POLYOXYETHYLENE 4-ALKYLPHENYLAMINES

In % (w/w); I and II denote the average degrees of ethoxylation and the number of oxyethylene groups, respectively.
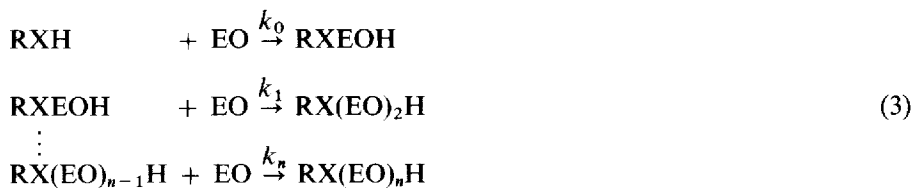
II	$n=1$						$n=3$						$n=5$						$n=8$					
	C_1	C_6	C_8	C_{10}	C_{12}	C_{16}	C_1	C_6	C_8	C_{10}	C_{12}	C_{16}	C_1	C_6	C_8	C_{10}	C_{12}	C_{16}	C_1	C_6	C_8	C_{10}	C_{12}	C_{16}
0	21.0	8.1	6.2	4.1	4.5	5.9	0	3.8	4.1	5.0	5.2	5.0	0	1.5	1.0	2.0	2.1	1.7	0	0	0	0	0	0
1	33.0	22.2	21.8	23.4	23.1	20.6	0	6.1	7.2	8.2	6.8	7.5	0	0.5	0.7	0.9	0.8	1.0	0	0.4	0.5	0.7	0.8	0.8
2	41.0	42.8	44.1	45.3	45.2	43.1	30.2	17.6	17.0	16.4	16.1	16.8	0.6	1.0	1.5	1.6	1.7	1.9	0	1.2	1.5	1.7	1.9	2.2
3		18.9	19.0	17.5	17.8	20.1	45.2	40.5	38.0	33.1	36.4	33.5	14.0	21.6	21.2	21.3	21.0	21.1	1.4	1.5	1.6	1.7	1.8	2.1
4							14.3	15.0	14.8	14.9	14.5	17.0	25.0	23.9	24.3	24.1	24.5	24.7	3.7	3.7	3.6	3.8	3.9	3.9
5							3.3	3.0	4.1	5.0	5.2	4.9	23.9	20.5	19.3	18.3	18.2	18.5	7.1	7.0	7.6	7.8	7.9	8.1
6							0	1.1	0.8	1.5	0	0.3	16.4	10.3	11.9	10.8	10.6	10.3	10.1	10.9	11.2	11.8	12.1	11.7
7													15.9	6.8	5.6	5.2	5.1	5.0	5.0	14.1	14.1	13.9	13.4	13.6
8													5.7	3.0	2.5	2.5	2.6	2.2	15.1	14.8	14.1	14.7	14.3	14.5
9													2.2	0.5	0.5	0.9	0.8	1.0	12.5	14.1	14.1	14.2	14.0	13.9
10													0.5	0.5	0.3				10.0	13.5	13.3	13.2	13.4	13.1
11																			8.6	4.3	2.0			
12																			3.8	2.1	1.9			
13																			1.0	0.9	0			
Other	4.9	8.0	7.9	9.7	9.4	10.3	9.0	12.9	14.0	15.9	15.8	15.0	5.8	9.9	11.7	12.4	12.6	12.6	12.6	12.5	14.7	16.7	16.5	16.1

oxyethylene group. The following values of this increment were obtained: 297.7, 298.1 and 297.6 for polyoxyethylene 4-alkylphenylamines having 1, 6 and 12 carbon atoms in the alkyl group, respectively. Thus, the average value is approximately equal to 298 and agrees well with the increment obtained previously for polyoxyethylene alkylamines ($\Delta I_A = 299$)[16]. Arithmetic retention indices of polyoxyethylene 4-hexylphenylamines are about 796–816 units higher than those obtained previously for polyoxyethylene hexylamines. These differences are equal to 816, 805, 808, 807, 806, 804, 800 and 796 for appropriate homologues having 2, 3, 4, 5, 6, 7, 8 and 9 oxyethylene groups, respectively. Thus, the aromatic ring increases the retention index by about 805 units, and this effect does not depend upon the length of the polyoxyethylene chain. The increments previously determined[16] can also be used to predict the values of the retention index for polyoxyethylene 4-alkylphenylamines. The average error of such an estimation is equal to 11 units, and only in one case does the error exceed 20 units.

The peak resolutions are similar to those reported previously for other groups of non-ionic surfactants[17]. They decrease as the lengths of the polyoxyethylene chain and/or of the alkyl group increase.

The contents of the successive homologues in the products analyzed are given in Table II. They were used as initial data for further computing of the distribution coefficients. The contents of other compounds, mainly polyoxyethylene glycols, which are eluted between the main peaks, are also given in Table II. Quite significant amounts of these compounds are formed and their contents increase in a typical way as the average degree of ethoxylation increases. Polyoxyethylene 4-alkylamines obtained from 4-methylphenylamine contain less polyoxyethylene glycols in comparison to products obtained from 4-alkylphenylamines containing from 6 to 16 carbon atoms in their alkyl groups.

The reaction between an initial 4-alkylphenylamine (RXH) and ethylene oxide (EO) can be described as follows

$$RXH \quad + EO \overset{k_0}{\rightarrow} RXEOH$$

$$RXEOH \quad + EO \overset{k_1}{\rightarrow} RX(EO)_2H \quad\quad (3)$$

$$\vdots$$

$$RX(EO)_{n-1}H + EO \overset{k_n}{\rightarrow} RX(EO)_nH$$

where k_0, k_1, ... k_n denote the rate constants for the successive steps of the process, X denotes N or NH and R a 4-alkylphenyl group.

The abbreviations used for 4-alkylphenylamine and its polyoxyethylene derivatives are the same as those used in our previous work[11] on polyoxyethylene alcohols, alkylphenols and alkylamines. This is possible because positional isomers having the same total number of oxyethylene groups but different distributions in the two polyoxyethylene chains are not separated, and consequently, they are not taken into consideration. In this case X denotes NH in 4-alkylphenylamines, 4-alkylphenyl-2-hydroxyethylamine and in some higher homologues having only one polyoxyethylene chain, while X is N in those typical homologues having two polyoxyethylene chains.

TABLE III

DISTRIBUTION COEFFICIENTS

Alkyl	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}	C_{11}	C_{12}	Correlation coefficient
CH_3	–	0.564	0.567	0.701	0.874	0.725	0.738	0.712	0.710	0.383	0.224	–	0.99
C_6H_{13}	1.345	1.133	0.750	0.976	0.957	0.974	0.892	0.844	0.715	0.349	0.544	0.401	0.91
C_8H_{17}	1.165	1.043	0.726	1.009	0.936	0.987	0.884	0.803	0.333	0.404	0.863	–	0.88
$C_{10}H_{21}$	1.772	1.697	0.773	0.840	0.818	0.808	0.820	0.708	0.492	–	–	–	0.93
$C_{12}H_{25}$	1.982	1.666	0.738	0.827	0.812	0.796	0.829	0.726	0.505	–	–	–	0.92
$C_{16}H_{33}$	1.252	1.044	0.786	0.925	0.903	0.902	0.872	0.748	0.519	–	–	–	0.86
Average	1.503	1.317	0.755	0.915	0.885	0.893	0.859	0.766	0.512	0.151	0.281	0.080	0.89

By using the computing method previously described by us[11], the distribution coefficients $c_1 = k_1/k_0$, $c_2 = k_2/k_0$, ..., $c_n = k_n/k_0$, defined as the ratio of the successive rate constants to the rate constant of the first step, were determined (Table III). They demonstrate that results obtained for polyoxyethylene 4-methylphenyl-amines differ from those obtained for polyoxyethylene 4-alkylphenylamines having long alkyl groups (C_6–C_{16}). The distribution constants are of similar order and a sharp decrease is observed between homologues containing 8 and 9 oxyethylene groups in polyoxyethylene 4-alkylphenylamines having from 6 to 16 carbon atoms in the alkyl groups. This clearly demonstrates that homologues having 9 or more oxyethylene groups are not eluted completely from the chromatographic column. Thus, their actual contents are higher than those given in Table II.

The correlation coefficients are approximately 0.9 and the value of 0.99 was obtained only for polyoxyethylene 4-methylphenylamines. This means that some important deviations of the computed values from those experimentally determined are observed for polyoxyethylene 4-alkylphenylamines having from 6 to 16 carbon atoms in their alkyl groups. This is not caused by the errors of the chromatographic analysis, the accuracy and precision of which are the same as in analyses of other non-ionic surfactants[18]. This is a result of some differences observed in the reaction course during the syntheses of polyoxyethylene 4-alkylphenylamines.

The molar mass distribution of the successive homologues for polyoxyethylene 4-octylphenylamines is presented in Fig. 2. The numbers on the curves denote the total numbers of oxyethylene groups present in the homologue considered. Similar distributions were obtained for other products although the concentrations of the individual homologues were somewhat different.

They demonstrate that the content of 4-alkylphenylamine does not decrease so quickly to zero as in the case of polyoxyethylene alkylamines, and small amounts of it are observed in the products having an average degree of ethoxylation equal to 6. As a result, it is impossible to obtain almost pure 4-alkylphenyldi(2-hydroxyphenyl)-amines as in the case of alkylamines. This is caused by the low basicity of the nitrogen atom in 4-alkylphenylamines and, as a result, by the relatively low reaction rates of the first two steps leading to the formation of 4-alkylphenyl(2-hydroxyethyl)amine and 4-alkylphenyldi(2-hydroxyethyl)amine.
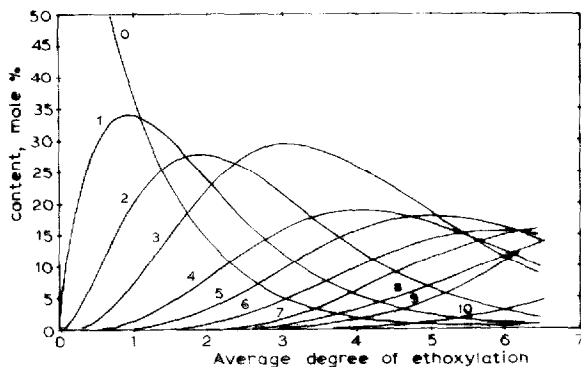

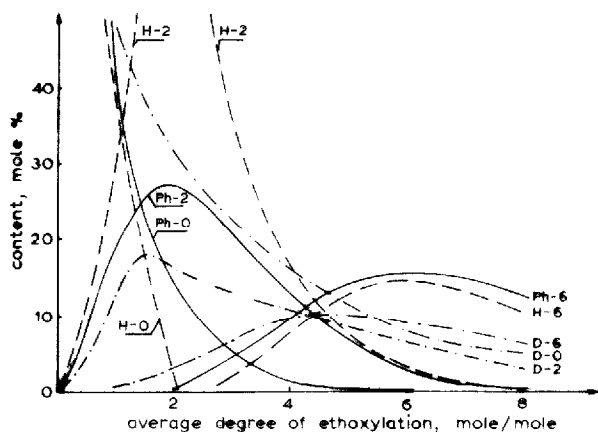Fig. 2. Molar mass distribution for polyoxyethylene 4-octylphenylamines.

Fig. 3. Comparison of molar mass distributions for polyoxyethylene 4-octylphenylamines (Ph-0, Ph-2 and Ph-6), polyoxyethylene hexylamines (H-0, H-2 and H-6) and polyoxyethylene dodecanol (D-0, D-2 and D-6). Numbers denote the numbers of oxyethylene groups in the homologues considered.

The distribution of the successive homologues is also different in comparison to polyoxyethylene alcohols, as is demonstrated in Fig. 3. The content of 4-alkylphenyl-amine (Ph-O) decreases more quickly than that of dodecanol (D-O), but more slowly than that of hexylamine (H-O). The content of 4-alkylphenyldi(2-hydroxyethyl)amine (Ph-2) never reaches the high value of alkyldi(2-hydroxyethyl)hexylamine (H-2) but is higher than that of the appropriate analogue of dodecanol having two oxyethylene groups (D-2). Thus, the molar mass distribution of polyoxyethylene 4-alkylphenyl-amines is between those reported previously for polyoxyethylene alkylamines and polyoxyethylene alcohols[11].

CONCLUSIONS

Successive homologues of polyoxyethylene 4-alkylphenylamines having differ-ent numbers of oxyethylene groups can be separated according to their increasing molar masses and their contents can be determined by gas chromatography. The separations are similar to those reported previously for other groups of non-ionic surfactants having polyoxyethylene chains. The retention index increments are similar to those obtained previously for polyoxyethylene alkylamines. Those for the polyoxyethylene group and the aromatic benzene ring are equal to 298 and 805, respectively. Retention indices of polyoxyethylene 4-alkylphenylamines can be estimated from the appropriate increments with an error of about 10 units. The molar mass distribution of polyoxyethylene 4-alkylphenylamines is between those reported previously for polyoxyethylene alkylamines and polyoxyethylene alcohols.

ACKNOWLEDGEMENT

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