MEASUREMENT OF THE POLARITY OF ALKYL DERIVATIVES OF DIAZAPOLYOXYETHYLENE ETHERS BY GAS CHROMATOGRAPHY

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SUMMARY

The polarity of alkyl derivatives of diazapolyoxyethylene ethers determined by gas chromatography was investigated. The influence of the structure of isomeric compounds on their polarity is discussed. It was found that the polarity depends on the lengths of the alkyl and polyoxyethylene chains, on the distribution of carbon atoms in alkyl groups linked with the nitrogen and oxygen atoms and the distribution of oxyethylene groups.
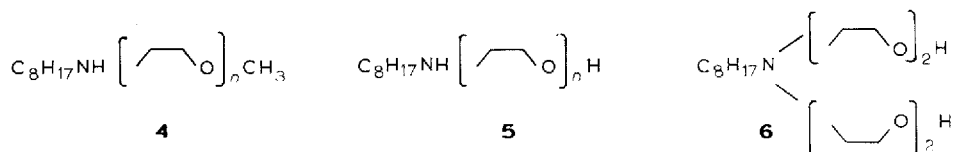
INTRODUCTION

The polarities of individual compounds containing one nitrogen atom[1,2] and of α,ω-diamino oligoether derivatives were studied previously[3]. The relationships between different polarity parameters and the increments of the polarity due to characteristic structural fragments were calculated.

The aim of this work was to examine the influence of the structure of alkyl derivatives of diazapolyoxyethylene ethers, which contain two nitrogen atoms bridged by an oligooxyethylene chain or by two methylene groups. The structures of investigated compounds are as follows:
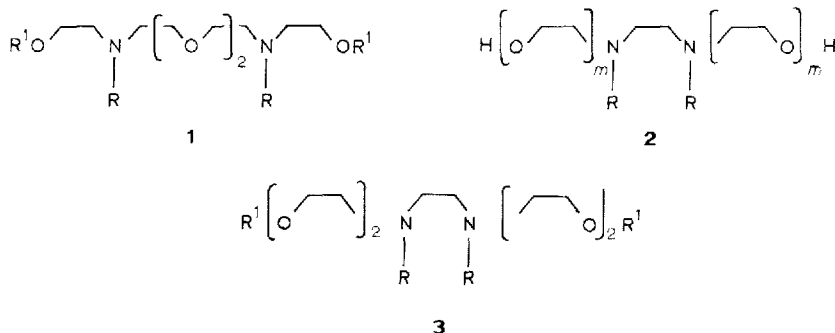
where R and R^1 denote alkyl groups (CH_3–C_8H_{17}) or hydrogen (R^1) and $m = 0, 1$ or 2.

The polarities of some individual octylaminooligooxyethylene methyl ethers (4) and octylamino N-mono- (5) and N,N-dioligooxyethylene glycols (6):

$$C_8H_{17}NH \left[\diagup \diagup \diagdown O \right]_n CH_3 \qquad C_8H_{17}NH \left[\diagup \diagup \diagdown O \right]_n H \qquad C_8H_{17}N \diagup \left[\diagup \diagdown O \right]_2 H \diagdown \left[\diagdown \diagup O \right]_? H$$

$$\textbf{4} \qquad\qquad\qquad \textbf{5} \qquad\qquad\qquad \textbf{6}$$

where $n = 1, 2$ or 3, were also determined.

Some of the compounds examined in this work have also been tested as crown ether analogues for the extraction of alkaline earth metals[4] and for mercury(II) chloride extraction[4-6].

EXPERIMENTAL

Eighteen pure model compounds (Table I) were used for polarity measure-

TABLE I

STRUCTURES OF AND PHYSICAL DATA FOR ALKYL DERIVATIVES OF DIAZAPOLYOXY-ETHYLENE ETHERS AND OF OXYETHYLENE OCTYLAMINES

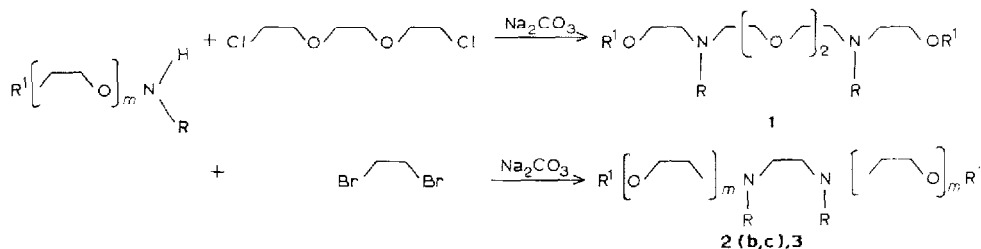| Compound	R	R'	m	n	B.p. ($^\circ C/mmHg$)	n_D^{20}
1a	C_8H_{17}	H	—	—	226–230/0.05	1.4677
1b	C_8H_{17}	CH_3	—	—	210–214/0.01	1.4578
1c	C_4H_9	C_4H_9	—	—	203/0.01	1.4524
1d	CH_3	C_8H_{17}	—	—	214/0.02	1.4548
1e	C_6H_{13}	C_2H_5	—	—	190–198/0.01	1.4533
2a	C_8H_{17}	—	0	—	150–152/0.01	—
2b	C_8H_{17}	—	1	—	196–198/0.01	1.4691
2c	C_8H_{17}	—	2	—	220–224/0.01	1.4701
3a	C_8H_{17}	CH_3	1	—	176–178/0.01	1.4551
3b	C_8H_{17}	CH_3	2	—	205–210/0.01	1.4561
3c	CH_3	C_8H_{17}	2	—	208–210/0.01	1.4560
3d	C_4H_9	C_4H_9	2	—	185–190/0.01	1.4526
4a	—	—	—	1	120/15	1.4342
4b	—	—	—	2	113–115/0.5	1.4395
5a	—	—	—	1	87–88/0.2*	1.4526
5b	—	—	—	2	108/0.05**	1.4538**
5c	—	—	—	3	170–172/0.01***	1.4568***
6	—	—	—	2*2	175–177/0.1§	1.4654§

    * B.p. 85–87°C/0.09 mmHg[9].
  ** B.p. 130–135°C/90 Pa; $n_D^{20} = 1.4540$[10].
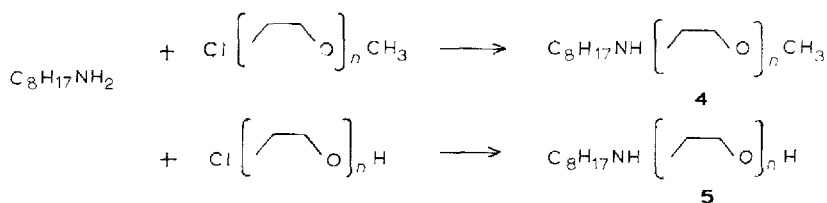 *** B.p. 190–195°C/0.06 mmHg; $n_D^{20} = 1.4644$[9].
   § B.p. 226–232°C/0.03 mmHg; $n_D^{20} = 1.4662$[9].

ments. They were obtained by treating the required amino alcohol derivatives in the presence of sodium carbonate with 1,8-dichloro-3,6-dioxaoctane for compounds 2b, 2c and 3:

$$R^1 \left[\diagup\diagdown O \right]_m N \diagdown^H_R + Cl\diagup\diagdown O\diagup\diagdown O\diagup\diagdown Cl \xrightarrow{Na_2CO_3} R^1 O\diagup\diagdown N \diagdown \left[\diagdown O\diagup \right]_2 \diagdown N \diagup\diagdown OR^1$$

1

$$+ \quad Br\diagup\diagdown Br \xrightarrow{Na_2CO_3} R^1 \left[O\diagup\diagdown \right]_m N \diagdown\diagup N \left[\diagup\diagdown O \right]_m R^1$$

2 (b,c),3

In the same way, 6 was obtained from octylamine and 2-chloroethyl-2-hydroxyethyl ether.

Compounds 4 and 5 were prepared according to known methods by reaction of the appropriate 2-chloroethyl ethers or 2-chloroethyl alcohols with an excess of octyl-amine:

$$C_8H_{17}NH_2 + Cl\left[\diagup\diagdown O\right]_n CH_3 \longrightarrow C_8H_{17}NH\left[\diagup\diagdown O\right]_n CH_3$$

4

$$+ Cl\left[\diagup\diagdown O\right]_n H \longrightarrow C_8H_{17}NH\left[\diagup\diagdown O\right]_n H$$

5

Analogous 2a was obtained by treating 1,2-dibromoethane with an excess of octyl-amine.

The reaction conditions were as described previously[4–6].

The purities and structures of all the compounds were confirmed by elemental analyses, ^{1}H NMR spectroscopy and gas–liquid and thin-layer chromatography. ^{1}H NMR spectra were recorded on a Tesla BS 487B 80 MHz instrument using [^{2}H]chloroform as solvent and HMDS as the internal standard. The structures and some physical data are given in Table I.

Chromatographic measurements

The conditions of the chromatographic measurements and the parameters used for the characterization of the polarities of the compounds have been reported previously[3].

RESULTS AND DISCUSSION

The values of the polarity parameters are given in Tables II–IV (compound numbering as in Table I). The precision of the determination of the polarity param-

TABLE II

EMPIRICAL POLARITY PARAMETERS

Compound	Temperature ($^\circ C$)	I_R		PI		ρ	
		CH_3OH	C_2H_5OH	CH_3OH	C_2H_5OH	CH_3OH	C_2H_5OH
1a	70	700	726	96.4	101.0	2.29	2.84
	90	688	708	94.1	97.8	1.94	2.25
1b	70	716	753	99.4	105.4	2.61	3.53
	90	721	751	99.3	105.2	2.45	3.06
1c	70	710	745	98.1	104.0	2.49	3.32
	90	721	748	100.2	104.7	2.48	3.04
1d	70	605	642	73.2	83.5	1.05	1.43
	90	604	634	72.6	81.4	1.03	1.29
1e	70	729	769	101.3	107.2	2.85	3.87
	90	740	775	103.5	108.7	2.83	3.65
2a	70	619	651	77.2	85.7	1.18	1.55
	90	621	642	77.8	83.8	1.18	1.40
2b	70	688	713	94.0	98.8	2.09	2.57
	90	690	700	94.6	96.4	2.00	2.15
2c	70	709	731	97.7	101.9	2.43	3.21
	90	711	730	98.4	101.8	2.26	2.60
3a	70	683	704	92.2	98.8	2.02	2.53
	90	681	701	91.8	97.4	2.00	2.13
3b	70	709	737	98.4	103.3	2.48	3.13
	90	686	740	93.3	103.1	1.91	2.86
3c	70	703	732	96.9	101.9	2.38	3.02
	90	705	722	97.2	100.3	2.23	2.54
3d	70	631	665	80.8	89.2	1.29	1.72
	90	630	655	80.6	86.8	1.26	1.52
4a	70	698	729	96.1	102.1	2.41	3.29
	90	677	703	94.6	99.2	1.98	2.47
4b	70	714	757	99.0	106.0	2.64	3.78
	90	704	742	97.1	103.7	2.23	2.98
5a	70	710	749	98.5	105.0	2.67	3.74
	90	694	742	95.5	104.1	2.15	3.15
5b	70	749	800	106.0	112.4	3.94	5.12
	90	744	799	102.7	111.7	3.86	4.93
5c	70	803	838	112.5	116.9	5.03	6.66
	90	797	829	111.8	115.9	4.12	5.02
6	70	778	823	109.1	115.3	4.16	6.01
	90	771	809	106.7	111.8	3.99	5.83

eters is good and similar to that reported in earlier studies[2,7,8]. The relationships between polarity parameters are similar to those presented previously[2,7,8].

As previously[2,3,7,8], linear relationships were observed between the examined polarity parameters and the sum of the first five McReynolds constants (Table V). The regression coefficients are not high but are still acceptable. These relationships indicate that the polarity parameters considered adequately describe solute–solvent intermolecular interactions.

The polarities of the investigated compounds depend significantly on their

TABLE III

THERMODYNAMIC POLARITY PARAMETERS

Compound	ΔG_s^m (OH) (kJ mol^{-1})		ΔG_s^m (C=O) (kJ mol^{-1})	
	CH_3OH	C_2H_5OH	2-Butanone	2-Pentanone
1a	− 10.9	− 9.2	− 9.3	− 9.0
1b	− 11.2	− 9.7	− 9.7	− 9.3
1c	− 11.3	− 9.7	− 9.2	− 8.9
1d	− 9.9	− 8.4	− 8.2	− 7.8
1e	− 11.9	− 10.4	− 9.5	− 9.0
2a	− 10.0	− 8.2	− 7.5	− 7.2
2b	− 10.7	− 9.0	− 8.9	− 8.6
2c	− 10.7	− 9.2	− 8.9	− 8.6
3a	− 9.8	− 8.3	− 8.0	− 7.7
3b	− 11.1	9.5	− 8.9	− 8.6
3c	− 11.4	− 9.7	− 8.8	− 8.5
3d	− 9.7	− 8.2	− 8.4	− 8.1
4a	− 11.0	− 9.9	− 9.2	− 9.0
4b	− 11.4	− 10.1	− 9.5	− 9.1
5a	− 11.3	− 9.8	− 9.5	− 9.2
5b	− 12.1	− 11.0	− 9.7	− 9.4
5c	− 12.6	− 11.1	− 10.1	− 9.7
6	− 12.0	− 11.0	9.7	− 9.3

TABLE IV

THE SUM OF THE FIRST FIVE McREYNOLDS CONSTANTS AND THE CONTRIBUTION OF

THE SUCCESSIVE TEST SOLUTES TO $\sum_{i=1}^{5} \Delta I_i$

Compound	Benzene (%)	1-Butanol (%)	2-Pentanone (%)	Pyridine (%)	1-Nitropropane (%)	$\sum_{i=1}^{5} \Delta I_i$
1a	9.4	31.8	15.4	20.6	22.8	1036
1b	9.6	31.6	15.2	18.9	24.6	1194
1c	9.4	33.7	14.6	17.9	24.3	1103
1d	9.5	35.0	14.3	16.9	24.3	732
1e	9.6	32.8	14.9	18.4	24.2	1223
2a	9.4	34.2	14.4	19.5	22.5	775
2b	9.4	33.1	14.2	20.9	22.4	947
2c	8.9	32.7	15.0	21.0	22.2	1084
3a	9.2	37.2	13.1	16.3	24.2	911
3b	9.0	34.1	14.4	18.7	23.8	989
3c	9.0	36.4	13.5	16.6	24.4	945
3d	9.1	34.5	14.6	17.1	24.6	808
4a	8.9	35.1	14.6	17.5	24.2	1091
4b	8.8	35.0	14.7	17.5	24.0	1152
5a	8.8	35.1	14.8	17.4	23.9	1180
5b	9.0	33.7	14.6	20.1	22.6	1316
5c	12.1	31.2	14.7	19.8	22.3	1458
6	9.2	33.5	14.0	16.9	23.4	1355
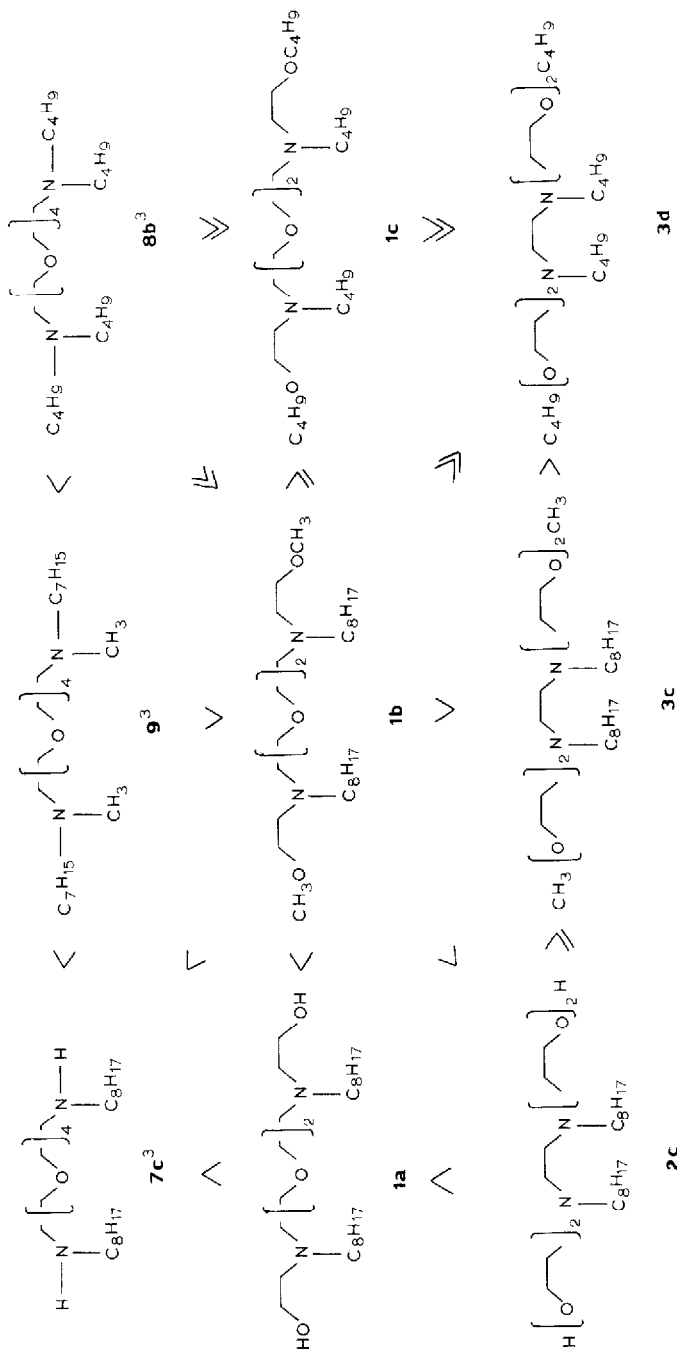
Scheme 1. Polarities of isomeric $C_{26}H_{52}N_2O_2$ and isomeric homologues $C_{28}H_{60}N_2O_4$.

TABLE V

REGRESSION AND CORRELATION COEFFICIENTS FOR THE RELATIONSHIP $PP = a + b \sum_{i=1}^{5} \Delta I_i$

PP	Solute	a	b	r
I_R	Methanol	452.1	0.234	0.9071
	Ethanol	463.7	0.255	0.9472
PI	Methanol	45.53	0.0470	0.8725
	Ethanol	56.25	0.0428	0.9165
ρ	Methanol	−2.53	$4.73 \cdot 10^{-3}$	0.8995
	Ethanol	−3.73	$6.66 \cdot 10^{-3}$	0.9186
ΔG_s^m (OH)	Methanol	−7.005	$-3.78 \cdot 10^{-3}$	0.8428
	Ethanol	−4.879	$-4.38 \cdot 10^{-3}$	0.8804
ΔG_s^m (C=O)	2-Butanone	−5.723	$-3.11 \cdot 10^{-3}$	0.8414
	2-Pentanone	−5.518	$-2.99 \cdot 10^{-3}$	0.8260

structures. The compounds examined differ rather in the position and distribution of the alkyl groups than in their length or the length of the oxyethylene chain.

The polarity of compounds 2, 4 and 5 increases as the length of the oxyethylene chains increases. This effect is stronger than that observed previously for compound 7:
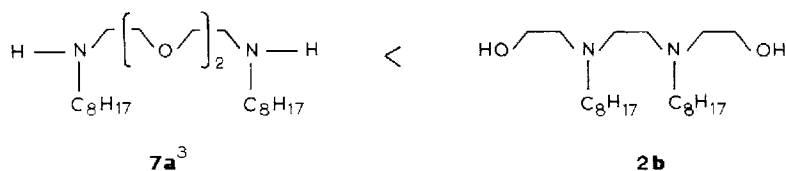

7	n
a	2
b	3
c	4

7^3
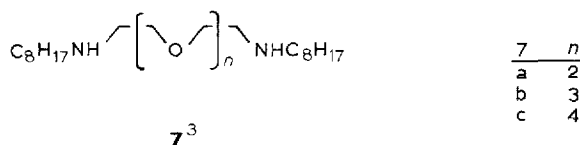
but similar (not stronger) to that reported for 8:
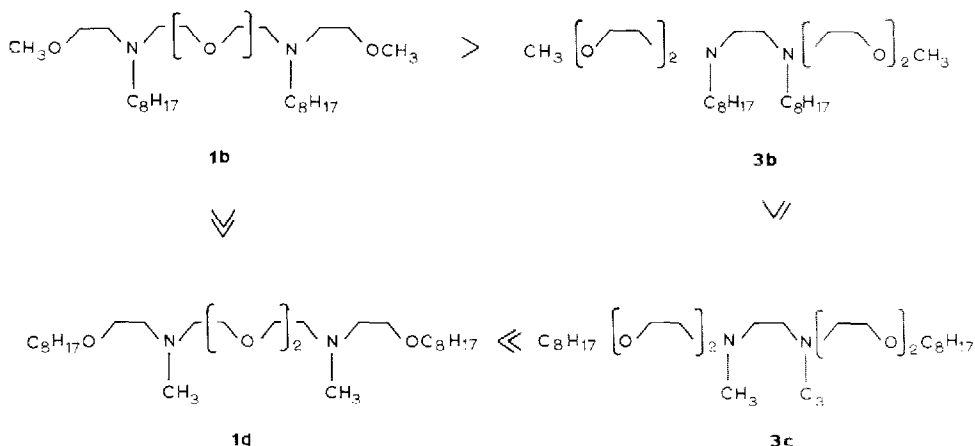

8	n
a	2
b	4

8^3
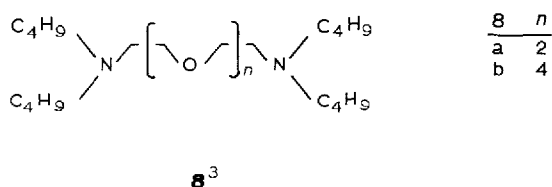
The sharp polarity increase that is observed for compound 2b may be attributed to the presence of hydroxyethyl groups (absent in 2a).

The important role of the distribution of carbon atoms in both alkyl groups was discussed in recent paper[3]. There it was indicated that compounds having two alkyl groups linked with the nitrogen atom (8) are much more polar than that having one, long alkyl chain linked to each nitrogen atom (7). Different distributions of four oxyethylene units significantly change the polarities of compounds, in the order shown in Scheme 1. It can be seen that the polarity depends significantly on the distribution of oxyethylene groups and alkyl chains in the molecule.

For compounds 7c, 1a and 2c, having heteroatom-bonded protons (= N–H; -O–H) the polarity increases as the oxyethylene groups are shifted from centre of the molecule into terminal positions (left-hand column of Scheme 1). An analogous effect is observed for compounds 7a[3] and 2b:

$$H - N \overset{}{\underset{C_8H_{17}}{|}} \left[\overset{}{\underset{}{O}} \right]_2 N \overset{}{\underset{C_8H_{17}}{|}} - H \quad < \quad HO \overset{}{\underset{}{}} N \overset{}{\underset{C_8H_{17}}{|}} N \overset{}{\underset{C_8H_{17}}{|}} OH$$

$$\mathbf{7a}^3 \qquad\qquad\qquad\qquad\qquad\qquad \mathbf{2b}$$

Opposite effects are observed for the second and third columns of compounds in Scheme 1 (9, 1b, 3b and 8b, 1c, 3d) having four alkyl substituents. The effect is stronger for compounds having four butyl groups (8b, 1c and 3d) than for compounds having two long and two methyl groups. For α,ω-bisamino oligoethers it was demonstrated that compounds having four short butyl groups exhibit higher polarities[3] (first row in Scheme 1). As a result, compounds 2c and 3b are more polar than 3d. The decrease in the polarity of compounds 1c and 3d is probably caused by the shortening of the oligooxyethylene chain present in the centre of the molecule and by the screening of the terminal oxygens by hydrophobic alkyl groups. As a result, oxyethylene groups linked with nitrogen and butyl groups become less polar or even act rather as non-polar groups. Such a supposition is confirmed by comparison of the polarities of compounds 1b, 1d, 3b and 3c:

$$CH_3O \overset{}{\underset{}{}} N \overset{}{\underset{C_8H_{17}}{|}} \left[\overset{}{\underset{}{O}} \right] N \overset{}{\underset{C_8H_{17}}{|}} OCH_3 \quad > \quad CH_3 \left[O \overset{}{\underset{}{}} \right]_2 N \overset{}{\underset{C_8H_{17}}{|}} N \overset{}{\underset{C_8H_{17}}{|}} \left[\overset{}{\underset{}{O}} \right]_2 CH_3$$

$$\mathbf{1b} \qquad\qquad\qquad\qquad\qquad\qquad\qquad \mathbf{3b}$$

$$\Vee \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad \mathbin{/\!/}$$

$$C_8H_{17}O \overset{}{\underset{}{}} N \overset{}{\underset{CH_3}{|}} \left[\overset{}{\underset{}{O}} \right]_2 N \overset{}{\underset{CH_3}{|}} OC_8H_{17} \quad \ll \quad C_8H_{17} \left[O \overset{}{\underset{}{}} \right]_2 N \overset{}{\underset{CH_3}{|}} N \overset{}{\underset{C_?}{|}} \left[\overset{}{\underset{}{O}} \right]_2 C_8H_{17}$$

$$\mathbf{1d} \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad \mathbf{3c}$$
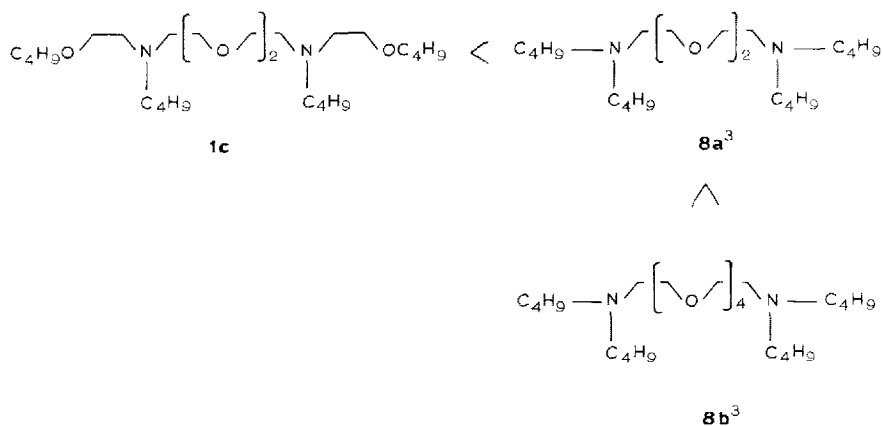
The lowest and highest polarities are shown by compounds 1d and 1b, respectively, having two oxyethylene groups in the centre of the molecule and two oxyethylene groups at periphery. The screening of the oxygen atom by the bulky octyl group is so effective that the polar character of this oxyethylene group disappears and compound 1d shows a low polarity. The methyl group is small and its effect is relatively weak. Compounds 3b and 3c are only slightly less polar than 1b but much more polar than 1d. This means that the presence of two oxyethylene groups on each side of the molecule significantly decreases the screening effect of the terminal alkyl groups.
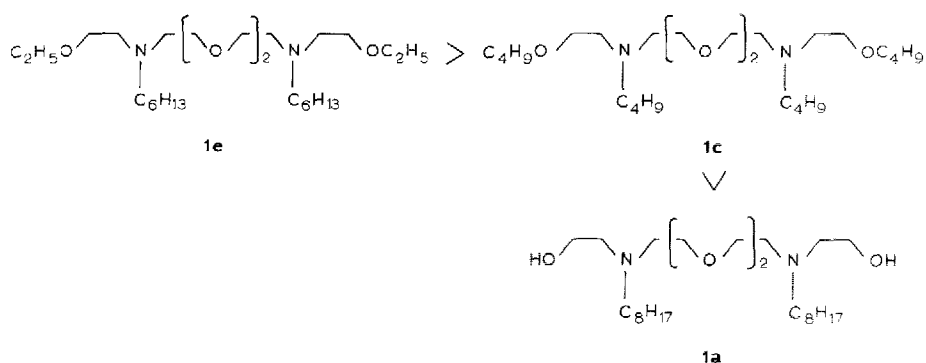
Moreover, the polarities of compounds 3b and 3c, having the bulky octyl group linked with nitrogen and oxygen, respectively, are almost the same. It also means that all compounds with the ethylenediamine structure exhibit only a weak influence of the number of oxyethylene chains and the distribution of alkyl chains in the molecule on their polarity, as shown for compounds 2 and 3.

The effect of the screening of oxygen atoms by alkyl groups is clearly observed when the polarity of compound 1c is compared with those of 8a[3] and 8b[3]:

C_4H_9O—N$\left[O \right]_2$N—OC_4H_9 $<$ C_4H_9—N$\left[O \right]_2$N—C_4H_9
             | | | |
           C_4H_9 C_4H_9 C_4H_9 C_4H_9

               1c   **8a**[3]

                                                                   $\wedge$

                           C_4H_9—N$\left[O \right]_4$N—C_4H_9
                                    | |
                                  C_4H_9 C_4H_9

                                        8b[3]

Compound 1c is not only less polar than 8b[3], having four oxyethylene units, but also less polar than 8a[3], having only two oxyethylene groups in the centre of the molecule. This means that the polar character of the oxygen atoms decreases so significantly that the oxyethylene groups linked with the terminal butyls become even non-polar.

Compounds 1a, 1c and 1e are isomers with different distributions of carbon atoms in their alkyl groups while the number and distribution of the oxyethylene groups are the same. Their polarities change in the following order:

C_2H_5O—N$\left[O \right]_2$N—OC_2H_5 $>$ C_4H_9O—N$\left[O \right]_2$N—OC_4H_9
             | | | |
         C_6H_{13} C_6H_{13} C_4H_9 C_4H_9

               1e   **1c**

                                                                   $\vee$

                         HO—N$\left[O \right]_2$N—OH
                               | |
                            C_8H_{17} C_8H_{17}

                                       1a

In this instance, compounds having short alkyl groups linked with each nitrogen atom and each terminal oxygen are more polar than compounds having the long alkyl group linked with each nitrogen atom. The conclusion is similar to that reported previously[3], where it was demonstrated that compounds having two short alkyl groups connected with the nitrogen atom are more polar than compounds having

only one long alkyl group. This effect is even more important than the screening of the oxygen atoms by short alkyl groups. However, the polarity decreases as the length of this alkyl groups increases. As a result, compound 1c is less polar than 1e. Similarly, compound 1d is less polar than 1b:
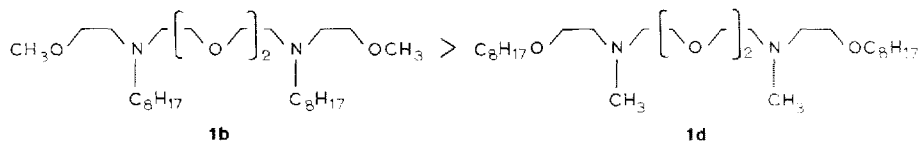
These last compounds are also less polar than compounds 1a, 1c and 1e as a result of the two additional methylene groups present in their molecules.

The effect of the lengths of the alkyl groups bonded with nitrogen and oxygen atoms can be described quantitatively (Fig. 1) when the differences between the number of carbon atoms in the alkyl groups are taken under consideration: $\Delta n = m - n$ for
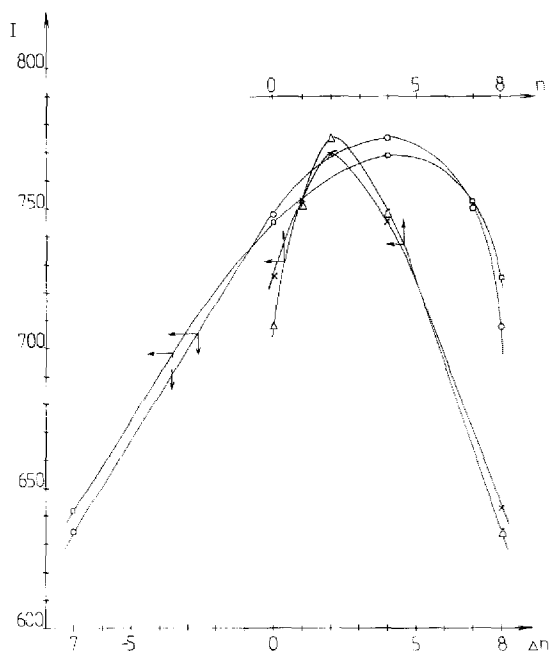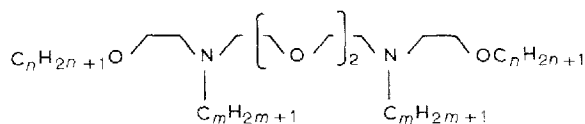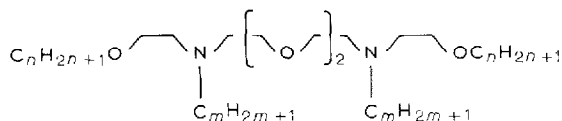

Fig. 1. Influence of the distribution of carbon atoms in alkyl chains on the retention index (I) of ethanol for compounds 1:

$\times \triangle = I$ vs. n; $\square, \bigcirc = I$ vs. Δn; $\times, \square$ = at 70°C; $\triangle, \bigcirc$ = at 90°C.

For low and high Δn values low polarity is observed, and the polarity increases as the differences between the numbers of carbon atoms in the alkyl groups decrease. However, the maximal polarity is not obtained for $\Delta n = 0$ but for $\Delta n = 4$. When the relationship between l and n is considered (Fig. 1), where n denotes the number of carbon atoms in the alkyl group bonded with the oxygen atom, the maximal polarity is observed for $n = 2$. This means that the polarity increases as the alkyl chain length increases only up to ethyl. A further increase in the alkyl chain length results in a decrease in polarity.

However, the influence of the lengths of alkyl groups linked to oxygen and nitrogen atoms should be examined in detail for the different types of compounds, and this problem will be investigated in the future.

The screening effect of the small methyl group is weak and almost negligible. As a result, compounds having free hydroxyl groups exhibit a polarity similar to that observed for compounds having terminal methyl groups, i.e., the polarities of compounds 2b and 2c are similar to those of 3a and 3b. The limited decrease in polarity for compound 1a may be attributed to the internal hydrogen bonding, which is much weaker for compounds 2b and 2c:
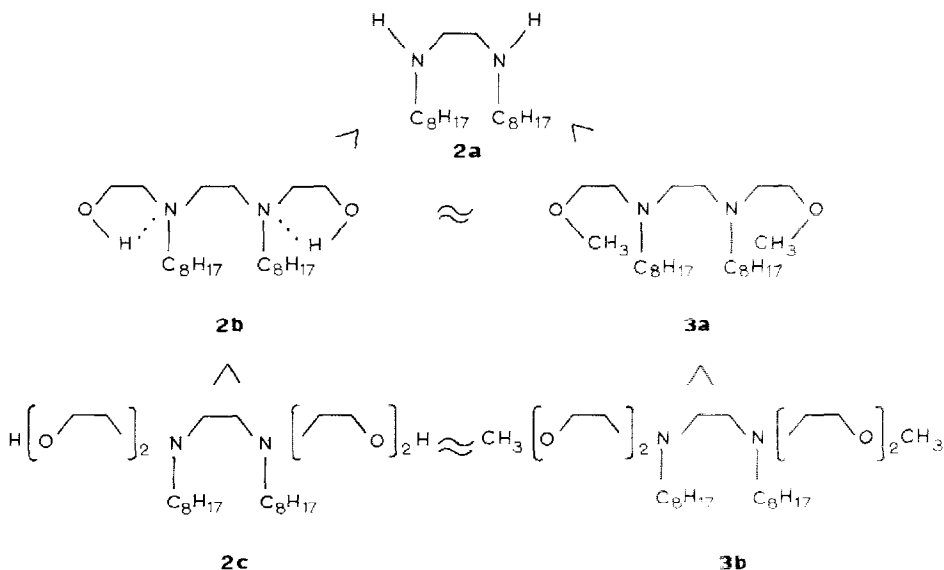
Hence the effects of methoxy and hydroxyl groups on polarity are similar. Similar relationships are observed for compounds 4a and 5a and for 4b and 5b, although the differences in their polarities are larger than those for compounds having two nitrogen atoms.

The effect of different groups and their position in the molecule can be quantitatively measured by means of the "hydrophobe effective length"[3]. As previously, $RNHCH_2(CH_2OCH_2)CH_2NHR$ (compounds 1 in ref. 3) were used as standards. The hydrophobe effective length is equal to the number of carbon atoms in both alkyl groups linked to the nitrogen atoms in a hypothetical standard which exhibits the same polarity as the compound being considered.

TABLE VI

HYDROPHOBE EFFECTIVE LENGTHS

Compound	Actual number of carbon atoms	Hydrophobe effective length				$\Sigma \Delta l_i$
		l_R		PI		
		CH_3OH	C_2H_5OH	CH_3OH	C_2H_5OH	
1a	16	9.6	11.1	10.3	11.4	8.9
1b	18	5.9	5.0	7.0	5.9	−0.2
1c	16	7.3	6.8	8.4	7.7	5.0
1d	18	32	30	36.3	34.1	26.5
1e	16	2.8	1.8	4.9	3.6	−1.9
2a	16	28.7	28.0	31.8	31.2	24.0
2b	16	12.5	14.0	13.0	14.4	14.1
2c	16	7.5	10.0	8.9	10.4	6.1
3a	18	13.6	16.0	15.0	14.4	16.2
3b	18	7.5	8.6	8.1	8.6	11.6
3c	18	8.9	9.8	9.8	10.4	14.2
3d	16	25.9	24.8	27.8	26.7	22.1
4a	18	10.1	10.4	10.7	10.1	5.7
4b	18	6.3	4.1	7.4	5.1	2.2
5a	16	7.3	5.9	8.0	6.4	0.6
5b	16	−1.9	−5.5	−0.4	3.1	−7.3
5c	16	−14.6	−14.1	−7.6	8.9	−15.5
6	16	−8.7	−10.7	−3.8	−6.8	9.6

Much lower values were obtained (Table VI) in comparison with the actual number of carbon atoms which demonstrates the weak effect of short alkyl groups linked with nitrogen and oxygen atoms in comparison with single alkyl groups linked to the nitrogen atoms in the standard. For compounds 5 and 6 even negative values were obtained. Hence the compounds investigated here are much more polar than the compounds $RNHCH_2(CH_2OCH_2)CH_2NHR$ used as standards.

CONCLUSIONS

The polarity of alkyl derivatives of diazapolyoxyethylene ethers depends on the lengths of the alkyl and polyoxyethylene chains, on the distribution of carbon atoms in alkyl groups linked with the nitrogen and oxygen atoms and on the distrtibution of the oxyethylene groups.

Compounds having the same number of carbon atoms are more polar when the atoms are distributed among several alkyl groups. The distribution of oxyethylene groups among different oligooxyethylene chains decreases the polarity as a result of screening of the single oxygen atom by non-polar alkyl groups.

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