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POLARITY OF SOME INDIVIDUAL DERIVATIVES OF α,ω-DIAMINO-OLIGOETHERS AS MEASURED BY GAS CHROMATOGRAPHY

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SUMMARY

The polarity of α,ω-diaminooligoether derivatives, as determined by inverse gas chromatography, was investigated. The effects of structures of the compounds on their polarities and on the hydrophobic effective lengths are discussed. Different relationships between polarity parameters are considered and appropriate increments of the polarity parameters were determined for characteristic groups.

INTRODUCTION

The polarities of several compounds containing one nitrogen atom were studied previously[1,2]. The relationships between different polarity parameters were discussed and the increments of the polarity parameters for different characteristic structural fragments were calculated.

The aim of this work was to study the relationships between the structures and polarities of some derivatives of α,ω-diaminooligoethers which contain two nitrogen atoms bridged by an oligooxyethylene chain, and each linked to combinations of hydrogen atoms and alkyl and acyl groups. Their structures are as follows:

C_8H_{17}—N $\quad$ N—C_8H_{17}

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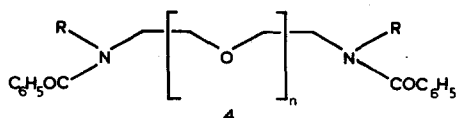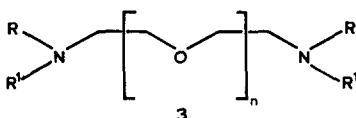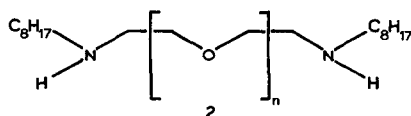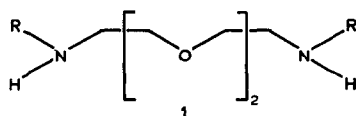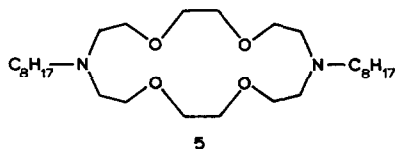
where R and R^1 denote alkyl groups (CH_3 to $C_{12}H_{25}$), a cyclohexyl or a benzoyl group and $n = 2$, 3 and 4.

Some of these compounds were obtained previously and tested as drugs[3,4] and pesticides[5]. Some new compounds are described in this work. They were tested as crown ether analogues for the extraction of mercury(II) chloride[6], alkali metals and alkaline earth metals[7].

EXPERIMENTAL

Individual derivatives of α,ω-*diaminooligoethers and their preparation*
        Nineteen pure model compounds (Table I) were used for polarity measurements.

TABLE I

STRUCTURES AND ANALYTICAL DATA FOR α,ω-DIAMINOOLIGOETHER DERIVATIVES

Compound	R	R^1	n	B.p. (°C/mmHg)	M.p. (°C)	n_D^{20}
1a	CH_3	—	2	85–88/0.3**	—	1.4453**
1b	C_2H_5	—	2	88–90/0.01***	—	1.4439***
1c	C_4H_9	—	2	124/0.01	—	1.4472
1d	C_6H_{13}	—	2	169–172/0.3	—	1.4514
1e	C_8H_{17}	—	2	167/0.01	—	1.4545
1f	$C_{10}H_{21}$	—	2	—	23	—
1g	$C_{12}H_{25}$	—	2	—	38–39§	—
1h	C_6H_{11}*	—	2	—	—	1.4829
1i	$C_6H_5CH_2$	—	2	198–200/0.01	—	1.5425
2a	C_8H_{17}	—	3	220/0.01	—	1.4553
2b	C_8H_{17}	—	4	226–281/0.1	—	1.4570
3a	C_4H_9	C_4H_9	2	139/0.01§§	—	1.4529
3b	C_4H_9	C_4H_9	4	206–208/0.08	—	1.4535
3c	CH_3	C_7H_{15}	4	197–206/0.02	—	1.4550
4a	H	—	2	—	120–122	—
4b	C_8H_{17}	—	2	Oil	—	—
4c	C_8H_{17}	—	3	Oil	—	—
4d	C_8H_{17}	—	4	Oil	—	—
5	C_8H_{17}	—	4	223–236/0.02	22	—

        * Cyclohexyl.
      ** 115°C/12 mmHg: 1.4453[12].
    *** 148°C/22 mmHg; 1.4420[12].
        § 39–40°C[8].
      §§ 122–39/0.02 mmHg[8].

They were synthesized according to methods described previously[3,8,9]. All reagents used for syntheses were of analytical-reagent grade.

Compounds 1 and 2 were obtained as follows:

$$2 \; RNH_2 \; + \; ClCH_2(CH_2OCH_2)_nCH_2Cl \; \longrightarrow$$

A 0.1-mol amount of the required α,ω-dichlorooligoether was added slowly with stirring at 70–120°C to the required primary amine (0.6–1.2 mol) and the reaction mixture was maintained at 70–120°C for 10–15 h. The cooled mixture was treated with aqueous sodium hydroxide (20 g in 40 cm³) and the precipitated salt was filtered off. The organic mother liquor was then dried over potassium hydroxide and distilled two to four times under reduced pressure. The yield was 50–80%.

Compounds 3 were prepared by heating (100–150°C) a mixture of 0.1 mol of the required α,ω-dichlorooligoether, 0.3 mol of the required secondary amine and 0.3 mol of sodium carbonate with stirring for 20 h. After the precipitated salt had been filtered off, the mother liquor was distilled three to five times under reduced pressure. The yield was 40–60%.

The bisbenzamides were prepared as follows:

$$+ \; 2 \; C_6H_5COCl \; \longrightarrow$$
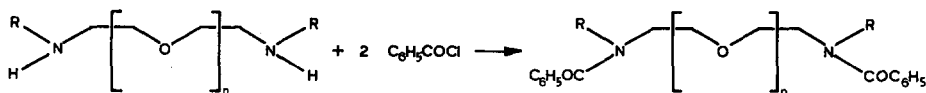
To a suspension of 0.05 mol of 1 in 30 cm³ of 1,4-dioxane and aqueous potassium hydroxide solution (10 g in 10 cm³) was added dropwise 0.11 mol of benzoyl chloride at 5–10°C. The mixture was stirred for 2 h at 50–70°C and, after cooling, diluted with 50 cm³ water. The solid product was collected on a glass filter, washed with water and recrystallized from ethanol. The oil obtained was washed five times with water and five times with n-heptane. The yield was 70–95%.

The crown ether 5 was obtained according to the method of Kulstad and Malmsten[10]:

$$+ \; ICH_2(CH_2OCH_2)CH_2I \; \longrightarrow$$
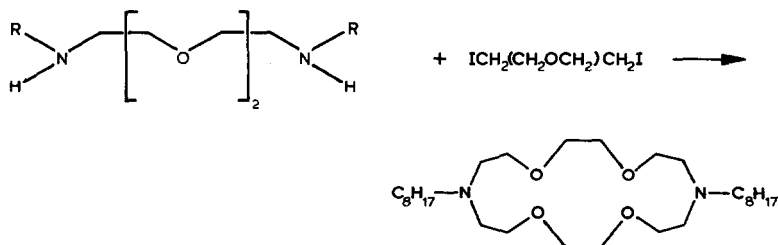
Treatment of 1e (0.05 mol) with 1,8-diiodo-3,6-dioxaoctane (0.05 mol) in the presence of sodium carbonate (0.1 mol) in acetonitrile afforded 5 in 28% yield. The product was purified by distillation and recrystallization.

The purities and structures of all the compounds were confirmed by elemental analyses, ^{1}H NMR spectra, and gas (GC) and thin-layer chromatography (TLC). Their structures and some analytical data are given in Table I. ^{1}H NMR spectra were recorded on a Tesla BS 487B 80-MHz instrument using C^2HCl_3 as solvent and hexamethyldisiloxane (HMDS) as internal standard. Compounds 1–3: 0.80–0.83 (t, CH_3), 1.22–1.32 (m, CH_2 in alkyls), 2.29–2.57 (t, CH_2 in alkyls bonded with hydrogen), 2.49–2.73 (4H, t, CH_2 in oligooxyethylene chain bonded with nitrogen), 3.47–3.54 (4H, t, CH_2 in oligooxyethylene chain in β-position), 3.52–3.60 ppm (s, CH_2 in oligooxyethylene chain).

The purity of α,ω-diaminooligoether derivatives was checked by GC using SE-30 as the stationary phase and by TLC on silica using toluene–acetone–methanol–25% ammonia solution (45:42:10:3) as the eluent and iodine vapour and cobalt(II) thiocyanate[11] for detection.

Chromatographic measurements

Chromatographic measurements were carried out using a gas chromatograph (Chrom 5, Kovo, Czechoslovakia) equipped with a flame ionization detector. The conditions were as follows: column, 1 m × 3 mm I.D.; column temperature, 70 and 90°C; column packing, 25% (w/w) of the compound on Porolith (mesh size 0.2–0.5 mm); carrier gas (helium) flow-rate, 40 ml/min; solutes, methanol, ethanol, 1-propanol, 1-butanol, 2-butanone, 2-pentanone, benzene, pyridine, 1-nitropropane and C_5–C_{12} alkanes; time for column stabilization, 10 h. The compounds examined were used as liquid stationary phases.

For each surfactant five different measurements were made and the average values of the polarity parameters were calculated. The following polarity parameters were considered; retention index of methanol and ethanol, I_R (ref. 13); polarity index of methanol or ethanol, $PI = 100 \log (C - 4.7) + 60$, where C is the apparent number of carbon atoms in a standard n-alkane having the same retention time as the alcohol[14]; coefficient ρ, defined as the ratio of the retention times of alcohol and n-hexane[15,16]; partial molal free energies of solution of hydroxyl group, $\Delta G_s^m(OH)$ and carbonyl group, $\Delta G_s^m(C=O)$; and McReynolds constants.

Partial molal Gibbs free energies of solution were calculated according to the procedure described by Risby and co-workers[17,18] and used in our previous work[2,19,20]. The sum of the first five McReynolds constants, $\sum_{i=1}^{5} \Delta I_i$, was calculated in the standard way using differences in retention indices, ΔI_i, values of benzene, 1-butanol, 2-pentanone, pyridine and 1-nitropropane, as determined on a considered compound and on squalane, respectively.

RESULTS AND DISCUSSION

The values of the polarity parameters obtained are given in Tables II–IV (the compounds are numbered as in Table I). The precision of the determination of the polarity parameters considered is good and similar to that in our previous work[1,2,19,20]. The relationships between the polarity parameters are also similar to those reported previously[2,19,20] and hence they are not discussed here.

TABLE II

EMPERICAL POLARITY PARAMETERS

Com-pound	Tempera-ture (°C)	I_R		PI		ρ	
		CH_3OH	C_2H_5OH	CH_3OH	C_2H_5OH	CH_3OH	C_2H_5OH
1a	70	920	1047	114.0	116.0	4.91	9.76
	90	–	–	–	–	–	–
1b	70	837	868	106.6	110.0	2.89	6.30
	90	–	–	–	–	–	–
1c	70	712	742	98.8	103.6	2.40	3.29
	90	703	726	96.9	101.1	2.36	2.67
1d	70	693	727	95.0	101.1	2.19	2.91
	90	675	699	90.4	94.9	1.79	2.14
1e	70	660	691	91.0	96.9	1.68	2.54
	90	655	681	86.0	94.4	1.60	2.06
1f	70	653	689	87.0	95.0	1.60	2.22
	90	618	656	79.9	93.5	1.52	2.25
1g	70	647	672	84.9	91.1	1.51	1.89
	90	610	650	74.7	85.7	1.08	1.78
1h	70	698	726	96.0	101.0	2.35	2.98
	90	683	703	92.9	96.9	1.90	2.22
1i	70	685	724	94.0	95.5	1.78	2.62
	90	683	703	92.8	93.6	1.27	2.18
2a	70	681	701	92.5	97.4	1.90	2.61
	90	693	696	95.1	95.6	2.04	2.09
2b	70	683	711	92.9	98.3	2.18	2.75
	90	692	707	94.7	97.7	2.00	2.25
3a	70	758	780	106.1	109.3	3.73	4.48
	90	778	783	109.0	109.7	3.78	3.93
3b	70	829	849	115.8	118.2	5.87	6.86
	90	853	874	119.4	121.2	6.20	6.95
3c	70	756	7.73	105.8	108.4	3.85	4.19
	90	727	765	101.6	106.2	2.66	4.14
4a	70	805	824	112.8	115.5	4.78	5.62
	90	803	803	114.0	113.6	4.27	4.18
4b	70	708	728	100.2	103.2	2.53	3.16
	90	737	764	103.2	107.4	2.73	3.31
4c	70	729	751	101.6	105.1	2.80	3.33
	90	722	749	100.5	104.9	2.38	2.88
4d	70	740	755	103.4	105.9	3.08	3.47
	90	723	752	101.8	105.3	2.72	2.97 ·
5	70	682	705	92.8	97.2	1.97	2.39
	90	699	703	96.0	96.8	2.10	2.17

The polarity of $RHNCH_2(CH_2OCH_2)_nCH_2NHR$ depends significantly on their structures, and increases as the lengths of the alkyl groups and of the oligooxyethylene chain decrease and increase, respectively. These effects are similar for the all polarity parameters and hence the relationships presented in Figs. 1 and 2 as examples have a general character. For the first homologues having short alkyl chains (methyl, ethyl

TABLE III

THERMODYNAMIC POLARITY PARAMETERS

| Compound	$\Delta G_s^m(OH)$ (kJ mol^{-1})		$\Delta G_s^m(C{=}O)$ (kJ mol^{-1})	
	CH$_3$OH	C$_2$H$_5$OH	2-Butanone	2-Pentanone
1a	—	—	—	—
1b	—	—	—	—
1c	−11.3	− 9.7	− 9.1	− 8.8
1d	−11.2	− 9.6	− 8.8	− 8.5
1e	−10.3	− 9.1	− 8.7	− 8.4
1f	− 9.9	− 8.4	− 8.4	− 8.2
1g	− 9.4	− 7.6	− 8.0	− 7.8
1h	−11.1	− 9.6	− 8.8	− 8.5
1i	−10.7	− 9.1	−11.0	−10.8
2a	−10.4	− 8.2	− 8.3	− 7.9
2b	−10.7	− 9.0	− 8.7	− 8.4
3a	−12.4	−10.6	− 9.2	− 8.8
3b	−12.4	−10.7	− 9.7	− 9.3
3c	−11.4	− 9.7	− 9.2	− 8.9
4a	−13.0	−11.2	−11.6	−10.0
4b	−11.3	− 9.6	−10.7	−10.4
4c	−10.5	− 8.8	−10.1	− 9.8
4d	−10.8	− 8.9	−10.2	− 9.9
5	−10.5	− 8.7	− 8.8	− 8.5

and butyl) their polarity decreases rapidly as the alkyl chain length increases. However, a further increase in the alkyl length causes a much smaller decrease in polarity, and approximately linear relationships are observed for compounds having 4–12 carbon atoms (m) in each alkyl group. The gradients of these relationships, which are different for each polarity parameter, do not depend significantly on the type of polar solute and they are similar for methanol and ethanol and for 2-butanone and 2-pentanone, respectively. The effect of the number of oxyethylene groups (n) on the polarity is also approximately linear. The gradients calculated for the relationships $PP_i = A + Bm$ and $PP_i = A + Bn$, where PP_i denotes the polarity parameter considered, give appropriate increments of the polarity parameter, which are negative and positive for a methylene group and an oxyethylene group, respectively (Table V). These increments and/or the relationships obtained for compounds 1 can be further used to estimate the polarity of other homologues, to determine the so-called "effective length of the hydrophobe" for other compounds and to compare the effect of cyclohexyl, benzyl and benzoyl groups on the polarity of the compounds and the effective length of their hydrophobes.

The use of these increments to calculate the polarity for the other compounds considered which have different structures is limited, because polarity depends significantly on the distribution of carbon in the X and Y groups. Isomers having each nitrogen atom linked with two short alkyl chains are much more polar than isomers in

TABLE IV

SUM OF McREYNOLDS CONSTANTS AND CONTRIBUTIONS OF SUCCESSIVE TEST SOLUTES

Compound	Benzene (%)	1-Butanol (%)	2-Pentanone (%)	Pyridine (%)	1-Nitropropane (%)	$\sum_{i=1}^{5} \Delta I_i$
1a	—	—	—	—	—	—
1b	—	—	—	—	—	—
1c	12.2	34.3	13.9	18.5	21.9	1032
1d	8.3	30.5	22.1	14.5	24.6	972
1e	9.3	33.8	14.2	17.0	24.4	936
1f	6.8	39.1	10.6	13.5	29.8	912
1g	9.4	38.2	12.9	16.7	22.6	717
1h	10.1	37.2	13.4	17.3	22.0	885
1i	10.2	22.9	22.4	18.5	25.8	1053
2a	9.4	36.2	14.1	17.0	23.3	875
2b	10.2	33.9	14.3	18.0	23.5	970
3a	1.8	38.3	14.6	19.1	26.1	1031
3b	9.8	32.9	14.2	18.6	24.4	1529
3c	9.3	35.4	14.0	17.5	23.7	1041
4a	11.6	15.2	26.2	23.1	22.1	1952
4b	10.1	26.3	15.6	24.2	23.2	1357
4c	10.8	27.4	16.5	19.8	25.4	1391
4d	11.0	27.2	16.3	20.4	24.9	1409
5	9.6	33.2	14.2	18.2	24.8	967
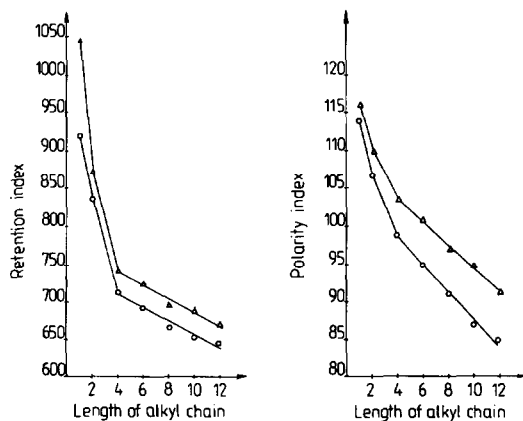
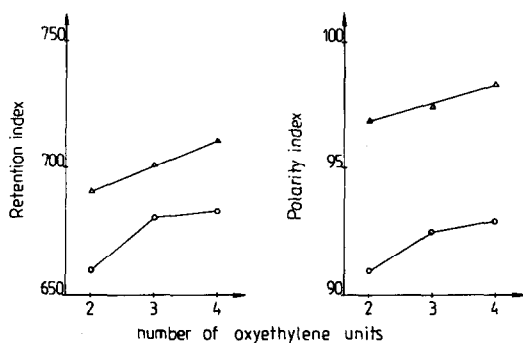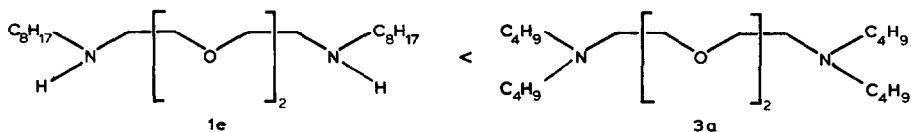Fig. 1. Effect of the length of alkyl chain on the polarity of compounds 1. ○, Methanol; △, ethanol.

Fig. 2. Influence of the number of oxyethylene units on the polarity of compounds 2. ○, Methanol; △, ethanol.

which each nitrogen atom is linked with only one but long alkyl group, as in compounds 1e and 3a:

The polarity parameters for compound 3a are higher than those for compound 1e by about 100, 15, 2, 2 and 100 units for I_R, PI, ρ, $\Delta G_s^m(OH)$ and $\sum_{i=1}^{5} \Delta I_i$, respectively. Hence

TABLE V

INCREMENTS OF POLARITY PARAMETERS

Polarity parameter	Polar solute	Temperature (°C)	Increment	
			$-CH_2-$	$-OCH_2CH_2-$
I_R	CH_3OH	70	−4.25	11.5
		90	−6.07	18.5
	C_2H_5OH	70	−4.45	10.0
		90	−4.87	13.0
PI	CH_3OH	70	−0.895	0.949
		90	−1.372	4.340
	C_2H_5OH	70	−0.777	0.700
		90	−0.905	1.650
ρ	CH_3OH	70	$-5.95 \cdot 10^{-2}$	0.250
		90	$-7.07 \cdot 10^{-2}$	0.200
	C_2H_5OH	70	$-8.67 \cdot 10^{-2}$	0.105
		90	$-7.92 \cdot 10^{-2}$	0.095

this effect is very strong and much more important than the effect of the lengths of the non-polar alkyl groups and of the polar oligooxyethylene chain. This effect becomes even stronger when the length of the polar oligooxyethylene chain increases. When compounds 2b and 3b are compared for which $n = 4$, the observed increase in the polarity parameters is about 50% higher than with compounds 1e and 3a. This increase is observed when the hydrogen atoms are replaced by methyl groups (compound 3c). This replacement causes a similar increase in the polarity parameters with a further change from methyl to butyl group (compounds 3c and 3b):
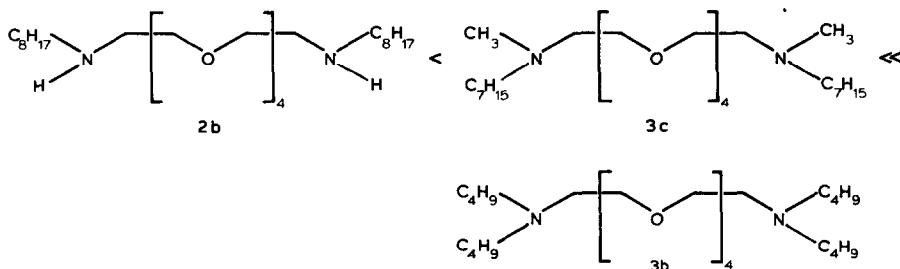

The effect of the oligooxyethylene chain length is also much stronger for compounds having two short alkyl chains linked with each nitrogen atom (for compounds 3 in comparison with compounds 1 and 2), e.g., for compounds 3a and 3b in comparison with compounds 1e and 2b. In this instance, $PP_i(3b) - PP_i(3a) \gg PP_i(2b) - PP_i(1e)$.

It is interesting that the linear compound 2b exhibits the same polarity as the cyclic compound 5. The same values of the polarity parameters, including the contributions for the McReynolds constants, were obtained for these two compounds:
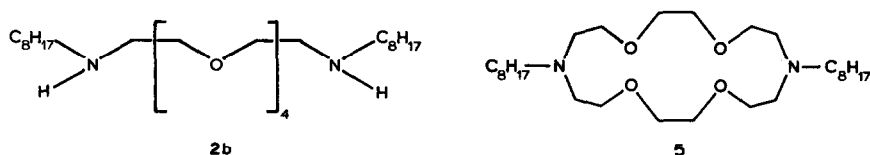
Probably this is a result of a hydrogen bonding in compound 2b between hydrogen atoms bonded with nitrogen atoms and oxygen atoms present in the oxyethylene groups linked with nitrogen atoms:
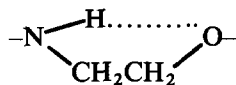
Comparison of the polarity parameters obtained for compounds 1d and 1h demonstrates that these compounds exhibit similar polarities as far as the retention times of alcohols and ketones are considered. The retention indices of alcohols, polarity indices, ρ values and partial molal Gibbs free energies of solution are almost the same for these two compounds. However, when more complex McReynolds constants are considered, a higher $\sum_{i=1}^{5} \Delta I_i$ is obtained for compound 1d.

1d   1h

The replacement of the octyl group by a benzyl group results in only a small polarity increase (compounds 1e and 1i), which rapidly increases when the octyl group is replaced by a benzoyl group (compounds 1e and 4a). Thus,

1e   <   1i   ≪

4a

This effect is so strong that compounds 4b, 4c and 4d are much more polar than compounds 1e, 2a and 2b, respectively, and they exhibit polarities near those of compounds 3a and 3b in which each nitrogen atom is bonded with two short butyl groups. Thus,

4b,4c,4d   ≫   1e,2a,2b

and

4b,4d   <   3a,3b

Compounds 4 have slightly acidic nitrogen atoms and they form two mesomeric structures:

As a result, they are more polar than appropriate compounds 1, 2, 3 and 5, in which the nitrogen atoms are strongly basic owing to the free electron pairs.

The effects of different groups on the polarities of the compounds can be quantitatively measured by means of the so-called "hydrophobe effective length". Compounds 1, $RNHCH_2(CH_2OCH_2)_2CH_2NHR$, were selected as the standard series and the hydrophobe effective length was obtained from the relationship of PP_i vs. $2m$, where m denotes the number of carbon atoms in each alkyl group and PP_i is the polarity parameter, valid for the considered standard series and from the polarity parameter determined experimentally for a compound considered. Thus the hydrophobe effective length equals the number of carbon atoms in both alkyl groups linked to the nitrogen atoms in a hypothetical $RNHCH_2(CH_2OCH_2)_2CH_2NHR$ which exhibits the same polarity as the compound considered.

The hydrophobe effective lengths obtained (Table VI) depend on the polarity parameter used for the calculations as a result of different interactions taken into consideration. They demonstrate that the polarities of cyclohexyl and benzyl groups are similar to those of the alkyl groups when only the interactions with the alcohol are considered. However, a much lower hydrophobe effective length was obtained for compound 1i, having two aromatic rings, when the McReynolds constants were considered. Compounds 3 have their lower hydrophobe effective lengths than the sum of the carbon atoms present in their alkyl groups. Thus, the second short alkyl group has only a small effect on the polarity. For compounds 4 negative values were obtained

TABLE VI

HYDROPHOBE EFFECTIVE LENGTHS

Compound	Actual number of carbon atoms	Hydrophobe effective length				
		I_R		PI		$\sum\limits_{i=1}^{5} \Delta I_i$
		CH_3OH	C_2H_5OH	CH_3OH	C_2H_5OH	
1h	12 (2 × C_6H_{12})	12.5	13.2	9.9	10.3	17.7
1i	14 (2 × $C_6H_5CH_2$)	14.2	13.3	13.0	18.2	7.9
2a	16	14.5	15.7	13.4	14.9	18.2
2b	16	14.2	14.6	12.9	13.6	12.7
3a	16	7.4	9.1	4.1	4.3	9.2
3b	16	4.0	5.6	1.8	1.7	5.7
3c	16	7.5	9.5	4.3	4.7	8.6
4a	12 (2 × C_6H_5CO)	5.0	6.7	2.3	2.2	−44.2
4b	14 (C_8 + C_6H_5CO)	11.4	13.0	6.9	8.1	− 9.7
4c	14 (C_8 + C_6H_5CO)	9.5	11.1	6.1	6.7	−11.7
4d	14 (C_8 + C_6H_5CO)	8.6	10.8	5.2	6.1	−12.7
5	16	14.3	15.2	13.0	15.3	12.9

TABLE VII

REGRESSION AND CORRELATION COEFFICIENTS FOR THE RELATION

$$PP_i = a + b \sum_{i=1}^{5} \Delta I_i$$

PP	Solute	a	b	r
I_R	CH_3OH	393.7	0.308	0.8953
	C_2H_5OH	427.8	0.296	0.9185
PI	CH_3OH	42.004	0.0533	0.8526
	C_2H_5OH	55.700	0.0422	0.9244
ρ	CH_3OH	−4.18	$6.67 \cdot 10^{-3}$	0.9378
	C_2H_5OH	−4.70	$7.61 \cdot 10^{-3}$	0.9466
$\Delta G_s^m(OH)$	CH_3OH	−7.316	$-3.64 \cdot 10^{-3}$	0.7688
	C_2H_5OH	−5.587	$-3.69 \cdot 10^{-3}$	0.7632
$\Delta G_s^m(C=O)$	MEK*	−6.737	$-2.09 \cdot 10^{-3}$	0.8812
	MPK*	−6.629	$-1.89 \cdot 10^{-3}$	0.8651

* MEK = 2-butanone; MPK = 2-pentanone.

for the hydrophobe effective lengths as a result of the high polarity of the benzoyl group present in these amides.

As previously[2], approximately linear relationships exist between the considered polarity parameters and the sum of the first five McReynolds constants. However, the correlation coefficients are lower but still acceptable. The values of the regression coefficients presented in Table VII were obtained for compounds that do not contain an aryl group in their molecules. For this group of compounds the contribution of ΔI values of 1-butanol in $\sum_{i=1}^{5} \Delta I_i$ is much lower than for the other compounds with non-aromatic hydrophobes (Table IV), as the contribution of the respective McReynolds solutes to the $\sum_{i=1}^{5} \Delta I_i$ values depends significantly on the chemical nature of the stationary phase used.

Linear relationships of PP_i vs. $1/C_n$ where C_n is the number of carbon atoms in the alkyl group, were found for the homologous series 1. For the retention index and ρ (solute ethanol) (Fig. 3a) the correlation coefficients are high (0.9939 and 0.9889, respectively). For the other polarity parameters considered the correlation coefficients are low (<0.9) and the errors are high. The polarity index may be correlated with the reciprocal of the molecular weight (M) of the stationary phase (Figs. 3b): for methanol, $PI = 93.33 + 7790/M, r = 0.9950$, and for ethanol, $PI = 79.39 + 6408M, r = 0.9874$.

CONCLUSIONS

Relationships between the polarity parameters and the structures of α,ω-diaminooligoether derivatives are much more complex than those obtained previously
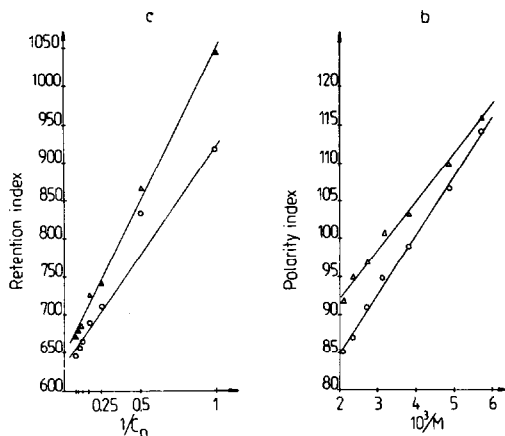
Fig. 3. (a) Retention index *vs.* reciprocal of the length of the alkyl chain; (b) polarity index *vs.* reciprocal of the molecular mass of the stationary phase. O, Methanol; △, ethanol.

for linear compounds. Linear relationships between the polarity parameters and the numbers of oxyethylene groups and carbon atoms present in the alkyl groups are only observed for homologous series and are observed for compounds having enough long alkyl chains and/or oligooxyethylene chain. Two short alkyl chains have a much smaller effect on the polarity than one long alkyl chain.

A cyclohexyl group is equivalent to an *n*-hexyl group. Amides having benzoyl groups are much more polar than the appropriate intermediate α,ω-diaminooligoether derivatives.

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