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POLARITY OF AMINOETHER ALCOHOLS AND THEIR ETHERS MEASURED BY REVERSED-PHASE GAS CHROMATOGRAPHY

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SUMMARY

Gas–liquid chromatography was used to determine the polarity of pure model aminoether alcohols and their ether analogues. Relationships between the polarity parameters are discussed. The polarity parameters are correlated with the compounds' structures and increments for characteristic groups have been determined. They can be used to estimate the polarity of compounds using only their formulae.

INTRODUCTION

The polarity parameters, as measured by reversed-phase gas chromatography (RP-GC), are of importance in determining the hydrophilic–lipophilic balance of non-ionic surfactants and their application has ben the subject of several reviews[1,2]. Recently, we demonstrated that the polarity is also an important parameter in the field of metal extraction[3,4]. Depending upon the extractant polarity, the extraction can proceed according to different mechanisms, *i.e.*, at the interface or in the bulk of the aqueous phase, and with different rates.

The aim of this work was (1) to determine the polarity of new model pure aminoether alcohols and their ethers which have found application as extractants[5], phase-transfer catalysts, surfactants[6] and therapeuticals[7]; (2) to discuss relationships between different polarity parameters and to estimate appropriate increments for characteristic groups present in the molecules, which can be used to predict the compounds' polarities using only their formulae. Thus, this work is a continuation of our previous studies concerning poly(oxyethylene glycol) dialkyl ethers and their sulphur analogues[8,9].

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TABLE I

STRUCTURES AND ANALYTICAL DATA OF THE INVESTIGATED COMPOUNDS

Compound No.	*R*	*n*	*B.p. (°C/Pa)*	n_D^{20}	*Molecular weight*	*Elemental analysis, calc. (found)*			*Yield (%)*	*Complexation**
						C	*H*	*N*		
3	n-C_4H_9**	1	104–105/20	1.4470	261.1	64.39 (64.43)	11.87 (11.57)	5.36 (5.31)	50	1
4	n-C_4H_9**	2	151–154/27	1.4519	349.2	61.91 (62.03)	11.17 (11.09)	4.01 (3.88)	59	2
5	n-C_6H_{13}	2	175–177/13	1.4541	405.2	65.20 (65.17)	11.60 (11.63)	3.45 (3.35)	54	2
6	n-C_8H_{17}	2	200–205/13	1.4558	461.3	67.70 (67.41)	11.92 (11.80)	3.03 (2.80)	50	2
7	n-C_4H_9**	3	218–222/7	1.4557	438.8	60.29 (60.22)	10.95 (10.80)	3.20 (2.96)	59	3
8	n-C_4H_9	1	134–235/11	1.4429	361.2	66.50 (66.49)	11.90 (11.79)	3.88 (3.52)	36	1
9	n-C_4H_9	2	196–206/20	1.4499	493.3	63.30 (63.55)	11.15 (11.15)	2.84 (2.73)	34	3
10	n-C_6H_{13}	2	215–220/7	1.4525	577.3	66.57 (66.53)	11.60 (11.66)	2.42 (2.3)	30	3
11	n-C_8H_{17}	2	242–245/13	1.4548	661.4	69.00 (69.02)	11.94 (11.83)	2.12 (2.00)	31	3

* Ability to dissolve solid potassium permanganate in chloroform: 1, no coloration; 2, a weak violet colour; 3, a strong violet colour.

** Compounds previously described[6].

EXPERIMENTAL

Reagents

Nine pure model compounds (Table I) were used. They were synthesized according to the folowing reaction schemes:

$$\underset{1}{H_2NCH_2CH_2OH} + \underset{2}{R(OCH_2CH_2)_nCl} \xrightarrow{Na_2CO_3} \underset{3\text{–}7}{[R(OCH_2CH_2)_n]_2NCH_2CH_2OH}$$

$$\underset{1}{H_2NCH_2CH_2OH} + \underset{2}{R(OCH_2CH_2)_nCl} \xrightarrow{NaOH} \underset{8\text{–}11}{[R(OCH_2CH_2)_n]_2N(CH_2CH_2O)_{n+1}R}$$

The aminoethanol (1) and the solid base (sodium carbonate or sodiumhydroxide) were placed in a four-neck round-bottom flask (500 ml) equipped with a stirrer, dropping funnel, thermometer and a reflux condenser. The flask was then heated to 80°C with vigorous stirring, and the alkylglycol chloride (2) was slowly added. The mixture was heated under reflux to 120–140°C for 15–20 h, then cooled to room temperature and the liquid was separated from the solids by suction. The precipitate was washed with acetone, and the cooled organic phases were dried over sodium sulphate. After removing the acetone, the residue was repeatedly distilled under reduced presure. The molar ratio of the reagents for aminoether alcohol (3–7) synthesis was 1:2:Na_2CO_3 = 1:2:1.2 (yields 50–60%) and for the aminoethers (8–11) was 1:2:NaOH = 1:3:3.2 (yields 30–40%).

The purity of the compound was demonstrated by thin-layer chromatography (TLC) and/or GC. Silufol plates (UV 254; Kavalier, Czechoslovakia) were used. The products were developed with toluene–acetone–methanol–aqueous ammonia (31:21:5:1.5, v/v) and detected by spraying with a solution of cobalt (II) thiocyanate or Dragendorffs reagent. For GC, the columns (1 m × 3 mm I.D. or 2 m × 3 mm I.D.) were filled with SE-30 as a liquid phase. The column temperature was 230–310°C.

Chromatographic measurements

Chromatographic measurements were carried out using a Chrom 5 gas chromatograph (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) extractant on Porolith (mesh size 0.2–0.5 mm); carrier gas (helium), 40 ml/min; solutes, methanol, ethanol, butanol, 2-pentanone, benzene, pyridine, nitropropane and C_5–C_{11} *n*-alkanes; time for column stabilization, 10 h.

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; polarity index of methanol and ethanol, PI = 100 log $(C-4.7)$ + 60, where C is the apparent carbon number of a standard *n*-alkane having the same retention time as the alcohol; coefficient ρ, defined as the ratio of the retention times of the alcohol and *n*-hexane; partial molal free energies of solution of hydroxyl, ΔG_s^m(OH), and carbonyl groups, $\Delta G_s^m(>C=O)$; McReynolds constants.

Partial molal Gibbs free energies of solution were calculated as described by Risby[10,11] and used in our previous work[12]. McReynolds constants were calculated in the standard way using the retention indices of benzene, butanol, 2-pentanone, pyridine and nitropropane as determined on the surfactant considered and on squalane, respectively.

RESULTS AND DISCUSSION

The values of the polarity parameters obtained are given in Tables II and III (the compound numbering is as in Table I). The precision of the determination of I_R, PI and ρ is good and similar to that in our previous work[8,9]. The confidence limits at the significance level of 0.05 amount to about 1, 0.1 and 0.01 for I_R, PI and ρ, respectively.

For ethanol (EtOH), higher values of I_R, PI, ρ and $\Delta G_s^m(OH)$ were obtained in comparison to methanol (MeOH). The two sets of parameters can be correlated according to the following linear equations:

$$I_R^{EtOH} = 1.0044 \cdot I_R^{MeOH} + 40.7 \quad , R = 0.9980$$

$$PI^{EtOH} = 0.8162 \cdot PI^{MeOH} + 25.22 \quad , R = 0.995$$

$$\rho^{EtOH} = 1.2509 \cdot \rho^{MeOH} + 0.322 \quad , R = 0.9890$$

$$\Delta G_s^m(OH)^{EtOH} = 1.0731 \cdot \Delta G_s^m(OH)^{MeOH} + 2.12 \quad , R = 0.9700$$

The values of the regression coefficient, R, are high and demonstrate the statistical significance of these equations.

The relationships between first three polarity parameters are similar to these found previously for other groups of compounds (Fig. 1). As the coefficient ρ increases the retention index and the polarity index also increase, both for methanol and ethanol.

The partial molal Gibbs free energies of solution of the hydroxyl and carbonyl groups, and the McReynolds constants, change in a similar order to that of the three previous parameters. However, the influence of the compounds' structures is different for each parameter considered. The coefficient ρ is the most sensitive and the quantity

TABLE II

POLARITY PARAMETERS

Compound No.	I_R		*PI*		ρ	
	MeOH	*EtOH*	*MeOH*	*EtOH*	*MeOH*	*EtOH*
3	695	740	95.4	103.0	2.15	3.40
4	720	765	99.7	107.5	2.70	3.86
5	666	706	89.5	97.4	1.73	2.40
6	638	683	82.8	93.1	1.37	1.99
7	736	785	102.0	109.3	3.16	4.28
8	644	687	84.4	94.0	1.45	2.10
9	761	800	107.6	111.9	3.99	5.15
10	660	705	87.3	97.2	1.95	2.63
11	624	666	79.6	89.7	1.23	1.77

TABLE III

POLARITY PARAMETERS

Compound No.	$\Delta G_s^m(OH)$ (kJ/mol)		$\Delta G_s^m(>C=O)$ (kJ/mol)	$\sum_{i=1}^{5} \Delta I$
	MeOH	EtOH		
3	−10.4	− 9.1	− 9.8	1071
4	−11.0	− 9.8	−10.0	1308
5	−10.2	− 8.7	− 9.3	1030
6	− 9.8	− 8.5	− 8.7	935
7	−11.6	−10.4	−10.3	1341
8	−10.1	− 8.7	− 8.8	864
9	−10.8	− 9.2	−10.0	1351
10	− 9.7	− 8.3	− 9.0	882
11	− 9.7	− 8.3	− 8.9	833

$(\rho_{max} - \rho_{min}/\rho_{min}) \cdot 100\%$, changes by about 200%. The McReynolds constants change by about 60%, but all other parameters change by only about 20%. Thus, the use of ρ and $\Sigma\Delta I$ to characterize the compounds' polarities should be favoured.

However, when the relationships between $\Sigma\Delta I$ and I_R, PI, ρ, ΔG_s^m(OH) and $\Delta G_s^m(>C=O)$ are considered, the parameters discussed usually increase as the $\Sigma\Delta I$ increases. However, the experimental points are scattered (Figs. 2 and 3), and the derivation of a simple and accurate relationship is impossible. Therefore linear relationships were derived as a first approximation, and their regression and correlation coefficients are given in Table IV. Although the correlation coefficients are relatively low, *i.e.*, in the range of 0.91–0.96, these approximately linear relationships between the polarity parameters calculated only from the retention times of ethanol and methanol demonstrate that proton donor–proton acceptor interactions are the most important for the group of compounds considered and can well characterize their polarities.

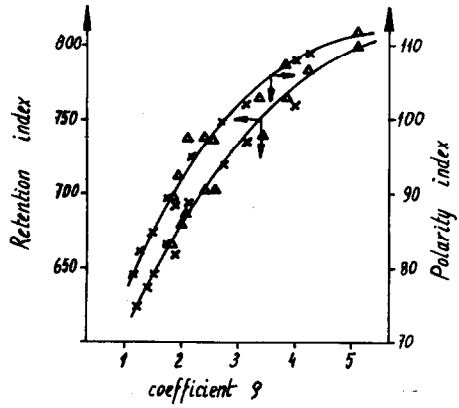

Fig. 1. Relationships between the retention index, the polarity index and the coefficient ρ for methanol (×) and ethanol (△).

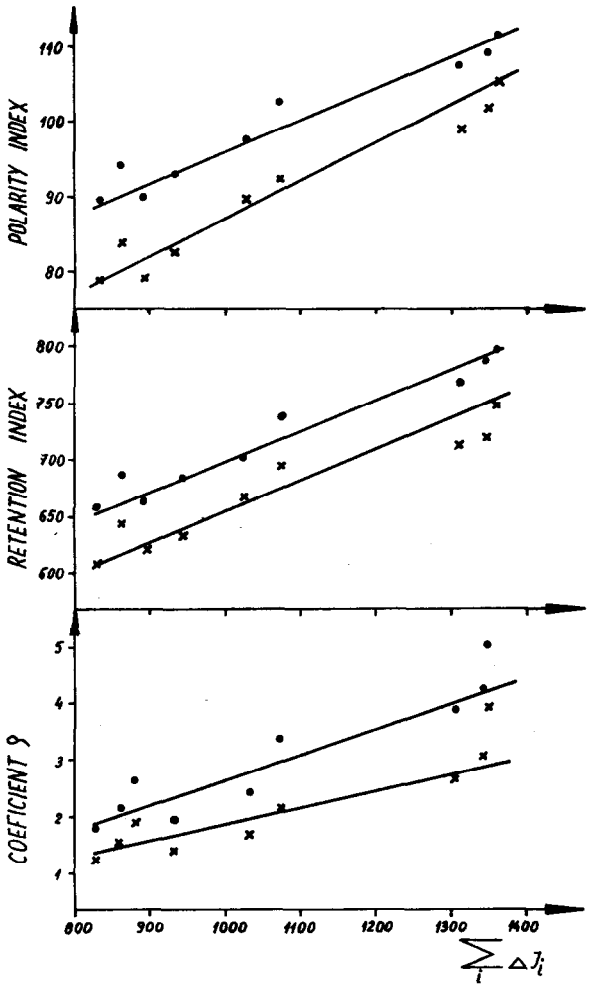

Fig. 2. Relationships between the polarity parameters determined from the retention times of alcohols (×, methanol; O, ethanol) and the McReynolds constants.

The influence of the compounds' structures upon their polarity parameters is shown in Fig. 4. The values of all the parameters considered increase almost linearly as the number of the oxyethylene units increases. Thus, the slopes of the straight lines give the increments in the polarity parameters per oxyethylene unit for each homologous series of compounds. The values of the polarity parameters decrease as the alkyl chain length increases. However, deviations from the straight lines are significant and the influence of the alkyl chain length decreases for compounds having longer chains.

The values of the parameters considered can be used to estimate the average increments for the characteristic groups present in the compounds. Assuming additivity of the polarity parameters, the polarity of a compound A_i (P_{A_i}), can be expressed as

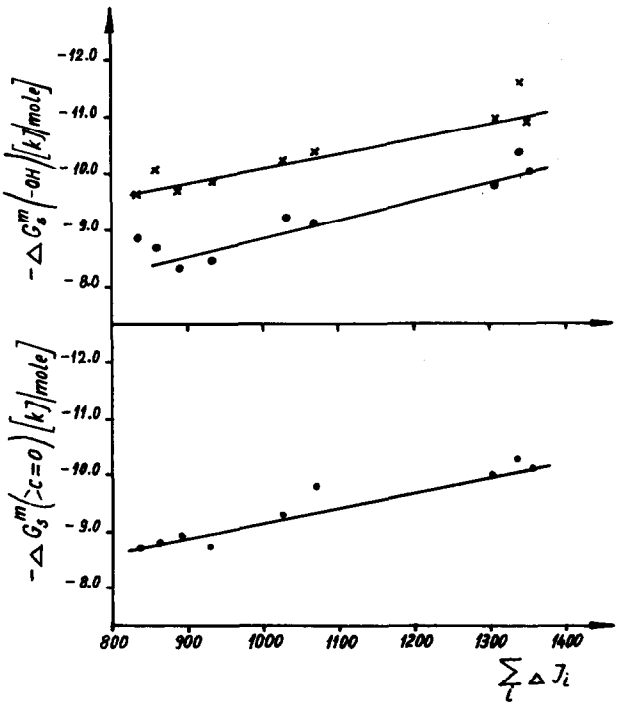

Fig. 3. Relationships between the partial molal Gibbs free energies of solution and the McReynolds constants for methanol (×) and ethanol (○).

TABLE IV

REGRESSION AND CORRELATION COEFFICIENTS FOR THE RELATIONSHIP

$P_i = a + b\Sigma\Delta I$

Polarity parameter, P_i	*Alcohol*	*a*	*b*	*Correlation coefficient*
I_R	MeOH	452.4	0.2155	0.9609
	EtOH	494.0	0.2174	0.9633
PI	MeOH	45.92	0.0432	0.9566
	EtOH	62.37	0.0355	0.9608
ρ	MeOH	−2.06	$3.981 \cdot 10^{-3}$	0.9159
	EtOH	−2.42	$5.137 \cdot 10^{-3}$	0.9346
ΔG_s^m(OH)	MeOH	−7.34	$-2.834 \cdot 10^{-3}$	0.9231
	EtOH	−5.86	$-2.935 \cdot 10^{-3}$	0.9346
ΔG_s^m(>C=O)		−6.56	$-2.679 \cdot 10^{-3}$	0.9385

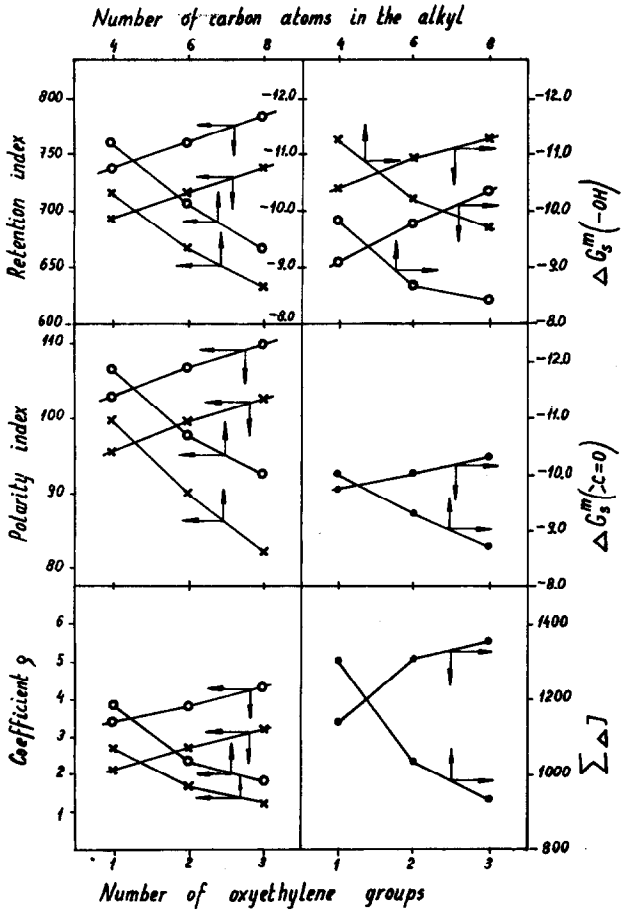

Fig. 4. Effect of the oligooxyethylene and alkyl chains upon the polarity parameters for methanol (×) and ethanol (○).

$$P_{A_i} = \sum_{j=1}^{m} a_{ji} \Delta P_{G_j} + \text{constant}$$

where it is assumed that the increment, ΔP, for a group G_j is constant for all compounds present in the system. The coefficient a_{ji} denotes the number of G_j groups in compound A_i, whose chemical formula can be expressed as

$$A_i = (G_1)_{a_{1i}} (G_2)_{a_{2i}} \ldots (G_m)_{a_{mi}}$$

where j denotes the characteristic group considered and $j = 1,2,\ldots, m$.

When the set of polarity parameters obtained for all compounds present in the system is considered (n being the number of compounds present) the following set of linear equations is obtained

TABLE V

INCREMENTS OF THE POLARITY PARAMETERS

Polarity parameter		*CH_2, CH_3*	*-O-*	*>NOH*	*>N-*	*Constant*	*Error*	
							Absolute	*Relative*
I_R	MeOH	−9.40	44.57	2838	2867	−3533	12	1.7
	EtOH	−9.47	45.34	4333	4300	−3594	11	1.5
PI	MeOH	−1.91	8.71	1055	1049	−959	2.4	2.5
	EtOH	−1.57	7.23	250.8	256	−354	1.8	1.7
ρ	MeOH	−0.374	0.905	23.62	23.2	−21.67	0.26	11.6
	EtOH	−0.288	1.107	49.8	50.4	−53.03	0.34	11.2
ΔG_s^m(OH)	MeOH	0.114	−0.546	−71	60.4	0.2	2.0	
	EtOH	0.114	−0.550	−95.1	−96.0	104	0.2	3.0
ΔG_s^m(>C=O)		0.108	−0.545	−40.9	−41.6	50.5	0.2	1.8
$\Sigma\Delta I$		−38.16	172	6357	6144	−5129	70	6.6

$$P = A \cdot \Delta P$$

where

$$P = [P_{A_1}, P_{A_2}, \ldots, P_{A_n}]^T$$

$$\Delta P = [\Delta P_{A_1}, \Delta P_{A_2}, \ldots, \Delta P_{A_n}]^T$$

$$A = (a_1, a_2, \ldots, a_n)$$

$$a_i = [a_{1i}, a_{2i}, \ldots, a_{mi}]^T$$

By solving these equations in the same way as in our previous work[13] the values of the increments were obtained (Table V). They can be used to predict the polarity parameters for the compounds considered and their homologues only from their formulae. The accuracies of such predictions are good and the errors amount to only 1.3–3% for I_R, PI, ΔG_s^m(OH) and ΔG_s^m(>C=O) and 7% for $\Sigma\Delta I$. The coefficient ρ is determined with lower precision, the error exceeding 10%.

CONCLUSIONS

The polarity parameters calculated only from the retention times of the alcohols (methanol or ethanol) and standard alkanes characterize well the polarity of the compounds considered. They are approximately linearly correlated with the McReynolds constants. The polarity increases as the number of oxyethylene units increases and as the length of the alkyl chain decreases. The increments determined for characteristic fragments of the compounds can be used to estimate the polarity parameters only from the compounds' formulae. The errors of such predictions are 1.3–3% for I_R, PI, ΔG_s^m(OH), ΔG_s^m(>C=O), 7% for $\Sigma\Delta I$ and above 10% for the coefficient ρ.

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