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POLARITY OF 1,3-BIS[ω-BUTOXYOLIGO(OXYETHYLENE)]PROPAN-2-OLS AS MEASURED BY REVERSED-PHASE GAS CHROMATOGRAPHY

ADAM VOELKEL and JAN SZYMANOWSKI*

Technical University of Poznań, Institute of Chemical Technology and Engineering, Pl. M. Skłodowskiej-Curie, Poznań (Poland)

and

JÖRG BEGER and KERSTIN EBERT

Mining Academy at Freiberg, Freiberg (G.D.R.)

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SUMMARY

Gas–liquid chromatography was used to determine the polarity of pure model 1,3-bis[ω-butoxyoligo(oxyethylene)]propan-2-ols. Relationships between the polarity parameters are discussed. The polarity parameters are correlated with the compounds' structures. The influence of the oxyethylene groups is evaluated.

INTRODUCTION

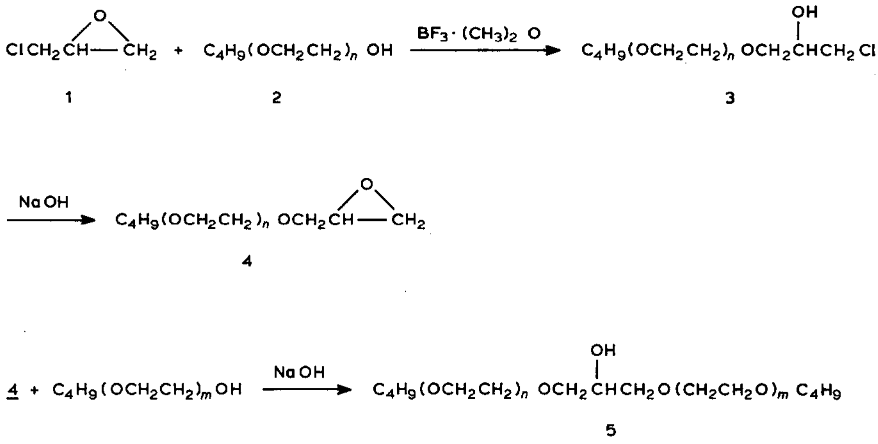
In previous studies[1,2] the polarities of poly(oxyethylene glycol)dialkyl ethers and some of their sulphur analogues were determined and correlated with the compounds' structures. The relationships between different polarity parameters were considered. The polarities of some aminoether alcohols and their ethers were also recently reported[3].

The aim of this work is to determine the polarities of pure individual 1,3-bis[ω-butoxyoligo(oxyethylene)]propan-2-ols containing different numbers of ethoxy units in the two butoxyoligo(oxyethylene) groups and to correlate these polarities with the compounds' structures. Compounds of this type have been tested as crown ether analogues for the extraction of alkaline and alkaline earth metals.

EXPERIMENTAL

Reagents

The model compounds used are listed in Table I. They were synthesized according to the following scheme:



The general procedure for synthesis of 1,3-substituted propan-2-ols was described previously[4–6], but physical data for these compounds are known only for (5, $n = m = 0$)[7].

Treatment of epichlorohydrin (1, 1 mol) with an excess of butoxyoligoethylene glycol (2, n = 0–3, 2 mol) in the presence of catalytic amounts of boron trifluoride (0.01 mol) afforded the corresponding chlorohydrin ether (3) in good yields. The product was purified by distillation, the excess of butoxyethylene glycol first being removed.

Treatment of the halohydrin ether (3) with a strong base (50% aqueous sodium hydroxide) resulted in epoxide ring closure to afford the glycidyl ethers (4), which for n = 0–2 were described previously[8–10]. The appropriate butoxyoligoethylene glycol (m = 0–4) was then added to the pure glycidyl ether (4) together with a basic catalyst (solid sodium hydroxide, 0.025 mol). The crude product was repeatedly distilled under reduced pressure.

The purity of the substituted propan-2-ols (5) was demonstrated by thin-layer chromatography (TLC) and/or gas–liquid chromatography (GLC), ^{1}H NMR spectroscopy and elemental analysis.

Chromatographic measurements

Chromatographic measurements were carried out using a Chrom 5 gas chromatograph (Kovo, C.S.S.R.) equipped with a flame ionization detector. The conditions were as follows: column (1 m × 3 mm I.D.), 25% (w/w) compound on Porolith (mesh size 0.2–0.5 mm); column temperatures, 70 and 90°C; carrier gas (helium) flow-rate, 40 ml/min; solutes, methanol, ethanol, *n*-butanol, 2-butanone, 2-pentanone, benzene, pyridine, 1-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 retention time and/or 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 number of carbon atoms in a standard *n*-alkane having the same retention time as that of the alcohol; coefficient ρ, defined as the ratio of the retention

TABLE I

STRUCTURE AND ANALYTICAL DATA FOR THE COMPOUNDS INVESTIGATED

Formula		*B.p.* *(°C/Pa)*	n_D^{20}	*Molecular weight*	*Elemental analysis, calc/found (%)*		*Yield (%)*
n	*m*				*C*	*H*	
0	0	83–84/13	1.4307	204.11	64.70/64.71	11.76/11.76	38
	1	123–124/53	1.4362	248.13	62.90/63.09	11.29/11.31	52
	2	147–153/27	1.4426	292.15	61.64/61.74	10.96/10.85	30
	3	165–168/27	1.4449	336.17	60.71/60.78	10.71/10.76	33
	4	178–180/13	1.4474	380.19	60.00/59.78	10.52/10.60	60
1	1	146–148/27	1.4409	292.15	61.64/61.70	10.96/10.81	27
	2	158–160/20	1.4446	336.17	60.71/60.98	10.71/10.71	30
	3	200–203/40	1.4478	380.19	60.00/59.92	10.51/10.31	39
	4	196–198/7	1.4495	424.21	59.40/59.44	10.40/10.54	31
2	2	175–177/27	1.4470	380.19	60.00/59.97	10.52/10.61	31
	3	223/53	1.4500	424.21	59.40/59.29	10.40/10.28	49
	4	220–222/7	1.4520	468.23	59.00/59.01	10.26/10.37	38
3	3	221–224/27	1.4519	468.23	59.00/59.00	10.26/10.40	50
	4	248–250/27	1.4535	512.25	58.60/58.52	10.16/10.31	45

times of the alcohol and *n*-hexane; partial molal free energies of solution of hydroxyl, ΔG_s^m (OH), and carbonyl groups, ΔG_s^m (C=O); McReynolds constants.

Partial molal Gibbs free energies of solution were calculated as described by Risby and co-workers[11,12] and as in our previous work[3]. McReynolds constants were calculated in the standard way using retention indices for benzene, *n*-butanol, 2-pentanone, pyridine and 1-nitropropane, as determined on a surfactant and on squalane, respectively.

RESULTS AND DISCUSSION

The values of the polarity parameters considered are given in Tables II and III. The precision of their determination is good and similar to that found in our previous work[1–3].

Using ethanol, higher values of the retention index, I_R, the polarity index (PI), the retention of the alcohol relative to *n*-hexane, ρ, and of the partial molal Gibbs free energies of solution of the hydroxyl group, ΔG_s^m (OH), are obtained in comparison to values determined for methanol. To a first approximation, these parameters can be correlated as follows:

$$I_R^{EtOH} = 202.176 + 0.7585\, I_R^{MeOH},\ R = 0.9686$$

$$PI^{EtOH} = 40.152 + 0.9487\, PI^{MeOH},\ R = 0.9897$$

$$\rho^{EtOH} = 0.6314 + 0.9487\, \rho^{MeOH},\ R = 0.9539$$

$$\Delta G_s^m\,(OH)^{EtOH} = -4.594 + 0.4423\, \Delta G_s^m\,(OH)^{MeOH},\ R = 0.9333$$

TABLE II

POLARITY PARAMETERS

Formula		*Solute*	I_R		*PI*		ρ	
n	*m*		*70°C*	*90°C*	*70°C*	*90°C*	*70°C*	*90°C*
0	0	Methanol	645	–	80.7	–	1.75	–
		Ethanol	680	–	92.3	–	1.98	–
	1	Methanol	655	646	86.9	84.5	1.85	1.41
		Ethanol	699	677	96.2	91.8	2.28	1.79
	2	Methanol	685	681	92.1	91.2	2.12	1.87
		Ethanol	727	709	99.5	98.1	2.66	2.22
	3	Methanol	716	710	97.5	96.1	2.69	2.43
		Ethanol	738	725	103.2	101.2	3.06	2.54
	4	Methanol	740	730	102.7	101.7	3.25	2.85
		Ethanol	755	743	105.7	103.9	3.42	2.85
1	1	Methanol	674	673	91.2	91.0	2.01	1.93
		Ethanol	714	706	98.9	97.3	2.51	2.27
	2	Methanol	700	687	96.4	94.0	2.26	2.10
		Ethanol	738	725	102.9	101.1	3.01	2.63
	3	Methanol	728	720	100.0	97.8	2.80	2.50
		Ethanol	752	739	105.4	103.9	3.40	2.86
	4	Methanol	750	740	103.9	102.5	3.41	2.81
		Ethanol	767	755	107.7	105.6	3.76	3.08
2	2	Methanol	709	705	98.2	97.4	2.41	2.38
		Ethanol	755	739	104.5	103.6	3.34	2.92
	3	Methanol	737	734	103.2	102.5	3.13	2.63
		Ethanol	767	756	107.5	106.1	3.68	3.09
	4	Methanol	754	750	106.3	104.4	3.57	2.95
		Ethanol	776	771	108.9	108.1	3.92	3.30
3	3	Methanol	753	746	105.2	104.4	3.33	2.80
		Ethanol	778	764	109.1	107.2	4.04	3.17
	4	Methanol	770	756	108.3	105.0	3.85	3.80
		Ethanol	782	772	110.0	108.6	4.24	3.40

A similar relationship was found for the partial molal Gibbs free energies of solution of the carbonyl group, ΔG_s^m (C=O), calculated from retention data obtained for 2-pentanone (P) and 2-butanone (B):

$$\Delta G_s^m\,(\mathrm{C{=}O})^P = 0.8128 + 1.0333\Delta G_s^m\,(\mathrm{C{=}O})^B,\ R = 0.9172$$

However, in this case, there are large deviations and as a result the correlation coefficient is low.

The relationship between I_R, PI and ρ are similar to those found previously for other groups of compounds[1–3]. As the retention index increases the polarity index and coeffcient ρ also increase; similar relationships are obtained for methanol and ethanol (Fig. 1).

TABLE III

POLARITY PARAMETERS AT 363 K

Formula		*ΔG_s^m (OH) (kJ/mol)*		*ΔG_s^m (C=O) (kJ/mol)*		$\sum_{i=1}^{5} \Delta I_i$
n	*m*	*Methanol*	*Ethanol*	*2-Butanone*	*2-Pentanone*	
0	0	—	—	—	—	—
	1	−10.3	−9.3	−9.4	−8.6	1007
	2	−10.6	−9.1	−9.7	−9.4	1155
	3	−10.8	−9.3	−10.0	−9.6	1262
	4	−11.0	−9.4	−10.1	−9.8	1319
1	1	−10.4	−9.2	−9.7	−9.3	1128
	2	−10.6	−9.3	−10.1	−9.5	1223
	3	−10.9	−9.4	−10.2	−9.8	1320
	4	−11.1	−9.5	−10.3	−9.9	1406
2	2	−10.8	−9.3	−10.1	−9.4	1339
	3	−11.0	−9.5	−10.4	−9.8	1399
	4	−11.2	−9.6	−10.6	−10.0	1476
3	3	−11.2	−9.5	−10.6	−10.1	1460
	4	−11.4	−9.6	−10.7	−10.3	1503

The partial molal Gibbs free energies of solution of the hydroxyl and carbonyl groups, and the McReynolds constants, exhibit similar trends to those of the previous three parameters. However, some important deviations are observed, which are probably connected with the much higher errors of determination of these thermodynamic parameters. Generally higher errors are observed for more volatile compounds which are more rapidly eluted, *e.g.*, methanol in comparison to ethanol. Moreover, the influence of the compounds' structures is somewhat different for each parameter considered. Coefficient ρ and the McReynolds constants are the most sensitive parameters while the thermodynamic functions are the least sensitive.

When relationships between $\Sigma \Delta I$ and I_R, PI, ρ, ΔG_s^m (OH) and ΔG_s^m (C=O) are considered, straight lines are obtained (Figs. 2 and 3), as in the case of aminoether

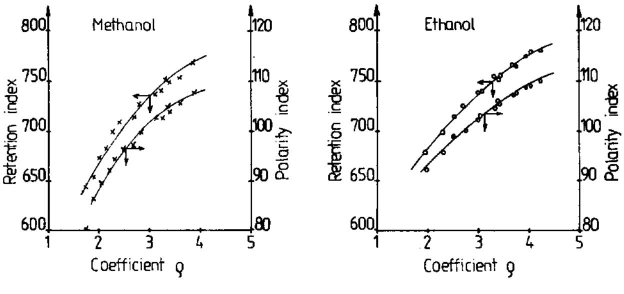
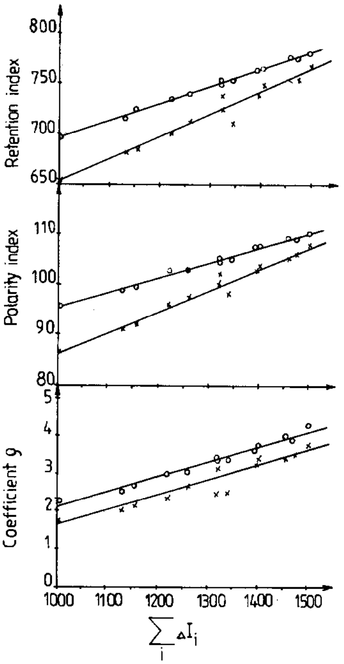


Fig. 1. Relationships between the retention index, the polarity index and the coefficient ρ for methanol (×) and ethanol (O).



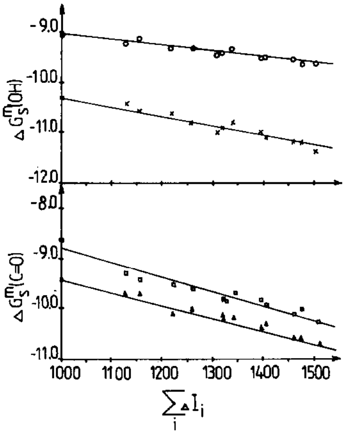


Fig. 2. Relationships between the polarity parameters determined from the retention times of the alcohols and the McReynolds constant for methanol (×); ethanol (○).

Fig. 3. Relationships between the partial molal Gibbs free energies of solution and the McReynolds constant for methanol (×), ethanol (○), 2-butanone (△) and 2-pentanone (□).

TABLE IV

REGRESSION AND CORRELATION COEFFICIENTS FOR THE RELATIONSHIPS $P_i = a + b \Sigma \Delta I$

P_i = Polarity parameter.

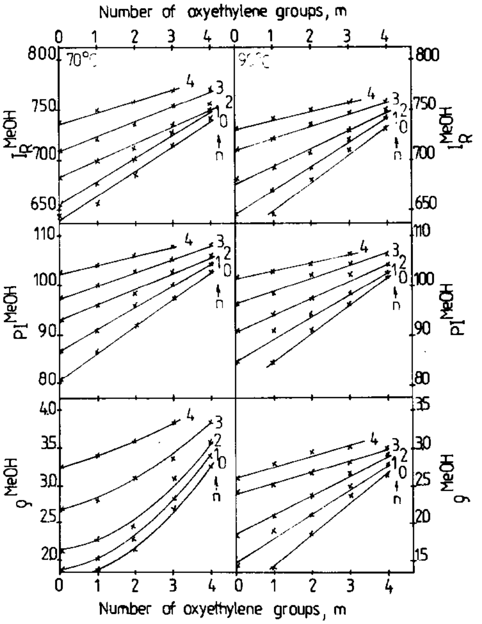
Polarity parameter	*Solute*	*a*	*b*	*Correlation coefficient*
I_R	Methanol	432.767	0.220	0.9690
	Ethanol	517.773	0.177	0.9950
PI	Methanol	39.879	0.045	0.9771
	Ethanol	64.991	0.030	0.9920
ρ	Methanol	−2.016	$3.176 \cdot 10^{-3}$	0.9333
	Ethanol	−1.794	$3.925 \cdot 10^{-3}$	0.9913
ΔG_s^m (OH)	Methanol	−8.016	$-2.176 \cdot 10^{-3}$	0.9767
	Ethanol	−8.231	$-8.9371 \cdot 10^{-3}$	0.9851
ΔG_s^m (C=O)	2-Butanone	−6.948	$-2.435 \cdot 10^{-3}$	0.9821
	2-Pentanone	−6.285	$-2.579 \cdot 10^{-3}$	0.9832

alcohols[3]. The values of the regression coefficients given in Table IV demonstrate the statistical significance of these relationships. In one case the correlation coefficient is 0.93, but in all other cases the values are in the range of 0.97–0.99.

The linear relationships between the McReynolds constants and the polarity parameters calculated only from the retention times of methanol and ethanol demonstrate that proton donor–proton acceptor interactions are the most important for the group of compounds considered, and thus the polarities are well characterized.

The influence of the compounds' structures upon their polarity parameters is shown in Figs. 4–6. Similar changes are observed for all polarity parameters obtained from the retention data for methanol and ethanol. Differences are observed only for low polarity compounds. All the polarity parameters, increase approximately linearly as the number of oxyethylene units increases. The opposite effect is observed for the molal free energies of solution of the hydroxyl and carbonyl groups, which approximately linearly decrease as the number of oxyethylene groups increases.

The values of the slopes which denote the appropriate increments of the polarity parameters for one oxyethylene group are given in Tables V and VI. The values of the regression coefficients calculated for the linear relationships are also given. The influence of the oxyethylene group upon the polarity depends upon the number of such groups in the first butoxyoligooxyethylene chain, *n*, and as this number increases the influence of the oxyethylene groups present in the second butoxyoligooxyethylene chain significantly decreases. As a result, gentler slopes were obtained for compounds having higher "*n*" values.



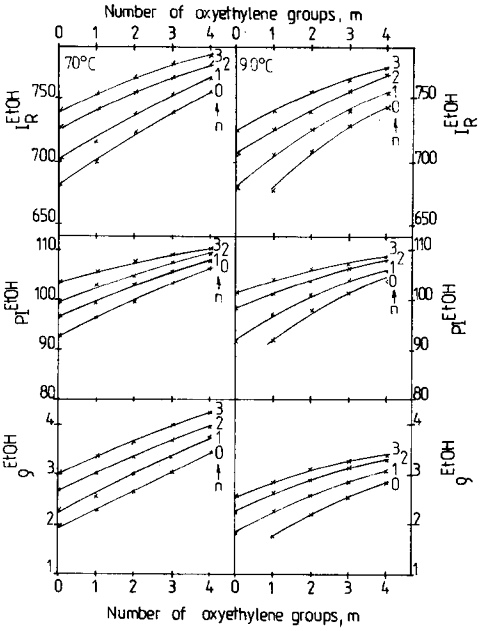


Fig. 4. Effect of the oligooxyethylene chain upon the empirical polarity parameters for methanol.

Fig. 5. Effect of the oligooxyethylene chain upon the empirical polarity parameters for ethanol.

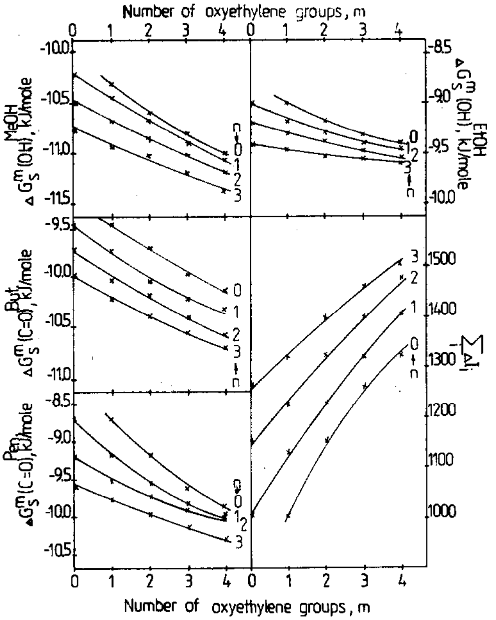


Fig. 6. Effect of the oligooxyethylene chain upon the thermodynamic polarity parameters.

TABLE V

SLOPES AND CORRELATION COEFFICIENTS FOR THE RELATIONSHIPS $P_i = a + bm$

P_i = Polarity parameter; n = constant; R = correlation coefficient.

Polarity parameter	*n*	*Methanol*				*Ethanol*			
		70°C		*90°C*		*70°C*		*90°C*	
		b	*R*	*b*	*R*	*b*	*R*	*b*	*R*
I_R	0	25.1	0.9856	28.1	0.9928	18.9	0.9907	21.4	0.9800
	1	24.4	0.9982	23.5	0.9946	17.4	0.9957	18.9	0.9886
	2	17.5	0.9866	18.5	0.9803	12.4	0.9950	15.5	0.9997
	3	13.3	0.9927	11.8	0.9984	11.4	0.9822	11.9	0.9866
	4	9.4	0.9726	8.8	0.9939	9.0	0.9891	10.0	0.9573
PI	0	5.46	0.9994	5.65	0.9981	3.38	0.9976	3.94	0.9773
	1	4.28	0.9980	4.28	0.9925	2.95	0.9952	3.42	0.9780
	2	3.52	0.9920	3.49	0.9930	2.34	0.9907	2.49	0.9978
	3	2.68	0.9981	2.44	0.9650	1.73	0.9881	1.81	0.9836
	4	1.92	0.9923	1.18	0.9793	1.41	0.9888	1.66	0.9738
ρ	0	0.38	0.9639	0.49	0.9986	0.37	0.9989	0.35	0.9967
	1	0.34	0.9921	0.34	0.9909	0.38	0.9954	0.32	0.9846
	2	0.38	0.9557	0.27	0.9985	0.32	0.9980	0.20	0.9818
	3	0.28	0.9889	0.30	0.9833	0.30	0.9915	0.20	0.9814
	4	0.20	0.9798	0.30	0.9873	0.26	0.9967	0.19	0.9865

The asymmetry of the compounds had some effect upon their polarity parameters, *e.g.*, compounds 5, 8 and 10. However, this effect is relatively weak; more symmetrical compounds exhibit somewhat lower polarity than their asymmetrical isomers.

The influence of the oxyethylene group upon the polarity also depends upon the type of compounds considered. Table VII shows data on the polarity index of methanol determined for three types of compounds: 1,3-bis[ω-butoxyoligo(oxyethylene)]propan-2-ols (A), $BuO(EO)_nCH_2CH(OH)CH_2(OE)_nOBu$; oligooxyethylene monooctyl ethers (B), $OctO\ (EO)_nH$; oligooxyethylene dibutyl ethers (C), $BuO(EO)_nBu$; containing a total of eight carbon atoms in the hydrophobic groups and different numbers of oxyethylene groups. The polarity indices for compounds A are similar to those for compounds B, and much higher than for compounds C. The influence of the additional oxyethylene group upon the polarity index of the more

TABLE VI

SLOPES AND CORRELATION COEFFICIENTS FOR OTHER POLARITY PARAMETERS

Details as in Table V.

Polarity parameter	*Solute*	*n*	*b*	*R*
ΔG_s^m (OH)	Methanol	0	−0.23	0.9944
		1	−0.21	0.9877
		2	−0.16	0.9701
		3	−0.15	0.9847
		4	−0.13	0.9827
	Ethanol	0	−0.14	0.9899
		1	−0.12	0.9783
		2	−0.12	0.9863
		3	−0.07	0.9707
		4	−0.07	0.9839
ΔG_s^m (C=O)	2-Butanone	0	−0.24	0.9797
		1	−0.23	0.9777
		2	−0.21	0.9707
		3	−0.05	0.9883
		4	−0.21	0.9845
	2-Pentanone	0	−0.38	0.9387
		1	−0.31	0.9846
		2	−0.15	0.9714
		3	−0.17	0.9734
		4	−0.16	0.9562
$\sum_{i=1}^{5} \Delta I_i$	—	0	104	0.9814
		1	99	0.9980
		2	82	0.9952
		3	62	0.9866
		4	62	0.9707

TABLE VII

COMPARISON OF THE POLARITY INDEX FOR 1,3-BIS[ω-BUTOXYOLIGO(OXYETHYLENE)]PROPAN-2-OLS (A), OLIGOOXYETHYLENE MONOOCTYL ETHERS (B) AND OLIGOOXYETHYLENE DIBUTYL ETHERS (C)

Methanol as the solute; 70°C.

Total length of oligooxyethylene chain	*Polarity index*			
	*A**		*B*[13,14]	*C*[2,14]
2	91.2	1,1	93.2	60.5
4	98.2	2,2	101.5	72.3
5	103.2	2,3	–	–
5.2	–		102.3	80.0
6	105.2	3,3	–	–
6.4	–		105.4	87.0
7	108.3	3,4	–	–
8	–		107.7	93.8

* With the distribution of oxyethylene groups in the two oligooxyethylene chains.

polar compounds A and B is much weaker than in the case of the less polar oligooxyethylene dibutyl ethers. For the group of compounds A considered, the influence of the oxyethylene group is similar to that observed previously for oligooxyethylene monoalkyl ethers.

CONCLUSIONS

The polarity parameters considered, which were calculated only from the retention time of the alcohol (methanol or ethanol) and standard alkanes, characterize well the polarity of the compounds. They are approximately linearly correlated with the McReynolds constants. The polarity increases as the number of oxyethylene groups increases, but in a different way for compounds having different structures. The influence of the number of oxyethylene groups upon the polarity depends upon the number of these groups in the first butoxyoligooxyethylene chain, and as this number increases the influence of the oxyethylene groups present in the second butoxyoligooxyethylene chain significantly decreases.

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