Journal of Chromatography, 387 (1987) 233–240
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

CHROM. 19 052

EFFECT OF END GROUP AND SOLVENT ON GEL PERMEATION CHROMATOGRAPHY OF OLIGO(OXYETHYLENE) COMPOUNDS

JOHN R. CRAVEN*, HELEN TYRER, STEPHEN POK LAI LI and COLIN BOOTH
Department of Chemistry, University of Manchester, Manchester M13 9PL (U.K.)
and
DAVID JACKSON
Imperial Chemical Industries PLC, Petrochemicals and Plastics Division, Wilton, Middlesbrough, Cleveland TS6 8JE (U.K.)

(Received August 18th, 1986)

SUMMARY

Samples of three series of homogeneous oxyethylene oligomers: (i) $H(OCH_2CH_2)_mOH$, m in the range 1 to 45; (ii) $CH_3(OCH_2CH_2)_mOCH_3$, m in the range 2 to 45; (iii) $H(CH_2)_n(OCH_2CH_2)_4O(CH_2)_nH$, n = 2, 3, 7, 9; were eluted through a PL-gel low-porosity gel permeation chromatographic column with several solvents; dichloromethane, tetrahydrofuran, 1,1,1-trichloroethane, 1,2,4-trichlorobenzene, and N,N′-dimethylacetamide. The elution volumes of the oligomers were determined by a combination of size-exclusion and partition–adsorption effects.

INTRODUCTION

In the gel permeation chromatography (GPC) of chain compounds the ideal separation mechanism is size exclusion[1]. In practice the elution volume is affected by partitioning of solute between the mobile phase (*i.e.* the solution in the void and the pores) and the gel-surface phase[2–4].

The partition effect (*i.e.* non-size-exclusion effect) can be described most generally in terms of adsorption. The balance of interactions in the system, *i.e.* solvent + solute + gel-surface, may favour positive adsorption of solute on the gel surface and so a larger than ideal elution volume for an injected sample, or negative adsorption and a smaller than ideal elution volume. When specific interactions (*e.g.* H-bonds, charge-transfer complexes, etc.) are involved the effects may be referred to simply as *adsorption, i.e.* a specific interaction between solute and gel resulting in positive adsorption, and *solvation, i.e.* a specific interaction between solute and solvent resulting in negative adsorption.

The concept of adsorption is most useful when the gel surface is not penetrated by the other components, *e.g.* for inorganic gels and organic solvents. With organic gels, or indeed with inorganic gels with surface-bonded phases, the gel-surface phases is swollen with solvent and, in principle at least, can be penetrated by solute. In the

0021-9673/87/$03.50

GPC of high polymers in good solvents the long-chain solute is largely excluded from the surface phase by the excluded volume effect[5]. It is this feature which, in the absence of specific effects, ensures that the GPC of high polymers is predominantly a size-exclusion effect.

In the GPC of oligomers, as in that of small molecules, partitioning is important[2–4,6]. A description of the effect can follow the conventions of solution theory, *e.g.* solubility parameter theory[4]. Thus a positive effect, *i.e.* an increase in elution volume, can be ascribed to a decrease in solubility of solute in the mobile phase relative to that in the gel-surface phase, while a negative effect, *i.e.* a decrease in elution volume, can be ascribed to a relative increase in solubility of solute in the mobile phase.

In a composite separation mechanism involving both size exclusion and partition, a positive partition effect will enhance the separation of two homologues while a negative partition effect will diminish it. This is because the effect of partition is itself size dependent, since smaller molecules more readily penetrate the pores of the gel and thereby have access to a greater gel-surface area.

For a homologous series of oligomers eluted in a single solvent, the contributions of size exclusion and partition to the overall GPC separation are not readily distinguishable. However a change of end group or of solvent provides a means of investigating the process and with this in mind, and also with a view to exploring conditions for GPC of the commercially important alkyl ethoxylate surfactants, we have investigated the elution of three series of homogeneous oxyethylene oligomers: (i) $H(OCH_2CH_2)_mOH$, m in the range 1 to 45; (ii) $CH_3(OCH_2CH_2)_mOCH_3$, m in the range 2 to 45; (iii) $H(CH_2)_n(OCH_2CH_2)_4O(CH_2)_nH$, $n = 2, 3, 7, 9$; through a PL-gel low-porosity column with several solvents; dichloromethane (DCM), tetrahydrofuran (THF), 1,1,1-trichloroethane (TCE), 1,2,4-trichlorobenzene (TCB) and N,N'-dimethylacetamide (DMA).

EXPERIMENTAL

Oligomers

(i) The oligo(oxyethylene) glycols $m = 1$–6 were obtained from commercial sources (BDH, Fluka, Lancaster Synthesis). The higher oligo(oxyethylene) glycols ($m = 9$–45) had been prepared earlier[7–9].

(ii) The oligo(oxyethylene) dimethyl ethers $m = 2$ and 3 were obtained from commercial sources (Hopkin and Williams, Fluka). The dimethyl ethers $m = 4$–6 were prepared by reaction of the glygols with methyl iodide in a modified Williamson reaction[10]. The higher dimethyl ethers had been prepared earlier[11–13].

(iii) The tetra(oxyethylene) dialkyl ethers ($n = 2, 3, 7, 9$) were prepared by reaction of the glycol with an appropriate alkyl bromide, following the procedures described earlier[11–13].

All oligomers were purified and analysed by the procedures described earlier[7–9,11–13]: conversions from glycol to ether were practically complete.

Solvents

THF (Fisons, SLR grade, stabilised), DCM and TCE (BHD, GPR grade) TCB (origin unknown) and DMA (Lancaster Synmthesis) were either distilled (TCB) or filtered before use.

Gel permeation chromatography

Degassed solvent at room temperature (*ca.* 20°C) was pumped (Waters Assoc. Model M45) at 0.5–1.0 cm^3 min^{-1}, depending on viscosity, through a 2-μm prefilter to an injection valve (Rheodyne Model 7010) fitted with an 80 mm^3 loop and then through a second 2-μm filter to a 60 cm × 7.5 mm I.D. PL-gel column (Polymer Labs.) of porosity 50 Å, bead diameter 5 μm, and plate count 47 000 for *o*-dichlorobenzene in THF. Oligomer solutions in the concentration range 0.5 to 9 g dm^{-3}, depending on refractive index increment, were injected through a 1-μm filter. Emerging solute was detected by a Waters Assoc. Model 401 differential refractometer attached either to a strip-chart recorder or to an Apple microcomputer via an Excalibur interface card. The elution volume of an internal marker was also recorded and used to correct the results for a given solvent for possible variation in pumping rate.

RESULTS

Due to differences in refractive index increment the concentration of injected solution varied with the solvent, being usually 5 g dm^{-3} for DCM, TCE and DMA, 2.5 g dm^{-3} for THF and 0.5 g dm^{-3} for TCB. The effect of changing concentration within the range used was checked for selected solvents and found to be small, the variation of peak elution volume (V_{pk}) and of peak width at half-height ($\Delta V_{1/2}$) being within the estimated errors of their determination, *i.e.* ± 0.1 cm^3 for V_{pk}, ±0.03 cm^3 for $\Delta V_{1/2}$.

Impurity peaks at high elution volumes interfered with some of the sample peaks when TCE, TCB and DMA were used as solvents. Also the refractive index increment was small for some of the oligomers in DMA and TCE. Any doubtful results have been omitted from the tables and figures below.

All peaks were slightly skewed, as illustrated in Fig. 1, the effect being least

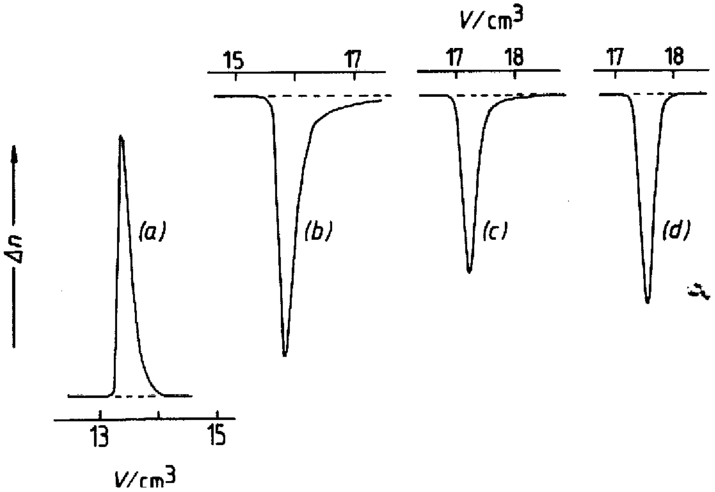

Fig. 1. GPC curves (refractive index difference between solution and solvent, Δn, *versus* volume V) for tetra(oxyethylene) glycol in (a) THF and (b) TCB and for tri(oxyethylene) dimethyl ether in (c) TCE and (d) DMA. The ordinate is arbitrarily scaled.

TABLE I

CONDITIONS FOR GPC

Solvent	*Flow-rate (cm^3 min^{-1})*	*Concentration range (g dm^{-3})*	*Marker*	*Average marker elution volume (cm^3)*
THF	1.0	2.5 ± 0.5	ODCB*	16.17
DCM	1.0	5.0 ± 3.0	ODCB	16.78
			Toluene	14.67
TCE	1.0	7.0 ± 2.0	**	18.28
TCB	0.5	0.75 ± 0.25	Toluene	18.77
			THF	19.85
DMA	0.8	4.0 ± 1.0	ODCB	20.07

* ODCB = *o*-dichlorobenzene.

** Impurity peak (origin unknown) used as marker.

TABLE II

ELUTION VOLUMES (cm³) OF OLIGO(OXYETHYLENE) GLYCOLS AND DIMETHYL ETHERS

Elution volume at peak corrected, for a given solvent, for variation in marker time.

Chain length in oxyethylene units (m)	*Solvent*				
	THF	*DCM*	*TCE*	*TCB*	*DMA*
Oligo(oxyethylene) glycols					
1	14.42	–	–	–	–
2	13.97	13.99	–	–	–
3	13.43	13.22	16.90	–	13.40
4	13.32	12.95	16.20	15.82	13.16
5	12.87	12.52	15.87	15.39	12.94
6	12.54	12.25	15.39	14.75	12.74
15	11.21	10.79	–	12.59	11.65
20	10.90	–	–	–	–
25	10.69	10.33	–	–	–
30	10.47	10.17	–	11.26	10.91
45	–	–	–	–	10.44
Oligo(oxyethylene) dimethyl ethers					
2	–	13.52	16.09	16.35	–
3	14.29	12.91	15.12	15.35	16.70
4	13.70	12.56	14.45	14.65	15.94
5	13.08	12.16	13.91	14.14	15.35
6	12.89	11.92	13.49	13.59	14.84
9	12.18	–	–	–	–
15	11.33	–	–	–	12.43
25	10.67	–	–	–	–
30	10.53	–	–	–	11.24
45	–	9.85	–	10.72	10.57

TABLE III

ELUTION VOLUMES (cm^3) OF TETRA(OXYETHYLENE) DIALKYL ETHERS

Elution volume at peak corrected, for a given solvent, for variation in marker time.

Alkyl chain length (n)	*Solvent*			
	THF	*DCM*	*TCE*	*DMA*
1	13.70	12.56	14.45	15.94
2	13.25	12.54	13.87	16.29
3	13.04	12.54	13.53	16.75
7	12.21	12.10	12.52	17.95
9	11.82	11.85	12.14	–

noticeable for the solvent (DMA) pumped at the lowest flow-rate[1]. Pronounced tailing of peaks towards the high elution volume side was observed with TCB and TCE, particularly for the glycols and the longer diethers (see Fig. 1).

The conditions used for GPC are summarised in Table I, together with values of V_{pk} for the markers. Values of V_{pk} for the samples are listed in Tables II and III. Semi-logarithmic plots of x against V_{pk}, where x is the chain length of the oligomer in C and O chain atoms, are shown in Figs. 2–5.

DISCUSSION

Oligo(oxyethylene) dimethyl ethers

As seen in Fig. 2, V_{pk} for the oligo(oxyethylene) dimethyl ethers increases smoothly as log x decreases. This regularity of behaviour is in keeping with a size-exclusion + partition separation mechanism. The differences in V_{pk} which are observed on changing the solvent are consistent with DCM being the best solvent for the oligomeric diethers, followed by THF, TCE ≈ TCB and DMA the worst. The effect of changing the solvent can be very large, *e.g.* an elution volume of $V_{pk} = 12.9$ cm^3 corresponds to a chain of 12 atoms in DCM but 40 atoms in DMA. Also the

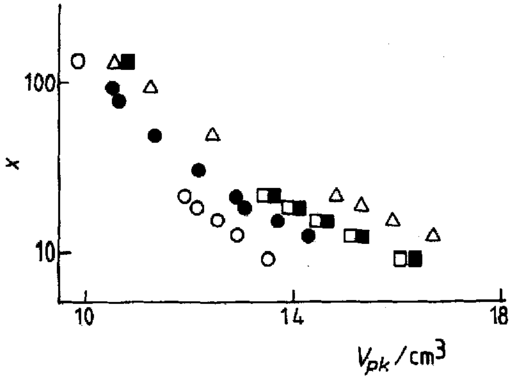

Fig. 2. GPC of oligo(oxyethylene) dimethyl ethers. Chain length x in chain atoms (C or O) on logarithmic scale *versus* elution volume at the peak, V_{pk}, for (○) DCM, (●) THF, (□) TCE, (■) TCB and (△) DMA.

effects are greatest for the smallest oligomers. These results are consistent with an important contribution of partition to the separation process.

Oligo(oxyethylene) glycols

The effects observed on changing the chain-end groups from methoxy to hydroxy are illustrated in Fig. 3. Compared with oligo(oxyethylene) dimethyl ethers of the same chain length the glycols elute: (i) at equivalent elution volumes (V_{pk}) in DCM; (ii) at lower elution volumes in THF, and markedly lower volumes in DMA; (iii) at higher elution volumes in TCB (and in TCE; not illustrated).

Judged by the GPC results DCM is an equally good solvent for both glycols and diethers (see Fig. 3a).

Both THF and DMA solvate the hydroxy end group, by hydrogen bonding to the ether oxygen or to the amido nitrogen and, in consequence, are good solvents for the glycols. The effect of the change in end group is most dramatic for DMA (see Fig. 3c) but is also clearly seen in the results for THF (see Fig. 3b).

A feature of the results for the glycols in THF is the similarity of the elution volumes of the tetramer and the trimer (13 and 10 chain atoms respectively) shown in Fig. 3b. This co-elution of the two glycols is reproducible in the independent THF + PL-gel systems in the two laboratories involved in this work.

As might be expected, TCB and TCE are poorer solvents for the glycols than for the diethers: see Fig. 3d. The skewing of peaks observed in these two solvents is

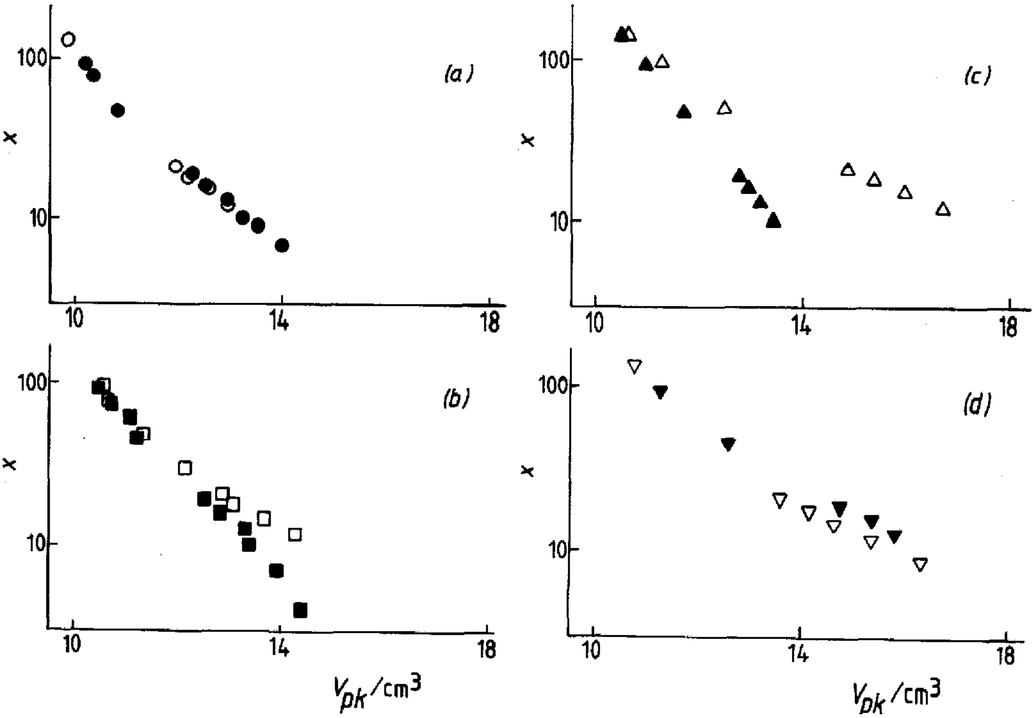

Fig. 3. GPC of oligo(oxyethylene) dimethyl ethers (open symbols) and oligo(oxyethylene) glycols (closed symbols). Chain length x in chain atoms (C or O) on logarithmic scale *versus* elution volume at the peak, V_{pk}, for (a) DCM, (b) THF, (c) DMA and (d) TCB.

suggestive of a specific adsorption process at a limited number of sites, with a slow equilibration time relative to the permeation and partition processes. Presumably end groups of the polystyrene chains of the gel are involved.

The elution volumes of the lowest oligomeric glycols are very similar in the three good solvents, DCM, THF and DMA (see Fig. 4). Since partition between the solution phase and the gel-surface phase is least important in these good solvent systems, the elution behaviour observed approaches most closely to that expected for a size-exclusion process. The differences between the curves for the higher oligomers (see Fig. 4, $x > 20$) can therefore be ascribed mainly to differences in coil expansion in the three solvents, *i.e.* DCM > THF > DMA. The increase in slope of the curve of log x against V_{pk} when $V_{pk} > 13$ cm^3, seen for the three good solvents in Fig. 4, is consistent with this argument since it can be attributed to the reduced selectivity of the size-exclusion effect when the pore size greatly exceeds the solute size.

Oligo(oxyethylene) dialkyl ethers

The effects of changing the chain-end groups of tetra(oxyethylene) compounds from methyl groups to longer alkyl chains, *i.e.* ethyl, propyl, *n*-heptyl and *n*-nonyl, are shown in Fig. 5. Comparison is made with results described earlier for dimethyl ethers.

With DMA as solvent the effect is to increase V_{pk} as the chain length is in-

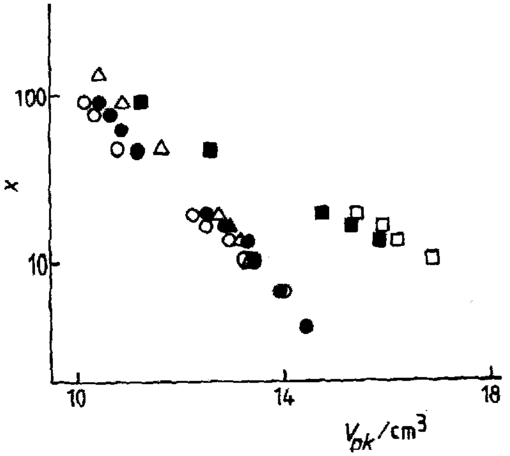

Fig. 4. GPC of oligo(oxyethylene) glycols. Chain length x in chain atoms (C or O) on logarithmic scale *versus* elution volume at the peak, V_{pk}, for (○) DCM, (●) THF, (□) TCE, (■) TCB and (△) DMA.

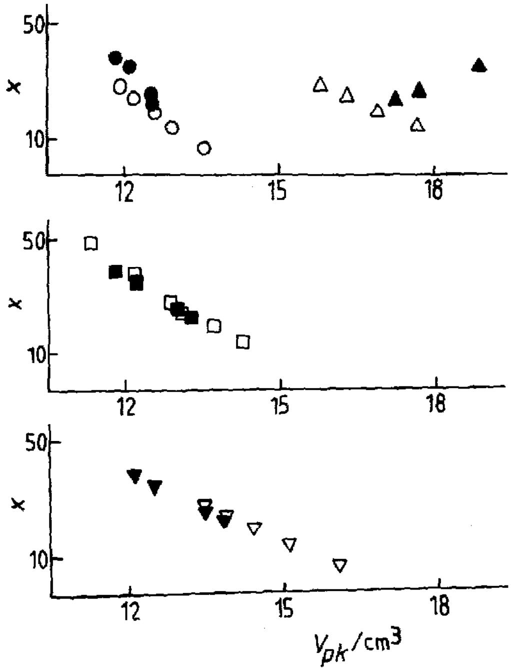

Fig. 5. GPC of oligo(oxyethylene) dimethyl ethers (open symbols) and oligo(oxyethylene) dialkyl ethers (closed symbols). Chain length x in chain atoms (C or O) on logarithmic scale *versus* elution volume at the peak, V_{pk}, for (○, ●) DCM, (△, ▲) DMA, (□, ■) THF and (▽, ▼) TCE.

creased, presumably because DMA is a very poor solvent for the alkyl blocks and partition dominates to such an extent that the usual size effect is reversed.

The effects noted for the other solvents are less spectacular. Compared with TCE, both DCM and THF are better solvents for the dialkyl ethers, as they are for the dimethyl ethers. Dialkyl and dimethyl ethers of equivalent chain length are not separated either in THF or in TCE, presumably because they are solvents which dissolve the oxyethylene and alkyl blocks with roughly equal efficiency. The relative behaviour of the dialkyl and dimethyl ethers in DCM is not easy to explain. However, the later elution of the dialkyl ethers in this solvent, compared with that of dimethyl ethers of the same chain length, is consistent with DCM being a poorer solvent for the alkyl block than for the oxyethylene block.

CONCLUSIONS

The interacting effects of end group and solvent on the GPC behaviour of the oligo(oxyethylene) compounds described here illustrate complexities in the chromatography of the model compounds which will also be met in the chromatography of non-ionic surfactants. None of the solvents used in this work meet the requirement of a separation process related directly to size for the full range of oligomers studied. On balance the best solvent is THF.

ACKNOWLEDGEMENTS

We wish to thank Mr. D. J. Roy for help with the chromatography and Dr. W. C. Campbell for his interest and advice.

REFERENCES

1 W. W. Yau, J. J. Kirkland and D. D. Bly, *Modern Size-Exclusion Liquid Chromatography*, Wiley, New York, 1979.
2 J. V. Dawkins and M. Hemmings, *Makromol. Chem.*, 176 (1975) 1777; 1795; 1815.
3 J. V. Dawkins, *J. Polym. Sci., Polym. Phys. Ed.*, 14 (1976) 569.
4 D. H. Freeman and D. Killion, *J. Polym. Sci., Polym. Phys. Ed.*, 15 (1977) 2047.
5 P. J. Flory, *Principles of Polymer Chemistry*, Cornell University Press, 1953, p. 519.
6 R. B. Walter and J. F. Johnson, *J. Liq. Chromatogr.*, 3 (1980) 315.
7 A. Marshall, R. H. Mobbs and C. Booth, *Eur. Polym. J.*, 16 (1980) 881.
8 H. H. Teo, R. H. Mobbs and C. Booth, *Eur. Polym. J.*, 18 (1982) 541.
9 S. G. Yeates, H. H. Teo, R. H. Mobbs and C. Booth, *Makromol. Chem.*, 185 (1984) 1559.
10 D. R. Cooper and C. Booth, *Polymer*, 18 (1977) 164.
11 R. C. Domszy and C. Booth, *Makromol. Chem.*, 183 (1982) 1051.
12 H. H. Teo, T. G. E. Swales, R. C. Domszy, F. Heatley and C. Booth, *Makromol. Chem.*, 184 (1983) 861.
13 S. G. Yeates and C. Booth, *Makromol. Chem.*, 186 (1985) 2663.