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## GAS CHROMATOGRAPHIC AND SORPTION PROPERTIES OF MACROPOROUS METHACRYLATE COPOLYMERS

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### SUMMARY

The chromatographic properties of copolymers of 2,3-epoxypropyl methacrylate and 2,3-epithiopropyl methacrylate with ethylene dimethacrylate and of their derivatives modified with amines were investigated by means of gas chromatography and by the sorption of sulphur and carbon dioxides. The relative retention volumes and the changes in the free energy of adsorption of various compounds depend on the extent of the specific surface area of copolymers and on the content of functional groups. A study of the sorption of different compounds revealed that with increasing specific surface area the non-specific interactions increase while specific interactions decrease. This suggests that the accessibility of functional groups decreases with increasing extent of cross-linking of the sorbent.

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### INTRODUCTION

In recent years, porous polymers have become widely used as supports in the size-exclusion chromatography of oligomers and polymers, in affinity and gas and liquid adsorption chromatography and also as sorbents of gases and vapours<sup>1,2</sup>. Numerous applications of such polymers have been made possible by the easy chemical modification of some polymer surfaces, by means of which various functional groups can be introduced. Some years ago the chromatographic properties of methacrylate copolymers were investigated<sup>3–5</sup>. This paper describes the sorption and chromatographic properties of methacrylate copolymers with various degrees of cross-linking containing epoxy and epithio groups.

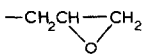
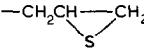
## EXPERIMENTAL

*Materials*

Copolymers based on 2,3-epoxypropyl methacrylate (EPMA) and 2,3-epithiopropyl methacrylate (ETPMA) cross-linked with ethylene dimethacrylate (EDMA) were prepared by suspension radical copolymerization in the presence of inert solvents, as described elsewhere<sup>6,7</sup>. Table I summarizes the chemical compositions and pore characteristics of the synthesized macroporous copolymers.

TABLE I

PROPERTIES OF SORBENTS BASED ON COPOLYMERS OF EPMA AND ETPMA WITH EDMA PREPARED IN THE PRESENCE OF CYCLOHEXANOL-DODECANOL AS A POROGENIC AGENT

Sorbent No.	Functional groups	Content of groups (mmol/g) <sup>a</sup>	EDMA <sup>b</sup> (%)	Cyclohexanol <sup>c</sup> (%)	S <sub>g</sub> <sup>d</sup> (m <sup>2</sup> /g)	V <sub>p</sub> <sup>e</sup> (ml/g)
1		5.52	20	100	18.5	0.22
2		4.83	30	85	30	1.13
3		4.14	40	91	56	1.47
4		2.76	60	85	94	1.21
5		3.76	38	85	51	1.25
6		3.50	38	91	66	1.10
7		2.20	60	91	109	1.66
8		1.20	80	91	224	1.87
9 <sup>f</sup>	-CH <sub>2</sub> CH(OH)CH <sub>2</sub> NH <sub>2</sub>	1.40			42	
10 <sup>g</sup>	-CH <sub>2</sub> CH(OH)CH <sub>2</sub> NH(CH <sub>2</sub> ) <sub>2</sub> NH <sub>2</sub>	2.45			53	
11 <sup>h</sup>	-CH <sub>2</sub> CH(SH)CH <sub>2</sub> NH <sub>2</sub>	1.20			66	
12 <sup>i</sup>	-CH <sub>2</sub> CH(SH)CH <sub>2</sub> NH(CH <sub>2</sub> ) <sub>2</sub> NH <sub>2</sub>	1.20			224	

<sup>a</sup> Calculated from elemental analysis of oxygen, sulphur and nitrogen.

<sup>b</sup> Percentage of EDMA in monomer mixtures.

<sup>c</sup> Percentage of cyclohexanol in porogen mixture.

<sup>d</sup> Specific surface area measured by thermal desorption of nitrogen.

<sup>e</sup> Pore volume calculated from cyclohexane regain.

<sup>f</sup> With ammonia-modified sorbent 3.

<sup>g</sup> With ethylenediamine-modified sorbent 3.

<sup>h</sup> With ammonia-modified sorbent 6.

<sup>i</sup> With ethylenediamine-modified sorbent 6.

*Chromatographic measurements*

Chromatographic measurements were carried out using a chromatograph provided with flame ionization detection. The copolymers were packed into a glass column (0.8 m × 0.3 cm I.D.) with a flow-rate of nitrogen in the column of 10–20 ml/min.

For chromatographic standards chosen from alkanes, aromatic hydrocarbons, alcohols, ketones and esters of carboxylic acids, specific retention volumes ( $V_g$ ) were determined and used to determine the relative retention volumes ( $V_{rel}$ ) with respect to

hexane, Henry adsorption constants ( $K_1 \text{ ml/m}^2$ )<sup>8</sup> using eqn. 1 and changes in the free energy of adsorption ( $-\Delta F$ ) according to eqn. 2.

$$K_1 = V_g/S_g \quad (1)$$

$$-\Delta F = RT \ln K_1 + \text{constant} \quad (2)$$

where  $S_g$  is the specific surface area of the sorbent. The retention data were corrected to non-ideality.

The extent of specific interactions was determined from the retention volumes in relation to alkanes or from the difference in changes in the free energy of adsorption:

$$-\Delta F = \Delta F_{\text{spec}} - \Delta F_{\text{alk}} \quad (3)$$

for alkanes (alk) and other sorbates (spec) having the same number of carbon atoms.

It should be borne in mind, however, that in addition to the sorption of organic compounds on polymeric sorbents at 150°C, dissolution of the compounds occurs together with adsorption. In this case changes in the partial molar free energy of the methylene group,  $\Delta G^E(\text{CH}_2)$ , are usually determined<sup>9</sup>.

The specific surface area was determined in the dry state by the three-point BET method using a Quantasorb apparatus (Quantachrome, Greenvale, NY, U.S.A.) and nitrogen as the sorbate with an experimental error of 5%.

The sorption of gases (sulphur and carbon dioxides) was investigated by using the static method and a vacuum apparatus.

## RESULTS AND DISCUSSION

The EPMA-EDMA and ETPMA-EDMA polymers investigated are characterized by the monomer composition in the polymerization mixture, by the content of functional groups in the polymer, by the specific surface area ( $S_g$ ) and by the specific pore volume ( $V_p$ ) summarized in Table I. Fig. 1 shows the dependences of the specific

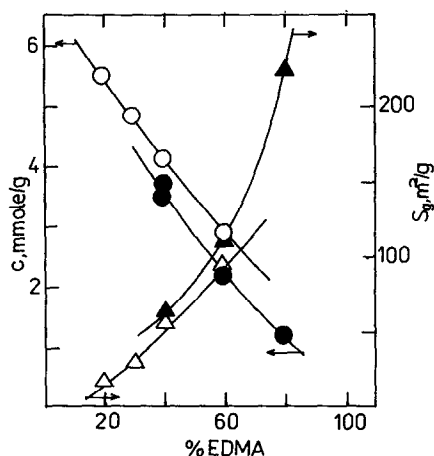


Fig. 1. Dependence of the content of (○) epoxy and (●) epithio groups and of the specific surface area ( $S_g$ ) of (△) EPMA and (▲) ETPMA copolymers on the content of the cross-linking agent (EDMA) in the mixture of monomers.

TABLE II

RELATIVE RETENTIONS ( $V_{rel}$ ) AND HENRY CONSTANTS ( $K_1$ ) OF VARIOUS COMPOUNDS ON COLUMNS PACKED WITH SORBENTS 3 AND 5 AT 150°C

Sorbate	EDPMA-EDMA		ETPMA-EDMA	
	$K_1$	$V_{rel}$	$K_1$	$V_{rel}$
$n\text{-C}_6\text{H}_{14}$	0.1	1.0	0.2	1.0
$n\text{-C}_7\text{H}_{16}$	0.2	1.8	0.4	1.9
$n\text{-C}_8\text{H}_{18}$	0.4	3.5	0.7	3.7
$n\text{-C}_9\text{H}_{20}$	0.7	6.4	1.3	7.1
$n\text{-C}_{10}\text{H}_{22}$	1.3	11.5	2.5	13.1
$\text{C}_6\text{H}_6$	0.3	2.7	0.7	3.4
$\text{C}_6\text{H}_5\text{CH}_3$	0.7	6.4	1.4	7.1
$\text{C}_6\text{H}_5\text{C}_2\text{H}_5$	1.2	10.5	2.5	13.2
$\text{CH}_3\text{OH}$	0.1	1.3	0.3	1.6
$\text{C}_2\text{H}_5\text{OH}$	0.2	1.7	0.5	2.4
$\text{C}_3\text{H}_7\text{OH}$	0.4	3.2	1.0	5.2
$\text{C}_4\text{H}_9\text{OH}$	0.7	6.3	2.1	11.2
$\text{C}_5\text{H}_{11}\text{OH}$	1.3	11.6	—	—
$\text{CH}_3\text{COCH}_3$	0.2	1.9	0.4	2.1
$\text{CH}_3\text{COC}_2\text{H}_5$	0.4	3.2	0.8	4.0
$\text{CH}_3\text{COC}_3\text{H}_7$	0.8	7.1	1.4	7.6
$\text{CH}_3\text{COC}_4\text{H}_9$	1.1	10.4	2.9	15.2
$\text{CH}_3\text{COOCH}_3$	0.2	1.7	0.3	1.7
$\text{CH}_3\text{COOC}_2\text{H}_5$	0.3	2.6	0.6	3.2
$\text{CH}_3\text{COOC}_3\text{H}_7$	0.5	4.8	1.2	6.4
$\text{CH}_3\text{COOC}_4\text{H}_9$	1.0	9.4	2.4	12.8
$\text{CH}_3\text{NO}_2$	0.6	5.6	0.8	4.3

surface area and of the concentration of functional groups on the amount of cross-linking agent for both polymer groups. With increasing EDMA content in the polymerization mixture the specific surface area of the polymers increases, but the concentration of functional groups decreases. These values are close for both types of polymers, and the dependences are parallel.

#### Chromatographic properties

Gas chromatography allows the properties of the sorbents to be investigated at a low surface coverage, under conditions where the sorbate-sorbate interactions are minimal. Table II summarizes the Henry adsorption constants ( $K_1$ ) and relative retentions ( $V_{rel}$ ) of various groups of compounds on sorbents 3 and 5, which have approximately the same concentrations of epithio and epoxy groups and similar geometries of the porous structure. As shown in Table II and Fig. 2,  $K_1$ ,  $V_{rel}$ ,  $\Delta F$  and Kováts retention indices ( $I$ ) for all sorbates, except for nitromethane in the case of  $V_{rel}$  and for aromatic hydrocarbons in the case of  $\Delta F$ , are higher on the sulphur-containing polymer than on that with epoxide groups. This suggests that stronger specific

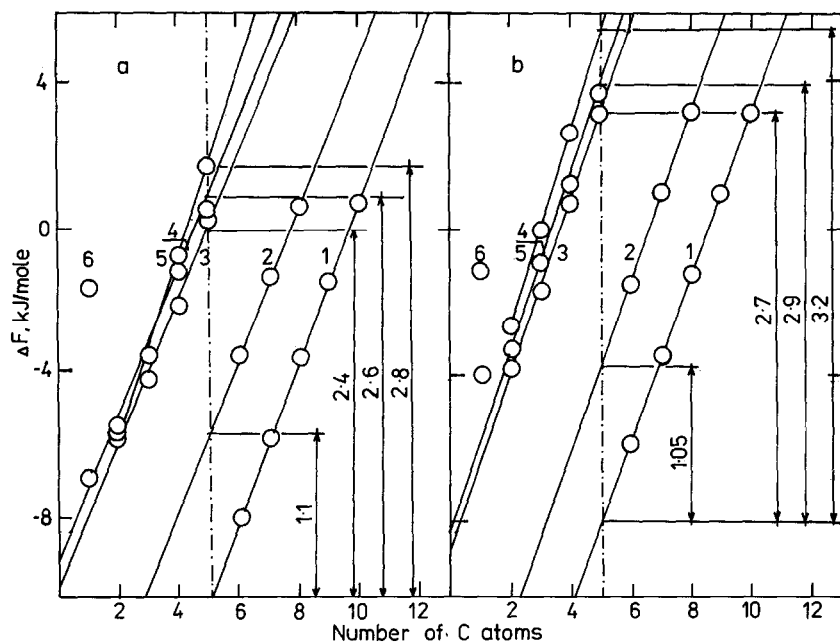


Fig. 2. Dependence of free energy of adsorption ( $\Delta F$ , kJ/mol) of various compounds on the number of carbon atoms for EPMA-EDMA (a, sorbent 3) and ETPMA-EDMA copolymers (b, sorbent 5). 1, alkanes; 2, aromatic hydrocarbons; 3, acetates; 4, ketones; 5, alcohols; 6, nitromethane.

interactions occur between sorbed molecules and sulphur-containing groups. The largest contribution of specific interactions was found with nitromethane ( $\mu = 3.6$  D), corresponding to the orientational forces.

Table III gives values of the constants  $a$  and  $b$  in the equation

$$-\Delta F = a + bn \quad (4)$$

TABLE III

COEFFICIENTS OF THE EQUATION  $-\Delta F = a + bn$  (kJ/mol) DETERMINED USING RETENTIONS OF HOMOLOGOUS SERIES OF VARIOUS COMPOUNDS ON METHACRYLATE COPOLYMERS AT 150°C

Sorbent No.	Alkanes		Aromatic hydrocarbons		Alcohols		Ketones		Acetates	
	$a$	$b$	$\Delta a^a$	$b$	$\Delta a^a$	$b$	$\Delta a^a$	$b$	$\Delta a^a$	$b$
1	4.6	0.37	2.2	0.27	2.8	0.36	2.9	0.29	2.8	0.28
2	4.7	0.41	1.7	0.39	2.7	0.45	2.8	0.41	2.7	0.37
3	5.0	0.52	1.2	0.49	2.7	0.50	2.7	0.50	2.1	0.70
4	5.5	0.73	1.1	0.67	3.2	0.53	3.2	0.64	3.1	0.67
5	4.0	0.46	0.5	0.57	1.0	0.61	2.2	0.58	2.1	0.57
6	4.7	0.54	1.0	0.56	2.8	0.64	2.7	0.61	2.6	0.56
7	5.0	0.66	0.6	0.67	2.3	0.70	2.6	0.64	2.6	0.62
8	5.7	0.80	0.40	0.79	2.5	0.83	2.9	0.75	2.7	0.81

<sup>a</sup>  $\Delta a$  denotes differences from values for alkanes.

where  $n$  is the number of methylene groups for various types of compounds relative to alkanes. The  $b$  values are a measure of changes in the free energy of the methylene group, *i.e.*, a measure of dispersion interactions, and characterize the selectivity with respect to the individual homologues. Changes in  $a$  for various types of compounds characterize the specific interactions of compounds containing the same number of methylene groups but having functional groups of different types.

Table III indicates that for the same sorbent the  $b$  values of the compounds investigated vary only slightly, *i.e.*, the character of the functional groups has only a weak influence on the contribution of dispersion forces. With increasing specific surface area, the contribution of non-specific interactions increases for both types of sorbent. The contribution of specific interactions is also affected by the number of accessible functional groups of the sorbent.

Fig. 3 shows the dependences of  $\ln K_1$  for various sorbates on the content of groups localized on the sorbent surfaces. The functional groups accessible on the inner surface ( $c_p$ ) were determined from the ratio of the total content of groups ( $c_0$ ) to the specific surface area ( $S_g$ ). This value was corrected for the size of the globules ( $R$ ) forming the sorbent bead ( $R = 3000/\rho S_g$ , nm) and by the size of the structural unit of EPMA or ETPMA,  $l = 1.0$  nm. The correction factor for the monomer EPMA (or ETPMA) distribution in the globule is then given by

$$A = 1 - \left( \frac{3000}{\rho S_g} - 1 \right)^3 \left( \frac{\rho S_g}{3000} \right)^3 \quad (5)$$

where  $\rho$  is the copolymer density (1.3 g/ml).

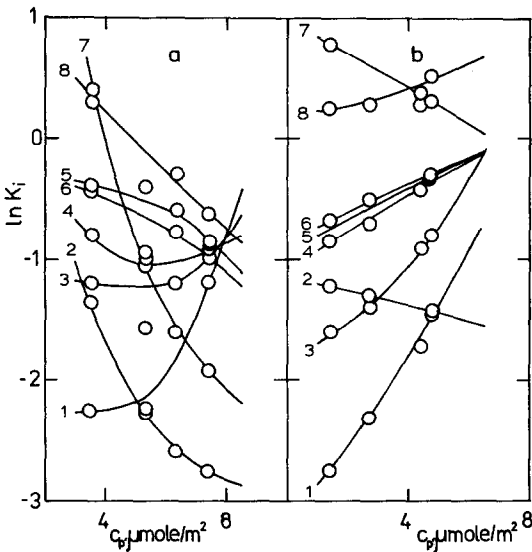


Fig. 3. Henry adsorption constant ( $\ln K_1$ ) as a function of the specific surface concentration of oxirane and epithio groups ( $c_p$ ) in (a) EPMA-EDMA and (b) ETPMA-EDMA copolymers. Sorbates: 1 = methanol; 2 = hexane; 3 = acetone; 4 = propanol; 5 = ethyl acetate; 6 = benzene; 7 = *n*-octane; 8 = toluene.

The content of surface groups ( $c_p$ ) is given by

$$c_p = \frac{c_0}{S_g} \cdot A \quad (6)$$

As follows from the calculations, there are no differences in proportionality between surface concentration and total content of groups.

The dependences in Fig. 3 confirm the preceding observations regarding the polar character of both types of sorbent. The non-linearity of the  $\ln K_i$  vs.  $c_p$  dependence can be interpreted as a deviation from the regular distribution of functional groups of the polymers prepared. With increasing content of surface glycidyl or epithio groups, the distribution coefficients of alkanes decrease, whereas those of methanol and acetone increase.

The retentions of medium-polarity compounds and aromatic hydrocarbons increase with increasing concentration of surface groups with the copolymer ETPMA, but decrease with EPMA.

The retentions of alkanes decrease more with increasing concentration of surface groups the longer is the hydrocarbon chain. The retention of molecules that are sorbed specifically increases more markedly with increasing content of groups the shorter is the hydrocarbon portion of the molecule. With epoxy copolymers the effect of the hydrocarbon part of the sorbate molecules on their retention is stronger than that with epithio copolymers, which indicates a weaker polarity of the epoxy groups.

Table IV gives the Kováts retention indices of various types of compounds on EPMA-EDMA and ETPMA-EDMA copolymers. A comparison of copolymers with similar compositions (Table I, copolymers 3 and 6) shows that the Kováts retention indices on ETPMA-EDMA copolymers are higher than those on EPMA-EDMA copolymers, which suggests that the specific interactions of sulphur-containing polymers may be stronger than those of copolymers which contain only oxygen.

#### *Sorption of sulphur dioxide and carbon dioxide*

Unlike chromatographic methods, sorption methods applied under static conditions make possible measurements with saturated surfaces of the sorbent. Fig. 4 shows the sorption isotherms of sulphur dioxide on EPMA-EDMA and ETPMA-EDMA copolymers. For polymers 5-7 the absorption ( $a$ , mmol/g) decreases with increasing  $S_g$  from 51 to 109 m<sup>2</sup>/g and with decreasing sulphur content from 12 to 7%. The sorbent having the lowest sulphur content and the largest specific surface area (224 m<sup>2</sup>/g) usually exhibits a high sorption of sulphur dioxide.

Fig. 5 shows the dependence of the sulphur dioxide sorption relative to unit surface area on the amount of sulphur in epithio groups of the ETPMA copolymer. The increase in the adsorption of sulphur dioxide in polymers with a sulphur content above 7% can be related to an increasing amount of epithio groups contributing to specific interactions with sulphur dioxide, particularly due to orientational forces ( $\mu = 1.6$  D). The ascending part of the dependence on the left (content of sulphur below 7%) can be explained by increasing dispersion interactions with the surface of the adsorbent proportional to the specific surface area.

The dependence of the sorption of sulphur dioxide on the content of functional groups in polymers, and on the specific surface area (Fig. 5), is caused by the varying

TABLE IV

KOVÁTS RETENTION INDEXES OF EPMA-EDMA AND ETPMA-EDMA COPOLYMERS AT 150°C

Solute	Sorbent No.							
	1	2	3	4	5	6	7	8
C <sub>6</sub> H <sub>6</sub>	1042	956	766	709	816	781	702	653
C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub>	1119	1051	903	795	964	901	802	749
C <sub>6</sub> H <sub>5</sub> C <sub>2</sub> H <sub>5</sub>	1199	1136	984	—	1070	998	—	—
C <sub>6</sub> H <sub>5</sub> C <sub>3</sub> H <sub>7</sub>	1256	—	—	—	—	—	—	—
CH <sub>3</sub> COCH <sub>3</sub>	944	863	710	621	711	707	587	562
CH <sub>3</sub> COC <sub>2</sub> H <sub>5</sub>	1044	950	792	713	830	812	687	649
CH <sub>3</sub> COC <sub>3</sub> H <sub>7</sub>	—	1069	924	—	969	912	781	740
CH <sub>3</sub> COC <sub>4</sub> H <sub>9</sub>	1085	1116	992	—	1095	1019	—	843
CH <sub>3</sub> COOCH <sub>3</sub>	901	817	690	621	697	684	588	555
CH <sub>3</sub> COOC <sub>2</sub> H <sub>5</sub>	975	884	761	704	794	778	674	650
CH <sub>3</sub> COOC <sub>3</sub> H <sub>7</sub>	1054	979	860	801	932	885	775	741
CH <sub>3</sub> COOC <sub>4</sub> H <sub>9</sub>	1137	1080	968	—	1065	997	—	852
CH <sub>3</sub> OH	964	809	639	514	604	676	468	432
C <sub>2</sub> H <sub>5</sub> OH	976	846	693	588	690	735	566	524
C <sub>3</sub> H <sub>7</sub> OH	1046	951	790	625	822	851	677	631
C <sub>4</sub> H <sub>9</sub> OH	1166	1083	900	—	989	975	—	742
C <sub>5</sub> H <sub>11</sub> OH	1251	1169	1001	—	1113	—	—	—
CH <sub>3</sub> NO <sub>2</sub>	1269	1095	793	—	853	822	681	624
CH <sub>3</sub> CN	1148	1002	889	642	—	—	—	—

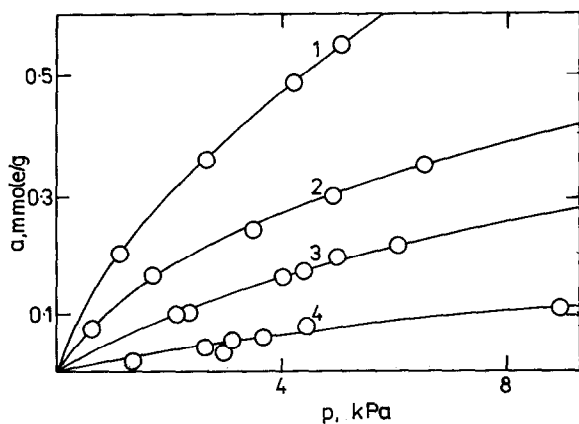


Fig. 4. Sorption isotherms of sulphur dioxide on ETPMA-EDMA copolymers measured at 30°C. 1 = sorbent 8; 2 = sorbent 5; 3 = sorbent 6; 4 = sorbent 7.



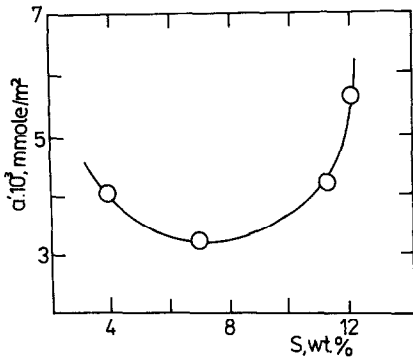


Fig. 5. Dependence of the amount of sulphur dioxide sorbed by unit surface area ( $a'$ ) of ETPMA-EDMA polymers as a function of the content of sulphur in epithio groups.

contributions of non-specific and specific interactions; in other words, it shows the role of the chemical nature of the surface, which is also reflected in the case of considerable saturation of the surface with the adsorbate.

Similarly to EPMA-EDMA copolymers, the ETPMA-EDMA copolymers modified with amines or with ethylenediamine<sup>10</sup> also adsorb more sulphur dioxide than the starting polymers (Fig. 6), but the sorption of sulphur dioxide and carbon dioxide on copolymers based on EPMA is several times higher. Different roles of the SH and OH groups of the polymer in the sorption of sulphur dioxide and carbon dioxide seem to be operative in this instance.

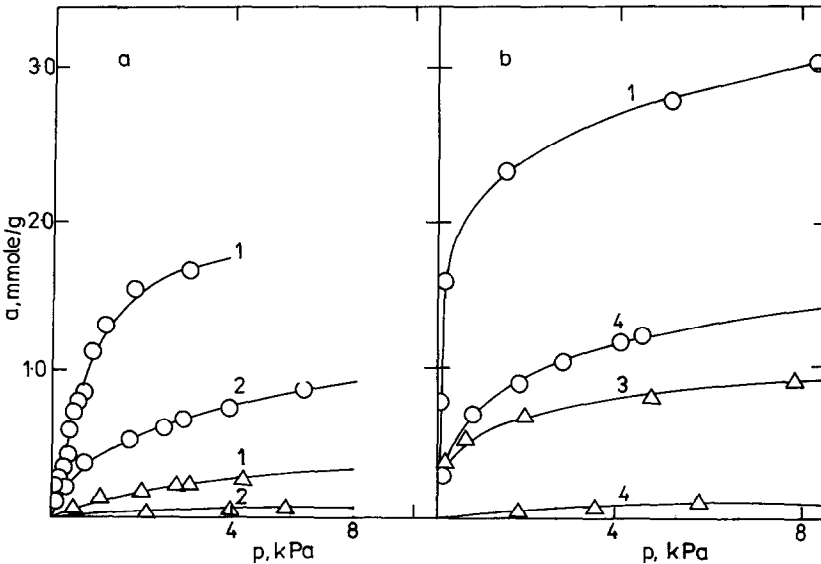


Fig. 6. Sorption isotherms of (O) sulphur dioxide and ( $\Delta$ ) carbon dioxide at 30°C on copolymers modified by (a) ammonia and (b) ethylenediamine; 1 = copolymer 9; 2 = copolymer 11; 3 = copolymer 10; 4 = copolymer 12.

## CONCLUSIONS

This chromatographic study of macroporous methacrylate copolymers has shown that with increasing specific surface area the non-specific interactions increase while specific interactions decrease. This confirms the suggestion that the accessibility of functional groups decreases with increasing amount of cross-linking agent in the sorbent.

The polar adsorbates are bound more strongly to the polymers with epithio groups than to those containing epoxy groups. The non-linearity or extremes of the dependences follow the changes in the ratio of specific and non-specific interactions caused by the irregular group distribution in the polymer globules.

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