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SOLUTE-SORBENT INTERACTIONS OF MACROPOROUS METHACRYLATE ION EXCHANGERS AND APPLICATION OF THESE SORBENTS IN GAS-SOLID CHROMATOGRAPHY

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SUMMARY

The chromatographic properties of macroporous methacrylate copolymers containing sulphopropyl groups in the H^+ , Li^+ , Na^+ , K^+ , Rb^+ , Cs^+ and Ag^+ forms were investigated. The retention values on the individual sorbents were determined and the Kováts retention indices were calculated using a number of aliphatic and aromatic hydrocarbons, alcohols and ethers. By assuming additivity, mathematical analysis of the particular factors operative in the solute-sorbent interactions was performed. The contribution of the formation of hydrogen bonds is of importance. The chromatograms indicate the possibility of separating mixtures of saturated and unsaturated hydrocarbons, alcohols, etc.

INTRODUCTION

Several papers have been published on the gas chromatographic properties of macroporous ion exchangers based on sulphonated styrene-divinylbenzene copolymer. Instead of commercial-type ion exchangers¹⁻³ that bear functional groups in the polymer bulk, attention is now concentrated on special ion exchangers with functional groups on the inner polymer surface, which possess more advantageous properties^{4,5}.

From this standpoint, we were interested in examining the properties of methacrylate macroporous copolymers^{6,7} in which the sulphopropyl functional groups are situated on the inner surface of the polymer due to the substitution conditions, which had not previously been studied.

EXPERIMENTAL

A macroporous copolymer* (G-70-85-SP), glycidyl methacrylate-ethylene dimethacrylate⁶ (with 30 mass-% of the cross-linking agent), subsequently substituted⁸ with sulphopropyl groups at a concentration of 0.745 mmol HSO⁻/g, was used in the chromatographic study. The specific pore volume of the copolymer was 1.227 ml/g, *i.e.*, porosity 61.3%, and its specific surface area was 30.5 m²/g.

Before use, the ion exchanger was washed under dynamic conditions with a 5% solution of hydrochloric acid, lithium, sodium, potassium, rubidium or caesium chloride or silver nitrate and distilled water and thus transformed into the H⁺, Li⁺, Na⁺, K⁺, Rb⁺, Cs⁺ or Ag⁺ form, respectively, and dried. After packing the chromatographic column (0.5 m × 0.3 cm I.D.), the ion exchanger was activated at 170°C for 24 h in a stream of helium (50 ml/min). An LXM-8MD chromatograph with a heat-conductivity detector was used.

Using the experimental retention values of a number of alkanes, aromatic hydrocarbons, alcohols and ethers, the retention times relative to pentane, Kováts retention indices, peak asymmetry and the height equivalent to a theoretical plate (HETP) were calculated. The dependence of HETP on the flow-rate of the carrier gas in the range 10-120 ml/min was ascertained with the aim of determining the optimal conditions of measurements; the optimal flow-rate was 50 ml/min and was used in all subsequent measurements.

RESULTS AND DISCUSSION

The methacrylate ion exchangers were prepared from macroporous glycidyl methacrylate-ethylene dimethacrylate copolymers⁶ by treating them, after hydrolysis, with propane sultone in alkaline medium⁷. The choice of the reaction conditions makes possible the introduction of functional groups on the inner surface of the polymer particles, as ensues from the distribution of sulphur in the polymer particles⁸ and from the fast kinetics of catalytic reactions in the gas phase⁷.

The chromatographic properties of this type of ion exchanger in the H⁺, Li⁺, Na⁺, K⁺, Rb⁺, Cs⁺ and Ag⁺ forms were investigated. The chemical structure of the sorbents is the cause of their elevated polarity, which is reflected in the Kováts retention indices of the reference standards (benzene, ethanol, acetonitrile, nitromethane and pyridine), summarized in Table I. The Kováts retention indices of solutes (except benzene) on the sorbents investigated here are distinctly higher than that of the structurally close methacrylate copolymer Chromosorb 107, and even than that of the strongly polar Chromosorb 104, *i.e.*, of a copolymer of acrylonitrile and divinylbenzene. It seems that the Kováts retention indices of benzene cannot be determined reliably, because methacrylate copolymers bearing a sulpho group are more polar than sulphonated styrene-divinylbenzene copolymers (Amberlyst A15¹, sulphonated Porapak Q^{4,5}).

We also tried to separate the contributions of the individual factors of the sorbent-solute interactions to the overall values of the Kováts retention indices. Us-

* The polymers were prepared at the Institute of Macromolecular Chemistry, Academy of Sciences, Prague 6, Academia, Czechoslovakia.

TABLE I

KOVÁTS RETENTION INDICES OF REFERENCE SOLUTES ON POLYMERIC SORBENTS G-70-85-SP (AT 100°C) AND CHROMOSORB (AT 150°C)

Solute	G-70-85-SP							Chromosorb		
	H ⁺	Li ⁺	Na ⁺	K ⁺	Rb ⁺	Cs ⁺	Ag ⁺	102	104	107
Benzene	776	617**	600	500	600	714	1031	672	650	835
	—		741*	756*	804*	—	—	1097*		
			—	644*	665**	—	—	814**		
660										
Ethanol	1183	1039	1051	1041	1091	1049	997	425	690	515
Methyl ethyl ketone	914	879	700	752	814	732	1007			
Nitromethane	1190	1155	1093	1087	1047	1018	1192	510	935	—
Acetonitrile	988	1095	1051	995	1003	915	1170	460	855	550
Pyridine	—***	920	934	1084	1080	810	—***	705	1025	—

* Amberlyst A-15 at 180°C¹.** Sulphonated Porapak Q at 175°C².

*** No elution.

ing the assumed additivity of contributions of the individual factors and the matrix calculation, mathematical analysis was performed on a data set including the Kováts retention indices of alkanes, aromatic hydrocarbons, alcohols and ethers on columns

TABLE II

KOVÁTS RETENTION INDICES OF AROMATIC HYDROCARBONS, ALCOHOLS AND ETHERS ON THE METHACRYLATE COPOLYMER WITH SULPHOPROPOPYL GROUPS (G-70-85-SP)

Solute	G-70-85-SP						
	H ⁺	Li ⁺	Na ⁺	K ⁺	Rb ⁺	Cs ⁺	Ag ⁺
Benzene	776	600	500	600	714	1031	672
Toluene	800	778	500	752	811	700	766
<i>p</i> -Xylene	883	1016	800	859	887	810	874
Ethylbenzene	883	1021	900	852	887	778	841
Cumene	910	1068	934	905	964	849	939
1,2,4-trimethylbenzene	1000	1092	982	949	1017	910	997
Methanol	1086	1094	1015	1011	1045	900	954
Ethanol	1183	1039	1051	1041	1090	949	997
<i>n</i> -Propanol	1255	878	800	925	1058	922	858
Isopropanol	—	640	700	789	850	720	725
<i>n</i> -Butanol	—	1000	960	924	1015	900	906
Isobutanol	—	917	908	900	943	818	822
<i>sec.</i> -Butanol	—	926	900	866	943	800	834
<i>tert.</i> -Butanol	—	779	800	800	880	720	784
<i>n</i> -Pentanol	—	1115	1028	737	1015	982	1000
Diethyl ether	883	550	500	544	600	600	550
Diisopropyl ether	600	700	700	737	710	651	672
Dibutyl ether	975	1021	948	924	933	856	929

TABLE III

CONTRIBUTIONS OF THE INDIVIDUAL TYPES OF INTERACTIONS OF SOLUTES AND SORBENTS TO THE OVERALL VALUES OF THE KOVÁTS RETENTION INDICES

For the radii of Li^+ , Na^+ , K^+ , Rb^+ , Cs^+ and Ag^+ cations, the values taken from ref. 10 are 0.6, 0.95, 1.33, 1.48, 1.69 and 1.26 Å, respectively.

Solute	I_{S1}	I_{S2}	I_{S3}	n_1	n_2	I_{A1}	I_{A2}	I_{A3}
Benzene	—	61	22	6	6	278	-62	243
Toluene	—	116	-9	6	8	64	-167	102
<i>p</i> -Xylene	—	88	5	8	10	131	-167	192
Ethylbenzene	—	77	19	8	10	79	-189	37
Isopropylbenzene	—	124	—	9	12	-205	-153	-176
1,2,4-trimethylbenzene	—	-115	—	9	12	-115	-114	-118
Diethyl ether	450	217	—	4	4	465	86	24
Diisopropyl ether	—	—	—	6	6	-252	-91	-66
Dibutyl ether	54	133	—	8	8	-143	-144	-8
Methanol	—	—	—	1	1	117	-175	205
Ethanol	742	227	—	2	2	-13	-84	-93
<i>n</i> -Propanol	1958	383	—	—	3	440	86	-65

packed with the methacrylate macroporous copolymer containing sulpho groups in the H^+ , Li^+ , Na^+ , K^+ , Rb^+ , Cs^+ and Ag^+ forms (Table II).

The Kováts retention index of a solute S_i on a sorbent A_j was defined as the sum of contributions of interactions of the solute, I_S , and of interactions of the sorbent, I_A . Contributions of interactions of the solute included hydrogen bonds (I_{S1}), induction effect (I_{S2}), steric effect (I_{S3}) and the size of the molecule defined by the total number of carbon atoms (n_1) and by the number of carbon atoms on which the chain is branched (n_2). The contribution of the sorbent again included hydrogen bonds in the case of the sorbent in the H^+ form (I_{A1}), the contribution of the type of the cation (I_{A2}) related to the ionic radius R and special interactions (I_{A3}) in the case of the sorbent in the Ag^+ form. The general relationship is given by eqn. 1.

$$I_{S_i A_j} = (I_{S1} + n_1 I_{S2} + n_2 I_{S3}) + (I_{A1} + R I_{A2} + I_{A3}) \quad (1)$$

The calculated values of the individual contributions are given in Table III.

Effects that may be operative in the solute-sorbent interactions were included in the contributions. One should bear in mind, however, that the Kováts retention indices are a macrophysical quantity that need not reflect the complicated relationships between the individual factors in terms of simple functions, and also the fact that the temperature at which the values were determined brings the polymer into a state where dissolution interactions become operative⁹, while substitution with cations gives the polymer the character of adsorption interactions. In spite of this simplification, and based on the mathematical analysis of the contributions, it can be said that hydrogen bonds are the main factor connected with efficiency, with respect to the contribution of both the solute and the sorbent. In the latter instance, these factors are especially operative in the interactions with alcohols, ethers and aromatic hydrocarbons. The contribution of the induction effects, and particularly that of the

steric effects, to interactions of the solute is much weaker than that of hydrogen bonds. It was also confirmed that the strength of interactions of the solute decreases with the ionic radius of the sorbents under study.

The positive or the negative values of the contributions I_{A1} and I_{A2} may be explained by the electron acceptor or donor character of the solute-sorbent interactions. These interactions were denoted as Van der Waals forces. Special interactions have been observed for the sorbent in the Ag^+ form with aromatic hydrocarbons. There is not enough experimental evidence for a quantitative determination of the contribution of the polymer matrix to the values of the Kováts retention indices. Comparison between the Kováts retention indices of aromatic hydrocarbons on sulphonated styrene-divinylbenzene copolymers and on methacrylate copolymers suggests a weaker intensity of the solute-sorbent interactions in the latter instance, in spite of the fact that they were recorded at a lower temperature (175 and 180°C, respectively, compared with 100°C). Whereas on the styrene copolymer the Kováts retention indices increase along the series of alkali metals, the methacrylate copolymer mostly shows a minimum in this series in its Na^+ form; the order of the hydrocarbons remains unchanged, however.

A more graphic view of the properties of these sorbents with respect to their separation properties is provided by the relative retention times of the solutes. As demonstrated by Fig. 1a, the retention diagram of the alkanes shows a linear increase in $\log t_{\text{rel}}$ with increasing chain length. Only the sorbent in its H^+ and Na^+ forms has lower retention times. Dependences observed with aromatic hydrocarbons are similar (Fig. 1b). The situation with solutes with the possibility of forming hydrogen bonds is different. Alcohols with a small molecule, such as methanol and ethanol, have higher retention values on sorbents in the salt form than further members of

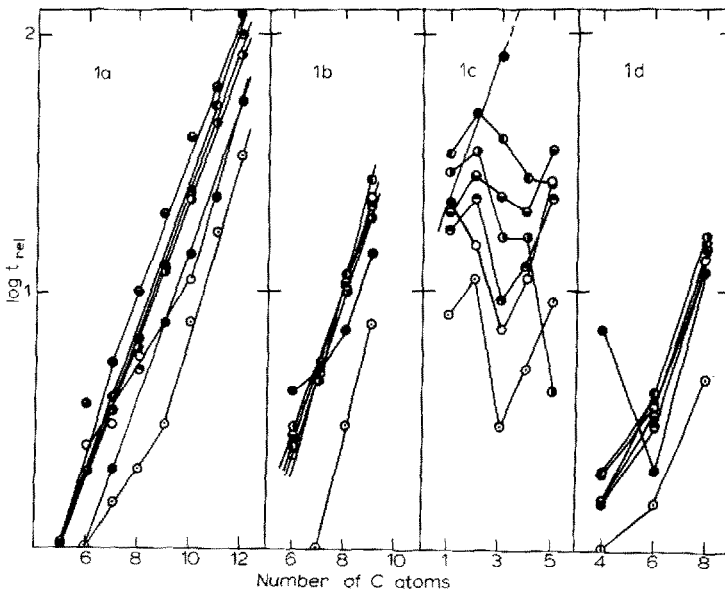


Fig. 1. Retention diagram of the homologous series of alkanes (a), aromatic hydrocarbons (b), alcohols (c) and ethers (d) on methacrylate copolymers bearing sulphopropyl groups in the H^+ (●), Li^+ (○), Na^+ (○), K^+ (●), Rb^+ (●), Cs^+ (●) and Ag^+ forms (●) at 150°C.

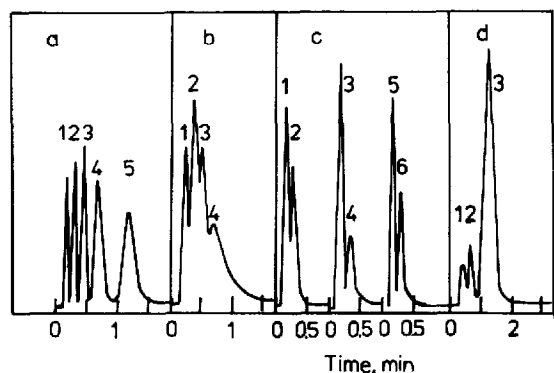


Fig. 2. (a) Chromatogram of alkanes (1 = decane, 2 = undecane, 3 = dodecane, 4 = tridecane, 5 = tetradecane) on the sorbent in the K^+ form at 150°C ; (b) chromatogram of a mixture of alcohols (1 = *tert.*-butanol, 2 = *sec.*-butanol, 3 = isobutanol, 4 = *n.*-butanol) on the sorbent in the Li^+ form at 100°C ; (c) chromatograms of the separation of alkanes and olefins (1 = hexane, 2 = 1-hexene, 3 = octane, 4 = 1-octane, 5 = cyclohexane, 6 = cyclohexene) on the sorbent in the Ag^+ form at 100°C ; (d) chromatogram of a mixture of polar compounds (1 = formaldehyde, 2 = methanol, 3 = water) on the sorbent in the Li^+ form at 120°C .

the homologous series, and in some instances also higher than *n*-pentanol (Fig. 1c). The highest retention values of alcohols were observed on the sorbent in the H^+ form where, however, they increase proportionately to the number of carbon atoms in the homologue. *n*-Butanol and higher alcohols, however, are not eluted from the column under these experimental conditions. With ethers (Fig. 1d), only an elevated retention of diethyl ether on the sorbent in its H^+ form is observed, compared with the further members of the series. In all other instances there was a continuous increase in the relative retention values.

Separations of mixtures of hydrocarbons, alcohols, olefins and polar compounds are illustrated in Fig. 2. Olefins and alkanes can be separated on the sorbent in the Ag^+ form, which is not feasible on sorbents modified with other cations. The anomaly in the separation of alcohols and ethers mentioned above may be utilized in special cases, *e.g.*, if combinations of columns are applied. The sorbents investigated in this study retain the ability of macroporous copolymers to separate aqueous solutions of organic compounds.

The chromatograms show that on the sorbents used, symmetrical peaks of all solutes were obtained, only the alcohols giving tailing peaks. The column efficiency was particularly high for alkanes and aromatic hydrocarbons (HETP = 0.21–0.13 cm); for alcohols and ethers it was low (HETP = 1.4–3.0 cm). For most of the compounds, the coefficient of peak asymmetry was 0.4–1.0; on the sorbent in the H^+ form it was lower (0.1–0.3).

It may be concluded that the sorbent studied not only proved useful in the interpretation of solute–sorbent interactions, but is also suitable for practical applications.

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