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SOLUTE–SOLVENT INTERACTIONS OF MACROPOROUS METHACRYLATE ION EXCHANGERS IN SALT FORM STUDIED BY GAS CHROMATOGRAPHY

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SUMMARY

Interaction of macroporous methyl methacrylate copolymers carrying strongly acidic sulphopropyl groups exchanged with metal ions of the IIb, VIb, VIIIb and rare earth groups of the Periodic Table with solutes —homologous alkanes, aromatic hydrocarbons, ketones, alcohols and organic acids— were studied by gas chromatography. The results show that the sorbents belong to class 3 according to Kiselev since, in addition to interactions due to dispersion forces, they also exhibit strong specific interactions. In comparison with the original copolymers, the ion exchangers carrying sulphopropyl groups exhibit stronger specific interactions, in particular with alcohols, due to hydrogen bonding. The methacrylate-based ion exchangers in salt form exhibit weaker specific interactions than the same sorbents in H^+ form. Non-specific interactions involving dispersion forces generally predominate.

INTRODUCTION

Interactions of methacrylate copolymers carrying sulphopropyl groups in the form of salts with group Ia ions were studied previously[1–3], and the magnitudes of non-specific and specific interactions were estimated by mathematical processing of experimental data.

With the aim of generalizing the conclusions obtained, we have broadened the scope of the interactions of methacrylate ion exchangers by including also salts of elements from groups IIb, VIb and VIIIb of the Periodic Table. We have tried to determine the selectivity of these sorbents, in particular applications, and the ability to vary their polarities by exchanging with different metal ions.

EXPERIMENTAL

Materials

Methacrylate ion exchangers were prepared from macroporous glycidyl methacrylate–ethylene dimethacrylate copolymers[4] by treating the hydrolyzed copolymer with propane-sultone in an alkaline medium[5]. The basic copolymer for the synthesis of type A ion exchanger was prepared from 85% (w/w) of the cross-linking agent and 15% (w/w) of glycidyl methacrylate in the inert solvent cyclohexanol–dodecanol (91:9). The type B ion exchanger was based on a copolymer prepared from 30% (w/w) of the cross-linking agent and 70% (w/w) of glycidyl methacrylate; the ratio of the inert solvents was 85:15. Ion exchanger A is identical with type A in ref. 3 and the present type B is identical with type C of ref. 3.

Chromatography

The ion exchangers were washed successively with 1 M hydrochloric acid, distilled water, a solution of the chloride or nitrate of the corresponding metal (from the group Cd^{2+}, La^{2+}, Cr^{3+}, Fe^{3+}, Co^{2+}, Ni^{2+}), distilled water and finally dried. Sorbents (particle sizes 180–250 μm) were packed into stainless-steel columns (50 cm × 0.3 cm I.D.) and activated by heating to 170°C for 24 h in a stream of helium. Retention times of homologous paraffins, aromatic hydrocarbons, ketones, organic acids and alcohols were measured at 100 or 150°C in helium at a flow-rate of 50 ml/min. The retention relative to pentane, the Kováts indices and the excess molar Gibbs energy of a methylene group[6], $\Delta G^E(CH_2)$, were determined from these data. The Kováts indices were calculated by interpolating the retention times, t_R, between the retention ties of adjacent paraffins, t_n, t_{n+1}. The contribution of solute–solvent interactions to the Kováts retention index was evaluated by multiple linear regression[3]

$$I = I_\alpha \alpha + I_\mu \mu + I_{c_p} c_p + I_R R \tag{1}$$

where α (Å^3) and μ (D, absolute electrostatic unit) are the solute electron polarizability and dipole moment respectively, c_p (μmol/m^2) is the surface concentration of active groups and R(Å) is the ionic radius of the cation; the coefficients I_α, I_μ, I_{c_p} and I_R characterize the magnitudes of the individual contributions.

The polarizability was evaluated from the molar refraction, R_m

$$\alpha = 3R_m/4\pi N \tag{2}$$

where N is the Avogadro number ($= 6.023 \cdot 10^{23}$). The molar refraction was evaluated from the molar mass, M, density, ρ, and refractive index, n, of the solutes:

$$R_m = \frac{n^2 - 1}{n^2 + 1} \cdot \frac{M}{\rho} \tag{3}$$

Values of the dipole moments have been published elsewhere[6].

The partial molar excess free energy of the methylene group was determined from the relative retentions of homologous paraffins, using the formula[7]

$$\Delta G^E(CH_2) = -RT \ln \frac{V_{g(n+1)} P^0_{(n+1)}}{V_{g(n)} P^0_{(n)}} \tag{4}$$

where R is the universal gas constant (= 8.31423 J/K · mol), T is the column temperature (K), $V_{g(n)}$ and $V_{g(n+1)}$ are the specific retention volumes (ml/g) of neighbouring paraffinic hydrocarbons and $P^0_{(n)}$ and $P^0_{(n+1)}$ are the vapour pressures of pure solutes under the given conditions.

RESULTS AND DISCUSSION

Retention times of paraffins, aromatic hydrocarbons, alkenes, ethers, alcohols and carboxylic acids were determined for fourteen columns packed with methacrylate ion exchangers of two basic types, carrying sulphopropyl groups and in the forms H^+, Cd^{2+}, La^{3+}, Cr^{3+}, Fe^{3+}, Co^{2+} and Ni^{2+} (see Table I). The polymers under investigation are sufficiently stable for gas chromatography (GC), in particular in the salt form[8] where the decomposition temperature exceeded 300°C according to differential thermogravimetry (DTG).

The retentions of individual groups of compounds of the same carbon number increase in the series: paraffins < olefins < aromatic hydrocarbons < ethers < ketones < carboxylic acids. In comparison with similar ion exchangers in the form of salts with alkali metals[1–3], retention on the above ionic forms was always larger. Sorbent B, characterized by a smaller specific surface area and higher polarity, exhibited a stronger retention for water than for methanol; in the form of salts with Cd^{2+}, Co^{2+} and Ni^{2+} the retention of water was even greater than that of ethanol. Individual organic acids can be separated on sorbent A, but some tailing was observed in this case. The retention of formic acid on sorbent B was higher than that of the next homologues and the same was true for methanol, apparently owing to the formation of hydrogen bonds with the polar sorbent.

Kováts retention indices calculated from the retention times (cf., Table II) enable one to compare sorbent polarity on a more general basis. First, it is apparent that the original glycidyl methacrylate copolymers are much more polar than sulphopropyl derivatives in the salt form, as evidenced by the increased Kováts indices (by 350 units for benzene and by 200 units for methanol). In the case of ion exchangers in H^+ form the interaction with alcohols increases by 230 units, but interactions with benzene and methyl ethyl ketone decrease somewhat (by 200 and 500 units, respectively).

With the exception of interactions of ion exchangers in the form of Ag^+ salts (cf., ref. 3) and of those between the original methacrylate copolymers and aromatic hydrocarbons or ketones, the interactions of ion exchangers in salt form with alcohols represent the only selective interaction in this broad spectrum of sorbents (32 types). Specific interactions were so large that the retention order was reversed as discussed below. In the series of aromatic hydrocarbons and ketones the interactions increased in the series: styrene–divinylbenzene copolymers < methacrylate ion exchangers in the form of salts with alkali metals[3] < methacrylate ion exchangers in the form of salts with heavy metals ≪ glycidyl methacrylate–ethylene dimethacrylate copolymers ≪ methacrylate ion exchangers in Ag^+ form. On the other hand, interactions with alcohols increase in the series styrene–divinylbenzene copolymers ≪ glycidyl methacrylate–ethylene dimethacrylate copolymers < methacrylate ion exchangers in the form of salts with alkali metals[3] ≈ methacrylate ion exchangers in the form of salts with heavy metals.

The statistical significance of correlation between the Kováts indices and either

TABLE I

RETENTION TIMES RELATIVE TO PENTANE OF SOLUTES ON METHACRYLATE ION EXCHANGERS
AT 150°C

Solute	Form H^+		Form Cd^{2+}		Form La^{3+}	
	A	$B^\star$	A	$B^\star$	A	$B^\star$
Hexane	2.30	1.36	2.36	1.54	2.56	1.66
Heptane	2.95	2.27	5.70	2.54	6.83	2.33
Octane	16.38	4.27	17.5	4.72	18.16	4.00
Nonane	47.18	8.00	**	9.36	39.32	7.33
Decane	109.73	15.90	***	17.72	***	15.00
Undecane	***	32.54	***	35.38	***	29.33
Benzene	3.72	3.45	4.16	2.00	4.06	2.33
Toluene	10.26	6.81	13.08	3.90	11.32	3.66
Ethylbenzene	24.18	9.81	34.25	7.45	24.89	6.00
Isopropylbenzene	***	11.54	63.25	10.45	50.00	9.33
1,2,4-Trimethylbenzene	37.43	27.27	***	14.27	79.96	13.33
o-Xylene	26.80	10.27	27.91	7.90	39.64	6.66
m-Xylene	23.72	10.18	22.07	6.81	34.19	6.66
p-Xylene	18.07	10.27	22.25	6.63	28.74	6.00
Cyclohexane	2.89	1.36	3.42	1.54	4.01	1.00
1-Hexene	2.35	1.54	2.63	1.54	3.10	1.66
1-Octene	14.87	5.00	24.44	5.18	51.28	4.33
Diethyl ether	1.53	2.72	1.47	1.54	1.73	1.00
Di-*n*-butyl ether	58.46	15.18	**	12.00	***	10.66
Acetone	2.30	32.27	2.31	11.54	3.42	4.33
Methyl ethyl ketone	4.20	15.63	5.55	6.09	6.41	3.66
Diethyl ketone	11.03	14.36	14.36	5.72	16.66	4.00
Methyl butyl ketone	4.35	41.18	**	11.63	**	8.33
Water	0.80	34.54	1.52	45.18	1.25	29.00
Methanol	1.00	22.00	3.80	20.45	1.32	16.00
Ethanol	2.12	47.00	2.41	38.18	2.85	21.00
Propanol	5.89	40.90	7.31	61.36	3.74	15.66
Isopropanol	3.84	20.00	3.97	7.54	5.03	4.33
n-Butanol	18.27	41.09	33.61	21.54	14.10	11.66
Isobutanol	11.66	11.18	16.07	9.36	18.05	6.66
sec.-Buanol	9.35	18.18	12.58	9.27	11.85	5.66
tert.-Butanol	0.64	2.09	7.50	5.72	6.85	4.00
n-Pentanol	***	26.09	55.02	29.54	46.83	22.33
2-Pentanol	***	25.00	27.41	20.72	**	11.00
n-Hexanol	***	51.54	***	53.81	***	35.66
n-Heptanol	***	38.63	***	91.63	***	68.33
n-Octanol	***	58.45	***	109.4	***	69.33
Formic acid	0.87	60.63	1.07	42.90	***	152.3
Acetic acid	11.73	32.70	1.47	52.27	**	41.00
Propionic acid	22.43	55.27	2.36	52.00	**	244.3

     * At 100°C.
    ** No elution.
   *** Data were not obtained.

Form Cr^{3+}		Form Fe^{3+}		Form Co^{2+}		Form Ni^{2+}	
A	$B^\star$	A	$B^\star$	A	$B^\star$	A	$B^\star$
2.29	1.54	2.39	1.36	2.35	1.46	2.72	1.62
7.20	2.72	5.66	2.27	5.79	2.46	5.02	2.50
17.74	5.00	15.88	4.09	14.56	4.80	13.19	4.45
★★	8.45	43.54	8.36	35.15	9.13	37.84	9.12
★★★	18.00	113.2	16.36	87.26	20.2	85.02	17.25
★★★	41.36	★★★	29.54	★★★	38.00	★★★	32.25
5.10	2.09	4.94	2.00	3.92	2.20	2.31	2.25
11.82	4.27	12.96	3.45	10.13	3.80	7.38	4.12
35.75	8.45	31.13	6.18	27.50	4.00	18.86	6.50
★★	12.72	59.90	9.27	43.86	10.86	★★★	9.37
★★★	17.45	60.37	12.90	59.90	16.46	★★★	13.12
30.82	8.45	24.90	6.54	9.75	7.46	★★★	7.25
27.33	7.54	21.84	6.18	7.20	6.20	★★★	7.25
28.49	8.18	21.00	6.09	4.86	6.66	26.73	6.87
2.96	1.36	2.67	1.18	2.50	1.46	2.31	1.62
2.68	1.54	2.35	1.36	2.35	2.09	2.36	1.62
20.69	5.18	12.98	4.27	11.54	5.00	18.75	5.25
1.34	1.54	1.47	1.54	1.47	1.13	1.34	1.50
★★	14.72	47.79	10.63	1.11	11.13	42.36	11.25
2.11	9.54	2.35	13.90	2.03	14.66	2.25	10.37
5.19	5.18	4.49	5.45	4.47	7.40	5.20	4.12
16.45	5.27	12.49	4.81	12.41	7.20	12.84	4.75
★★	12.09	33.96	9.27	32.20	13.33	42.81	10.25
1.62	43.18	1.28	31.54	1.37	56.86	—	61.62
1.66	22.45	2.35	17.72	2.73	21.80	1.62	22.50
5.16	47.72	2.13	35.63	2.26	48.80	2.95	36.00
13.89	38.63	5.66	31.36	5.86	44.46	9.16	38.87
5.59	4.81	3.45	5.63	3.52	9.46	3.47	5.25
28.84	12.09	16.83	13.63	14.47	22.80	13.38	14.62
15.23	6.09	12.69	6.09	11.69	10.13	12.80	7.75
10.56	5.90	8.52	6.63	9.05	10.00	8.68	6.50
3.09	3.81	5.66	3.81	5.79	5.80	5.38	4.62
★★★	23.00	22.49	24.27	39.05	35.33	★★★	30.00
★★★	10.27	21.28	11.54	31.13	22.80	★★★	21.25
★★★	29.09	77.35	37.72	96.54	58.33	★★★	53.12
★★★	64.63	★★★	61.36	★★★	125.5	★★★	107.2
★★★	81.09	★★★	64.36	★★★	★★★	★★★	112.5
3.60	47.72	11.09	45.72	9.96	48.86	6.56	59.37
★★	37.90	23.58	40.90	15.33	68.86	9.48	112.5
★★	109.1	47.16	101.4	37.41	94.46	★★	110.4

TABLE II

KOVÁTS RETENTION INDICES ON METHACRYLATE ION EXCHANGERS AT 150°C

Solute	Copolymers		Form H^+		Form Cd^{2+}		Form La^{3+}	
	A	B	A	B*	A	B*	A	B*
Benzene	709	956	715	767	656	655	649	700
Toluene	795	1051	773	875	775	770	753	785
Ethylbenzene	***	1136	838	931	**	867	743	869
Isopropylbenzene	***	***	908	954	**	918	**	935
1,2,4-Trimethylbenzene	***	***	879	1076	**	968	**	985
Methanol	514	809	500	1046	655	1023	529	1010
Ethanol	588	846	590	**	603	**	613	1052
Propanol	625	951	741	**	723	**	640	1009
n-Butanol	***	1083	811	**	**	1031	776	967
Isobutanol	***	***	781	950	793	900	800	886
sec.-Butanol	***	***	768	1019	771	899	758	859
tert.-Butanol	***	***	**	686	726	829	701	800
n-Pentanol	***	1169	***	1070	**	1076	***	1062
2-Pentanol	***	***	***	1037	**	1025	***	901
n-Hexanol	***	***	***	**	***	**	***	**
Diethyl ether	553	607	551	729	545	600	558	500
Di-*n*-butyl ether	***	970	926	994	***	937	***	954
Acetone	621	863	600	1099	597	934	631	814
Methyl ethyl ketone	713	950	785	**	698	838	841	695
Diethyl ketone	***	***	800	**	783	829	823	793
Methyl butyl ketone	***	1116	724	724	***	935	***	818

* At 100°C.
** Data were not calculated.
*** Data were not obtained.

the ionic radius or the molar mass of the cation was tested on the whole set of data. Significant dependences were found for methanol and methyl ethyl ketone. In the case of benzene, although the values varied over a broad interval, the correlation was not significant, because these interactions were of a different nature, involving mostly the polymer matrix. The Kováts indices in general decrease with increasing ionic radius and increasing molar mass of the cation.

To conclude, three specific interactions are typical for the investigated methacrylate ion exchangers:

(1) between the methacrylate ion exchanger in salt form and alcohols and carboxylic acids, interpreted as due to the formation of hydrogen bonds;

(2) between glycidyl methacrylate–ethylene dimethacrylate copolymers and aromatic hydrocarbons and ketones, attributed to the formation of coordinate bonds;

(3) between the methacrylate ion exchangers in Ag+ form[3] and aromatic hydrocarbons and ketones, ascribed to the formation of coordinate compounds which involve a double bond.

Form Cr^{3+}		Form Fe^{3+}		Form Co^{2+}		Form Ni^{2+}	
A	B*	A	B*	A	B*	A	B*
670	656	685	678	657	618	584	680
757	777	781	772	761	765	740	789
**	900	868	858	874	773	810	856
***	955	935	916	926	922	***	908
***	997	936	966	959	975	***	960
561	1029	598	1015	617	1014	548	1044
672	**	587	**	595	**	634	**
774	1096	600	**	702	**	762	**
**	949	806	974	800	1021	801	977
785	841	779	856	777	913	797	880
704	835	740	868	749	913	757	856
627	758	700	789	700	830	707	808
***	1031	835	1067	913	1092	***	1089
***	928	830	949	888	1021	***	1036
***	1061	962	**	***	***	***	**
535	600	544	626	545	532	529	584
***	975	912	937	**	925	916	936
590	918	598	937	583	961	581	923
673	811	674	841	672	863	704	790
793	814	777	823	783	863	797	812
***	949	877	815	892	900	918	922

TABLE III

COEFFICIENTS CALCULATED USING EQN. 1 AND AVERAGE CONTRIBUTIONS TO THE KOVÁTS INDICES

Mean square deviations: * 35.6; ** 22.1; *** 94.8.

	Solution interaction		Sorbent interaction		Average contribution (%)			
	I_α	I_μ	I_{c_p}	I_R	$I_\alpha\bar{\alpha}$	$I_\mu\bar{\mu}$	$I_{c_p}\bar{c}_p$	$I_R\bar{R}$
Aromatic hydrocarbons*	−482	3.06	1.43	−149.5	75.2	0.1	2.4	22.3
Ethers**	−426	−56.2	2.33	−161	63.9	7.9	3.9	24.3
Alcohols***	−314	−427	14.6	−133	17.6	47.4	19.3	2.25

TABLE IV

VALUES OF PARTIAL MOLAR EXCESS GIBBS FREE ENERGY OF A METHYLENE GROUP, $\Delta G^{E}(CH_2)$ (kJ/mol), OF METHACRYLATE ION EXCHANGERS

Sorbent A; standard deviation $\pm$ 0.66 kJ/mol.

Form H^+	Form Cd^{2+}	Form La^{3+}	Form Cr^{3+}	Form Fe^{3+}	Form Co^{2+}	Form Ni^{2+}
−1.04	−1.42	−1.40	−1.19	−0.92	−0.80	−0.37

Multiple linear regression of Kováts indices (eqn. 1), which includes contributions of (i) the solute (characterized by electron polarizability and dipole moment) and (ii) the sorbent (characterized by the surface concentration of groups and by ionic radius), indicated that this equation is valid also for the ion exchangers containing heavy metal ions. The contribution of non-specific interactions in this case was somewhat smaller (75% as compared to 98% for aromatic hydrocarbons, Table III). Non-specific interactions involving dispersion forces further decrease to 17% for alcohols, where the contribution of dipole–dipole interactions rises to 46%. Contribution (ii) due to the sorbent remains approximately constant at 22–28%. These values and the general trends are similar to those established for the series which included salts with alkali metals[3]. Hence, the sorbents investigated belong to class 3 of the Kiselev classification[9].

Thermodynamic quantities can be used for correlating sorbent polarity. Values of the partial molar excess free energy of a methylene group, $\Delta G^{E}(CH_2)$, range between − 0.37 and − 1.04 kJ/mol for the ion exchanger based on polymer A with sulphopropyl groups in H^+ form (Table IV), and parallel the increase in polarity measured by the Kováts indices. However, $\Delta G^{E}(CH_2)$ is inferior to the Kováts indices in that it is not sensitive enough in reflecting the transition from the original polymer to the ion exchanger with sulphopropyl groups in different ionic forms: whilst the Kováts indices order the individual sorbents into well defined series, the overall difference in $\Delta G^{E}(CH_2)$ within the investigated series of sorbents (0.82 kJ/mol for series A) is comparable with the standard deviation ($\pm$ 0.66 kJ/mol). Moreover, the values are complicated by inaccuracies in the heats of evaporation. The molar excess enthalpy would be more exact but less sensitive still to the variation in solvent polarity.

The values of $\Delta G^{E}(CH_2)$ found in this study are smaller than those determined for Porapak P and T[7] but also negative, indicating that the heats of adsorption of all solutes are larger than their heats of evaporation.

CONCLUSIONS

Because of their macroporous structure the copolymers studied can be used also in the analysis of organic compounds in aqueous solutions. They can be used for separation of hydrocarbon isomers, ketones, ethers and alcohols.

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