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EVALUATION OF THE SELECTIVITY OF SOME ORGANO-SUBSTITUTED LAYER SILICATES*

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SUMMARY

The thermodynamic characteristics of the adsorption of individual C_8 alkylbenzenes on organo-substituted layer silicates and chromatograms of separation of artificial three- and four-component mixtures on these sorbents have been obtained by gas adsorption chromatography. The separation properties of chromatographic columns containing modified minerals have been determined, and it was established that with highly dispersed silicates (montmorillonite and fluorhectorite) the selectivity of the sorbent contributes considerably to the separation. It is shown that, depending on the type of modifying cations, the selectivity of organo-substituted layer silicates is determined by either the enthalpic or the entropic component of the Gibbs free energy change on adsorption.

INTRODUCTION

The separation of organic compounds with narrow boiling ranges is one of the most difficult problems in analytical gas chromatography. Multi-component sorbents based on organo-substituted clay minerals have been used successfully for this purpose[1–5]. The complicated composition of the sorbent makes it difficult to establish the role of each of the components in chromatographic separation and therefore there are no clear requirements for the characteristics of the organic complexes used. In order to work them out, a systematic investigation of the selectivity of organo-substituted clay minerals with respect to hydrocarbons of narrow boiling range is necessary.

It is known[6] that the separation properties of a chromatographic packed column with respect to substances that have similar boiling points is determined by the efficiency of the column itself and the selectivity of the sorbent. The latter, in accordance with Herington's equation[7], is directly connected with the retention volumes of adsorbates, which are proportional to the Gibbs free energy change in the

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system[8]. Therefore, if the separation efficiency of the column is determined mainly by the selectivity of the sorbent, it may be possible to calculate the potential separation efficiency of a packed column from the retention volumes of individual components of the mixture to be separated. Also, by measuring the different constituents of the Gibbs free energy, the role of the structure of the modifying layer in determining the selectivity of the sorbent may be established.

EXPERIMENTAL

Pyzhevsky montmorillonite, kovdorsky vermiculite and synthetic fluorhectorite, the basic characteristics of which are listed in Table I, were used. A standard sample of Bentone-245 was used for comparison. The minerals were modified with alkylammonium and alkylpyridinium chlorides and bromides. The methods for obtaining organo-substituted samples were analogous to those reported earlier[9].

The amounts of sorbed organic substances were determined by the combustion method[10]. The specific surface areas of the sorbents with respect to water and *n*-hexane were determined from adsorption isotherms obtained by the microbalance method. The gas chromatographic conditions were described earlier[11].

RESULTS AND DISCUSSION

The determination of the separation properties of columns containing the investigated sorbents showed that with highly dispersed minerals (montmorillonite, fluorhectorite) the selectivity of the sorbents contributes considerably to the separation. This was indicated by the relationship between the relative retention volumes of the components to be separated using the modified samples of the minerals and the separation ability of the columns. Table II shows that the degree of separation of a mixture of *p*-xylene and ethylbenzene by cetylpyridinium-montmorillonite is higher

TABLE I

PHYSICO-CHEMICAL CHARACTERISTICS OF LAYER SILICATES

Property	*Mineral*		
	Montmo-rillonite	*Fluor-hectorite*	*Vermic-ulite*
Cation-exchange capacity (mg-equiv./g)	0.90–1.0	0.75–0.82	1.40–1.50
Basic cation in exchange complex	Ca^{2+}	Na^+	Mg^{2+}
Elementary charge (charge units)	0.39	0.65	0.85
Exchange position area ($Å^2$)	60.0	37.7	27.5
Effective surface area determined from adsorption of water (m^2/g)	420–480	280	470–500
External surface area determined from adsorption of hexane (m^2/g)	30–40	20	8–10
Particle size (*μm*)	0.03–0.3	–	3–5

TABLE II

EFFICIENCY (NUMBER OF THEORETICAL PLATES, N), SELECTIVITY (V_{rel}) AND SEPARATION ABILITY (K_1, K_b) OF CHROMATOGRAPHIC COLUMNS CONTAINING MODIFIED MINERALS

Sorbent	Temperature (°C)	N	p-Xylene Ethylbenzene		m-Xylene p-Xylene		K_1
			V_{rel}	K_b	V_{rel}	K_b	
Bentone-245	93	2000	1.04	0.25	1.20	0.98	1.70
Cetyltrimethylammonium-montmorillonite	110	1880	0.97	0	1.26	—	3.50
Cetylpyridinium-montmorillonite	93	1070	0.92	0.84	1.17	0.98	1.79
Cetylpyridinium-fluorhectorite	94	1360	0.90	0.93	1.05	0.95	1.60
Cetylpyridinium-vermiculite	99	670	0.97	0.06	1.12	0.60	—

than by Bentone-245 (K_b = 0.84 and 0.25, respectively), which correlates with the relative retention volumes of the mixture on these sorbents (0.92 and 1.04), but not with the number of theoretical plates, N (1070 and 2000). An analogous situation is observed on comparing the separation criteria and the efficiency of columns containing cetylpyridinium-fluorhectorite and Bentone-245 with respect to the same pair of hydrocarbons. With a column containing cetyltrimethylammonium-montmorillonite, which gives a slightly different value of N to the column containing Bentone-245, the mixture of p-xylene and ethylbenzene is hardly separated; this is due to the insufficient difference in the retention volumes of the sorbates. At the same time, the separation criterion, K_1, for the m-xylene–p-xylene mixture on cetyltrimethylammonium-montmorillonite exceeds the K_1 values obtained with other sorbents. This agrees with the highest values of V_{rel} (Table III) of the sorbates when they are adsorbed by cetyltrimethylammonium-montmorillonite.

As the separation ability of highly dispersed adsorbents is determined by their selectivity, the preliminary investigation of the adsorption thermodynamics of individual substances allows a more certain determination of the potential separation properties of the sorbents. The chromatograms in Figs. 1 and 2 confirm that when analysing hydrocarbon mixtures over a narrow temperature range the same yields of the components and, to some extent, the same degree of separation remain, which may be expected from the differences in the retention volumes of individual sorbates. The retention volumes and heats of adsorption of o-, m- and p-xylene on cetyltrimethylammonium-montmorillonite (Q_a = 47, 52 and 46 kJ/mol, respectively) confirm the high separation ability of this sorbent with respect to the mixture examined. In fact, Fig. 1 shows that for this sorbent all three isomers are separated from each other and the peaks of m- and p-xylene are further apart than when other organocomplexes are used as sorbents (Fig. 2).

From the thermodynamic point of view, the selectivity of organo-substituted layer silicates is due in some instances to differences in the enthalpies and in other instances to differences in the entropies of adsorption of individual hydrocarbons.

TABLE III

RELATIVE RETENTION VOLUMES (V_{rel}) AND ENTHALPIES OF ADSORPTION ($\Delta \bar{Q}_a$, kJ/mol) of AROMATIC HYDROCARBONS ON ORGANO-SUBSTITUTED LAYER SILICATES AT 150°C

Sample mixture	Bentone-245		Montmorillonite Cetylpyridinium (a = 1.41)*		Cetylammonium (a = 1.36)*		Cetyltrimethyl-ammonium (a = 1.54)*		Vermiculite Cetylpyridinium (a = 1.34)*		Cetylammonium (a = 1.24)*		Cetylpyridinium-fluorhectorite (a = 1.39)*	
	V_{rel}	$\Delta \bar{Q}_a$	V_{rel}	$\Delta \bar{Q}_a$	V_{rel}	$\Delta \bar{Q}_a$	V_{rel}	$\Delta \bar{Q}_a$	V_{rel}	$\Delta \bar{Q}_a$	V_{rel}	$\Delta \bar{Q}_a$	V_{rel}	$\Delta \bar{Q}_a$
m-Xylene-p-xylene	1.20	0	1.17	1	1.11	3	1.26	6	1.12	0	1.17	2	1.05	0
p-Xylene-ethylbenzene	1.04	0	0.92	−1	1.00	−3	0.97	−2	0.97	−1	0.98	0	0.90	0

* a = Modifier sorbed in mg-equiv./g.

TABLE IV

SPECIFIC RETENTION VOLUMES (V_s, cm³/m²), ISOSTERIC ENTHALPIES ($\bar{Q}_a$, kJ/mol) AND DIFFERENTIAL ENTROPIES ($-\Delta \bar{S}_a$ J/mol·°K) OF ADSORPTION OF AROMATIC HYDROCARBON ON ORGANO-SUBSTITUTED LAYER SILICATES AT 150°C

Adsorbate	Bentone-245			Montmorillonite Cetylpyridinium (1.41 mg-equiv./g)			Cetylammonium (1.36 mg-equiv./g)			Vermiculite Cetylpyridinium (1.34 mg-equiv./g)			Cetylammonium (1.25 mg-equiv./g)			Cetylpyridinium-fluorhectorite (1.39 mg-equiv./g)		
	V_s	$\bar{Q}_a$	$-\Delta \bar{S}_a$	V_s	$\bar{Q}_a$	$-\Delta \bar{S}_a$	V_s	$\bar{Q}_a$	$-\Delta \bar{S}_a$	V_s	$\bar{Q}_a$	$-\Delta \bar{S}_a$	V_s	$\bar{Q}_a$	$-\Delta \bar{S}_a$	V_s	$\bar{Q}_a$	$-\Delta \bar{S}_a$
Benzene	0.29	44	72	0.73	40	53	−	−	−	3.38	46	55	1.82	34	32	1.30	42	53
Toluene	0.47	46	72	0.94	43	58	−	−	−	4.66	49	59	2.79	38	38	−	−	−
Ethylbenzene	0.70	51	79	1.44	45	59	0.82	38	47	6.58	54	68	4.69	43	47	2.50	44	54
p-Xylene	0.75	51	80	1.32	44	58	0.82	41	54	6.37	53	66	4.73	42	43	2.35	45	56
m-Xylene	0.90	51	78	1.55	45	60	0.91	44	60	7.11	53	65	5.57	44	46	2.63	45	55
o-Xylene	0.97	51	76	1.60	45	59	0.87	42	56	7.58	53	65	5.32	44	46	2.75	45	54

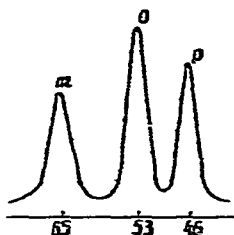Fig. 1. Separation of artificial three-component mixture on cetyltrimethylammonium-montmorillonite. p = p-Xylene; m = m-xylene; o = o-xylene.
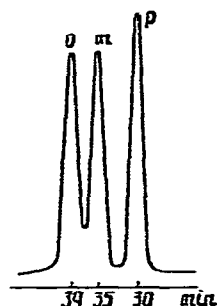
Fig. 2. Separation of artificial three-component mixture on Bentone-245. Symbols as in Fig. 1.

Therefore, the highest values of V_{rel} for the m-xylene–p-xylene system using cetyltrimethylammonium-montmorillonite correlate with the highest values of $\Delta\bar{Q}_a$ (Table III). The relative enthalpies of adsorption and retention volumes of m- and p-xylene on cetylammonium-montmorillonite and -vermiculite are lower. For these adsorbents, the series of increasing retention volumes of dialkylbenzene isomers correlates with the series of increasing enthalpies of adsorption. Therefore, the enthalpic factor plays the main role in the change in free energy when adsorption on organo-derivatives of these adsorbents takes place, and the separation effect is due mainly to the difference in the enthalpies of adsorption of the isomers. These differences are connected with the fact that the centres of Van der Waals forces of the molecular chains of the adsorbed structural isomers are not at the same distances from the solid surfaces[8,12]. Also, the different arrangements of the substituents in the benzene ring change the electronic density distribution in the skeleton of the ring, resulting in different energies of interaction between the sorbate molecules and the active centres of the adsorbents. However, the differences in the interactions between alkylbenzene molecules and the surfaces of the adsorbents depend rather on the accessibility of the active centres of the organo-complexes for the molecules adsorbed than on the dipole moment. This is confirmed by the discrepancy between the series of increasing enthalpies of adsorption of xylene isomers on the organo-substituted minerals (for cetyltrimethylammonium- and cetylammonium-montmorillonite m- > o- > p-) and the series of increasing dipole moments of the sorbate molecules (o- > m- > p-).

With cetylpyridinium-substituted layer silicates and Bentone-245, there is virtually no difference in the enthalpies of adsorption of xylene isomers (Table III). Therefore, the selectivity of these sorbents is determined by the same difference that is observed in the entropies of adsorption of the hydrocarbons examined (Table IV). The predominating influence of the entropic factor in separations on the sorbents is apparently connected with the fact that modifying groups with a cyclic function (cetylpyridinium) form geometrically less homogeneous layers on the surface. This creates conditions for greater differences in the entropies of rotation of xylene isomers when adsorption takes place; the symmetrical molecules of p-xylene lose more rotational degrees of freedom than m-xylene on adsorption and, as a result, are eluted first from the column.

Taking as a basis earlier investigations[5,9] and considering the relatively small

increase in the retention volumes of benzene on organo-substituted sorbents in comparison with the unsubstituted sorbents[13], it can be concluded that the separation of aromatic hydrocarbons takes place mainly at the external surface of modified layer silicates. Moreover, under the gas chromatographic conditions used (temperature 100–150°C and degree of surface coverage not exceeding 0.05), the polarity of the active centres of the modifying layer and its micro-relief would apparently affect the adsorption process. This assumption was supported by the fact that an increase in the enthalpy of adsorption of xylenes from 36–39 to 44–45 kJ/mol was observed on a montmorillonite sample that had been washed with aqueous ethanol in order to remove excess of sorbed cetylpyridinium groups.

In conclusion, this work indicates that under the gas chromatographic conditions used, the potential separation efficiency of highly dispersed sorbents may be determined from the thermodynamic adsorption characteristics of individual substances. The same thermodynamic characteristics allow the determination of the effect of the components of the Gibbs free energy change on adsorption on the selectivity of organo-substituted layer silicates.

REFERENCES

1 M. A. Hughes, D. White and A. L. Roberts, *Nature (London)*, 184 (1959) 1796.
2 D. White, in W. F. Bradley (Editor), *Clays and Clay Minerals, Proceedings of the 12th National Conference on Clays and Clay Minerals, Atlanta, Georgia, September 30–October 2, 1963*, Pergamon Press, Oxford, New York, 1964, p. 257.
3 W. H. Slabaugh and R. W. Vasofsky, *Clays Clay Miner.*, 23 (1975) 458.
4 R. W. Vasofsky and W. H. Slabaugh, *J. Colloid Interface Sci.*, 55 (1976) 342.
5 V. G. Berezkin, V. S. Gavrichev, L. N. Kolomiyets, A. A. Korolev, V. N. Lipavskii, N. S. Nikitina and V. S. Tatarinskii, *Gazovaya Khromatografiya v Neftekhimii*, Nauka, Moscow, 1975, p. 200.
6 A. V. Kiselev and Y. I. Yashin, *Adsorbtsionnaya Gazovaya i Zhidkostnaya Khromatografiya*, Khimiya, Moscow, 1979, p. 21.
7 E. F. G. Herington, in D. H. Desty (Editor), *Vapour Phase Chromatography*, Butterworths, London, 1957, p. 5.
8 A. V. Kiselev and Y. I. Yashin, *Gazo-adsorbtsionnaya Khromatografiya*, Nauka, Moscow, 1967, p. 116.
9 A. I. Zhukova, S. V. Bondarenko and Y. I. Tarasevich, *Neftekhimiya*, 21 (1981) 765.
10 J. L. McAtee, Jr., *Amer. Mineral.*, 44 (1959) 1230.
11 S. V. Bondarenko, A. I. Zhukova and Y. I. Tarasevich, *Ukr. Khim. Zh.*, 46 (1980) 370.
12 A. N. Korol, *Nepodvizhnaya Faza v Gazo-zhidkostnoi Khromatografii*, Naukova Dumka, Kiev, 1969, p. 116.
13 M. Taramasso and F. Veniale, *Control Miner. Petrol.*, 21 (1969) 53.