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ORGANIC DERIVATIVES OF HUNGARIAN BENTONITES IN HYDROCARBON ANALYSIS

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SUMMARY

As known from the literature, the dimethyldioctadecylammonium derivatives of clay minerals can be used as stationary phases in the gas chromatography of aromatic hydrocarbons.

Several Hungarian bentonites containing 40–90% of montmorillonite were examined in order to obtain such selective stationary phases. The investigations showed also that the Hungarian bentonites can be used as starting materials for the preparation of these substances, and the resulting organo-bentonites have properties that may in some cases have superior selectivity and efficiency compared with those of the well known stationary phase Benton 34. The differences in the relative volatilities of the individual derivatives make possible the choice of the appropriate derivative for a given separation, and in some cases a mixture of two or more derivatives may be used as the most suitable stationary phase for a given separation.

INTRODUCTION

Since the early work of HUGHES *et al.*[1], the dimethyldioctadecylammonium derivative of a montmorillonite-containing clay mineral, the so-called Bentone 34, has been widely used in gas chromatography (GC) as a stationary phase, on account of its high selectivity towards aromatic hydrocarbons. This stationary phase is very effective in separating *meta*- and *para*-isomers; the relative volatility for the *m–p*-xylene pair is about 1.3 in the case of Bentone 34.

The work of TARAMASSO and coworkers[2–5] has shown that not only montmorillonite but also other clay minerals can be used for the preparation of such stationary phases, and among these derivatives there are some substances that are more selective and more effective than Bentone 34.

The more selective stationary phases can be prepared by using such clay minerals as nontronites, beidellites and vermiculites. However, these minerals are rather rare, and in Hungary only traces of them can be found naturally. On the other hand, a great number of bentonites occur in Hungary, the composition and properties of which are very different, so we decided to examine several Hungarian bentonites in order to find those types which could serve as starting materials for the production of a selective stationary phase for the GC of aromatic hydrocarbons.

TABLE I

MOST IMPORTANT DATA OF THE BENTONITES INVESTIGATED

Bentonite	*Montmorillonite content (%)*	*Exchangeable cations, mg equiv./100 g*				
		Ca	*Mg*	*Na*	*K*	*Total*
Istenmezeje (Na_2CO_3-exchanged, 2:1)	concentr.	24	16	87	1.3	127
Golop II	63	49	15	0.6	2.2	66
Salgótarján	40	15	16	20	1	52
Mád	64	66	50	5.8	2.5	124
Nagymányok	90	51	55	1.2	–	107
Illite, Füzérradvány	—	13.5	12.6	2.6	2	30.7
Pákozd	63	55	43	4.3	1.5	105
Eger II	63	52	54	16	2.2	124
Bánd	75	71	34	2	0.9	108
Komlóska	50	42	24	2.3	1.8	70

Table I shows the more important properties of the bentonites investigated[6]. It can be seen that the Hungarian bentonites contain mainly Ca and Mg as exchangeable cations whereas the Wyoming montmorillonite[6], the starting material for Bentone 34, contains mainly sodium ions. Two of the materials investigated were submitted to cation exchange by treatment with sodium carbonate. In order to obtain reasonable retention times and efficiencies, the bentonite of Bánd was also treated with sodium carbonate, and as a result of this treatment both the efficiency and selectivity were increased.

EXPERIMENTAL

The derivatives were prepared by the following method. To a solution which contained the required amount of dimethyldioctadecylammonium chloride (Arquad 2 HT) was added an aqueous suspension of the bentonite (6 g/l) at a temperature of 40–60°. The proportion of bentonite to Arquad was 2:1 unless otherwise indicated. The mixture was stirred for 2 h, then filtered and washed. The resulting organo-bentonite was dried under an infrared lamp.

The organo-bentonite was applied to the surface of the support from a benzene suspension (it swells in benzene and after the removal of the benzene the organo-bentonite adheres well to the support). The ratio of the derivative to the support was 15:85.

The columns prepared with the different bentonite derivatives were tested in a Pye Argon Chromatograph. This apparatus is particularly suitable for such investigations since its 120-cm long straight column allows column packing to be carried out with a high reproducibility. The temperature of the column was maintained in most experiments at 100° and the argon flow-rate was 1.2 l/h. The samples were introduced with a micropipette having a volume of 0.025 μl.

The test substances were benzene, toluene, ethylbenzene, *p*-xylene, isopropylbenzene, *o*-xylene, *m*-xylene and *n*-propylbenzene. In order to make it possible to calculate retention indices, the C_7–C_{11} *n*-alkanes were also injected.

From the test chromatograms, the following data were measured or calculated.

TABLE II

RETENTION VALUES

Values are given in mm (2.2 mm corresponds to 1 min).

Bentonite	*Benzene*	*Toluene*	*Ethyl-benzene*	*p-Xylene*	*o-Xylene*	*m-Xylene*	*Isopropyl-benzene*	*n-Propyl-benzene*	*n-Heptane*	*n-Octane*	*n-Nonane*	*n-Decane*	*n-Undecane*
Istenmezeje (2:1)	36	62	105	114	144	157	130	191	11	24	51	108	—
Golop II	36	61	102	109	138	167	125	199	7	14	31	67	142
Salgótarján	16	29	51	59	70	76	67	100	5	11	23	55	115
Mád	36	61	103	109	131	171	127	196	7	15	33	70	149
Nagymányok	24	46	84	89	107	121	112	171	8	20	44	99	227
Illite, Füzérradvány	14	24	41	44	55	58	51	77	8	12	26	53	109
Pákozd	30	50	85	97	116	140	108	170	8	15	33	72	151
Eger II	28	50	86	93	118	131	112	203	9	20	44	96	207
Erdőbénye	24	43	71	81	100	107	90	138	9	16	37	79	168
Istenmezeje (3:1)	26	44	75	78	97	122	92	150	6	13	27	57	118
Komlóska	33	57	96	104	131	147	117	184	7	24	49	105	222
Bánd	36	62	105	112	139	169	133	210	8	16	35	77	166

(1) Retention times or distances. These data are characteristic for the retaining power of the derivative under investigation, but they seem to be independent of other properties.

(2) Relative volatilities of the aromatic hydrocarbon pairs in the order of elution. These values give an idea of the selectivity of the derivative and form the basis for further calculations.

(3) The number of theoretical plates and from it height to a theoretical plate (HETP) values. These data are also in themselves characteristic and are necessary for other calculations. Calculations are performed for *p*-xylene, *m*-xylene, *n*-propylbenzene and for an *n*-alkane. *p*-Xylene and *n*-propylbenzene are the aromatic hydrocarbons retained the least by the derivatives and *m*-xylene is retained the most, and the data referring to the aromatics compared with those of the *n*-alkane may throw some light on the difference in mass transfer of the two types of hydrocarbons.

(4) Retention indices of *p*-xylene and *m*-xylene. The deviation of the actual retention index of *p*-xylene from the value that could be obtained for a hypothetical *n*-alkane having the same boiling point as *p*-xylene is characteristic for the minimum selectivity shown by the derivatives towards aromatic hydrocarbons. The difference between the retention indices of *m*- and *p*-xylene indicates the maximum selectivity that can be obtained for aromatic hydrocarbons, except for those that have an unsaturated side-chain, *e.g.*, styrene. It should be remembered that the two xylenes have a difference in boiling point of only 0.75°.

(5) From the relative volatilities and efficiencies, column lengths were calculated that would be necessary to separate the *m*–*p*-xylene pair and the hydrocarbon pair most difficult to separate.

RESULTS AND DISCUSSION

Table II shows the retention distances of the columns of the derivatives in-

TABLE III

RELATIVE VOLATILITIES

Bentonite	*p-Xylene–ethylbenzene*	*Isopropylbenzene–p-xylene*	*o-Xylene–isopropylbenzene*	*m-Xylene–o-xylene*	*n-Propylbenzene–m-xylene*	*m-Xylene–p-xylene*
Istenmezeje (2:1)	1.09	1.14	1.12	1.09	1.22	1.38
Golop II	1.07	1.15	1.10	1.21	1.19	1.53
Salgótarján	1.15	1.13	1.05	1.10	1.32	1.29
Mád	1.06	1.16	1.04	1.31	1.14	1.57
Nagymányok	1.06	1.27	0.96	1.12	1.41	1.37
Illite, Füzérradvány	1.09	1.15	1.09	1.04	1.33	1.30
Pákozd	1.14	1.11	1.08	1.20	1.22	1.44
Eger II	1.09	1.20	1.05	1.11	1.55	1.40
Erbőbénye	1.13	1.11	1.11	1.07	1.29	1.32
Istenmezeje (3:1)	1.05	1.18	1.05	1.27	1.22	1.57
Komlóska	1.08	1.13	1.12	1.13	1.25	1.41
Bánd	1.07	1.18	1.23	1.22	1.25	1.50

vestigated for the test substances and the *n*-alkanes. All the conditions being identical, the differences in the retentions of the same constituent show the difference in the retaining power of the various derivatives. This value, however, does not mean anything in itself, and in fact a derivative having a relatively great retaining power can show a poor selectivity and low efficiency. On the other hand, a derivative with a small retaining power will have a small capacity and therefore a low loadability. It can be seen from Table II that the differences in the retention are considerable and this fact must be considered when evaluating the derivatives.

Table III shows the relative volatilities calculated for six pairs of component. It can be seen that it is not the *m*–*p*-xylene pair that gives rise to the greatest difficulty but in most cases the *p*-xylene–ethylbenzene pair. These data are useful in choosing the suitable derivative for a given separation problem and also yield the data

TABLE IV

HETP VALUES (mm)

Bentonite	*p-Xylene*	*m-Xylene*	*n-Propylbenzene*	*n-Undecane*
Istenmezeje (2:1)	1.21	1.37	1.13	1.15
Golop II	1.08	1.24	0.96	0.90
Salgótarján	1.67	2.16	1.05	0.80
Mád	1.25	1.25	0.98	1.27
Nagymányok	1.86	1.57	1.67	1.18
Illite, Füzérradvány	4.83	3.42	2.48	1.34
Pákozd	1.70	2.50	1.47	1.24
Eger II	1.60	2.02	1.55	1.20
Erdöbénye	1.40	2.37	1.59	1.18
Istenmezeje (3:1)	0.76	0.68	0.66	1.05
Komlóska	1.16	1.32	1.16	0.99
Bánd	1.23	1.07	1.05	—

necessary for calculating the column length for a given degree of separation. If the relative volatility for a given pair of components attains the value 1.10, it is high enough for a good separation ($R = 1.5$) when a 4–6-m long column is used.

Table IV gives the HETP values for four test compounds. These values are very important in the evaluation of the derivatives, and also give information on the nature of the selectivity. In some cases, the relatively high selectivity is not connected with the increased HETP values, as can be seen in the case of the Istenmezeje bentonite, where the HETP values do not differ greatly for *m*- and *p*-xylene nor in the case of the *n*-propylbenzene–*n*-undecane pair. An example of the opposite case is the Salgótarján bentonite, where the HETP values are considerably higher for *m*-xylene than for *p*-xylene and again higher for *n*-propylbenzene than for *n*-undecane. The same phenomenon can be observed for the Erdöbénye bentonite. In these cases, the selectivity properties result in decreased efficiency. It must be noted that higher HETP values are due mainly to increased tailing.

Table V shows the retention indices calculated for *p*- and *m*-xylene, and also the column lengths necessary for the separation of the *m*–*p*-xylene pair and for the pair most difficult to separate by the column under investigation. From the deviation of the retention index of *p*-xylene from the value for a hypothetical *n*-alkane boiling at the boiling point of *p*-xylene, the general selectivity of the derivative shown

TABLE V

RETENTION INDICES AND CALCULATED COLUMN LENGTHS

Bentonite	*Retention indices*		*Index differences (index units)*		*Column length (m)*	
	m-Xylene	*p-Xylene*	*p-Xylene*	*m-Xylene–p-xylene*	*m-Xylene–p-xylene*	*Max.*
Istenmezeje (2:1)	1051	1007	157	44	0.65	7.2
Golop II	1121	1064	214	57	0.37	10.42
Salgótarján	1143	1108	258	39	1.54	34.3
Mád	1118	1059	209	59	0.38	30.4
Nagymányok	1024	986	136	38	0.92	45.3
Illite, Füzérradv.	1012	976	126	36	3.26	117.0
Pákozd	1090	1040	190	50	0.96	16.4
Eger II	1040	997	147	43	0.89	32.0
Erdöbénye	1040	1003	153	37	1.45	20.0
Istenmezeje (3:1)	1105	1043	193	62	0.21	12.1
Komlóska	1045	999	149	46	0.56	8.7
Bánd	1103	1049	199	54	0.40	10.40
Mixture of Istenmezeje, Mád and Erdöbénye	1070	1018	168	52	0.39	4.7

towards aromatic hydrocarbons can be seen. The difference between the indices of the two xylenes is a measure of the special interaction between *m*-xylene and the derivative.

From the necessary column lengths, it can be seen that for the separation of the *m–p*-xylene pair in some cases a column length of about 20 cm is sufficient. Unfortunately, in this case for the separation of the *p*-xylene–ethylbenzene pair a column length of about 12 m would be necessary. Generally, it can be said that when a derivative shows high selectivity for the *m–p*-xylene pair, its selectivity for the *p*-xylene–ethylbenzene pair is rather low. The selectivity values, as shown by the example of the Istenmezeje bentonite, can be influenced by the bentonite–Arquad proportion and also by other parameters of the preparation. Another possibility is to use stationary phases prepared from two or more derivatives. In such manner it is possible to eliminate the too low relative volatilities for the critical pairs. In one experiment of this type we obtained a column which produced the best values in Table V. However, the calculation of the proportions to be used in this mixing is not yet clear, as the relative volatilities do not seem to be quite additive in this respect and the deviations due to interactions between the various derivatives in the mixtures must be taken into consideration. Also, the experimental data available for this calculation are not yet sufficient.

CONCLUSIONS

The investigations have shown that the Hungarian bentonites are suitable for the preparation of dimethyldioctadecylammonium derivatives which, in turn, can be used as selective stationary phases in the GC of aromatic hydrocarbons. The selectivity, efficiency and other properties of these substances may be very different, but these variations may prove very useful because it gives the possibility of solving

almost any analytical task in hydrocarbon analysis, using one of the derivatives studied or a convenient mixture of two or more of them.

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