CHROM. 12,484

MODIFICATION OF THE ROHRSCHNEIDER METHOD FOR THE CLASSIFICATION OF THE POLARITY OF POLYMERIC SORBENTS BASED ON METHACRYLIC ACID ESTERS

J. LUKÁŠ

Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences, 162 06 Prague 6 (Czechoslovakia)

SUMMARY

In order to express the polarity of polymeric sorbents based on methacrylic acid esters, the Rohrschneider method has been modified by replacing squalane with a non-polar adsorbent, Carbopack B. Using ethanol sorption as an example, it was shown that the modified Rohrschneider constants may be correlated with the thermodynamic function ΔH_a, describing the direct participation of specific adsorbate-polymeric sorbent interactions. Hence, by using the modified Rohrschneider constants it is possible to classify the polarity of these polymeric sorbents simply and with good accuracy.

INTRODUCTION

Characterization of the polarity of stationary phases in gas–liquid chromatography (GLC) has been attempted by many workers. The method most widely used is that suggested by Rohrschneider[1] and its modified form described by McReynolds[2]. Both procedures characterize the polarity of the stationary phase by means of five constants derived from the difference between the Kováts retention indices of five standard substances on the stationary phase under study and the retention indices obtained on a reference column with squalane (10%) at the same temperature. Disadvantages of the methods are the low thermal stability of the reference squalane[3], the possibility of changes in the retentions of compounds on squalane due to its oxidation[4] and the scatter of retention data obtained with different supports caused by the difference in their adsorptivities[5]. Bearing these objections in mind, several workers have suggested other means for the characterization of the polarity of stationary phases[3,6–10]. Despite these reservations, the polarity of stationary phases is now most frequently expressed in terms of Rohrschneider or McReynolds constants[11].

The problems of the systematic classification of the polarity of adsorbents in gas–solid chromatography (GSC) have so far been overcome to a much smaller extent. In this area preference should be directed to the work of Kiselev and his group[12]. In the molecular statistical theory of adsorption, they classified adsorbents

into four groups and adsorbates into three groups on the basis of chemical composition which pre-determines possibilities of specific or non-specific interactions. Using the retention volumes of adsorbates on the sorbents under investigation, they derived the thermodynamic quantities (potential of intermolecular interactions, heats of adsorption, free energy of sorption, entropy, etc.).

In the past 10 years, polymeric sorbents characterized with a macroporous structure due to the pore size, shape and distribution and to the specific surface area have been widely used in GSC. Interactions of adsorbates with polymeric sorbents have mostly been investigated by correlating retention data with thermodynamic quantities[13–16]; the retentions on styrene–divinylbenzene sorbents were interpreted in relation to the electron polarizability of adsorbate molecules[17,18], to their dipole moments[17] and to the number of carbon atoms in the adsorbate molecules[13,17]. In many instances these dependences were obtained on commercial polymeric sorbents, the chemical compositions of which were not exactly known, so that the interaction between the adsorbate and polymeric sorbent could not be interpreted from the standpoint of their chemical composition.

Earlier papers from this laboratory dealt with the investigation of the basic chromatographic properties of copolymers based on glycidyl esters of methacrylic acid[19], and of these copolymers modified by reactions with a number of amines, or by acid hydrolysis followed by cyanoethylation[20]. The effects of morphology on the chromatographic properties of these copolymers were also studied[21]. The polarity of polymeric sorbents mentioned above was characterized by employing modified Rohrschneider constants[19,20]. In the modification of the Rohrschneider method, the Kováts retention indices of five standard sorbates on squalane were replaced with their retention indices measured at the same temperature on a non-polar sorbent, Carbopack B. It is the aim of this paper to present a theoretical basis for the modification of the Rohrschneider method for the expression of the polarity of polymeric sorbents and to demonstrate that these empirical quantities, which represent the participation of specific interactions between the adsorbate and the polymeric sorbent, may be correlated with thermodynamic quantities.

EXPERIMENTAL

The procedure employed in the preparation of copolymer samples, the measurements needed for the calculation of the Kováts retention indices of the Rohrschneider standards, the modification of the Rohrschneider method and the characterization of Carbopack B (Supelco, Bellefonte, Pa., U.S.A.) as a non-polar standard for adsorbents have already been published[19].

The isosteric heats of sorption of ethanol were calculated from adsorption isotherms by a procedure described earlier[22]. Chromatographic measurements needed for the calculation of adsorption isotherms were carried out with a Perkin-Elmer F-11 apparatus (Perkin-Elmer, Beaconsfield, Great Britain), equipped with a flame-ionization detector (FID) and glass columns (100 × 0.3 cm I.D.), at 100°, 125°, 150° and 175°.

The differences between the isosteric heats of sorption and the heat of evaporation of ethanol were used to calculate the excess enthalpies of sorption (ΔH_a) on the individual copolymers. The average heat of evaporation of ethanol (26 kJ/mole) for

the given temperature range was calculated by means of the Clausius–Clapeyron equation; the general equation for the dependence of the logarithm of the vapour pressure of ethanol on temperature was derived from tabulated equilibrium data[23].

RESULTS AND DISCUSSION

When characterizing polymeric sorbents as adsorbents, one must first try to decide which of the processes involved in the chromatographic separation of compounds on macroporous copolymers plays the decisive role. It is well known that authors' views differ on this point and that no unambiguous evidence has been offered so far in support of the individual standpoints. For instance, Hollis[24] assumes that the decisive factor which affects the retention of compounds on macroporous copolymers is related to absorption. The view that predominates at present is that the mechanism of interaction of sorbates with macroporous copolymers is a combination of adsorption and absorption[15]. Results of the investigation of the chromatographic properties of a series of poly(glycidyl methacrylate–ethylene dimethacrylate) indicate, however, that the main separation process which takes place on these copolymers is physical adsorption. One of the indicators that confirm this statement are values of the Rohrschneider constants (Table I). If absorption were the process predominating in the chromatographic separation on glycidyl methacrylate copolymers, the Rohrschneider constants of these copolymers should be approximately the same as those of the stationary phases based on polyesters and mentioned above. As can be seen from Table I, the Rohrschneider constants for copolymers are lower, which indicates that sorbate–copolymer interactions are weaker than sorbate–stationary phase interactions of a similar type. To elucidate the mechanism of interactions between the sorbate and the macroporous copolymer, the properties of these copolymers were investigated over a wide temperature range, necessarily involving their glass transition temperatures. Within the range 75–175°, the dependence of the logarithms of the

TABLE I

ROHRSCHNEIDER CONSTANTS OF POLYMERIC SORBENTS AND OF SOME STATIONARY PHASES BASED ON POLYESTERS

For values of the modified Rohrschneider constants of the polymeric sorbents, see ref. 19.

Sample	x	y	z	u	s
G 3*	0.10	1.45	1.34	1.82	—
G 21*	0.17	1.49	1.34	1.93	—
G 44*	0.52	1.92	1.69	2.55	1.27
G 55*	1.14	2.77	2.40	3.76	2.45
G 71*	2.70	4.17	3.83	6.25	4.56
Porapak Q	−0.36	0.27	0.38	0.38	0.09
Porapak T	0.42	2.02	1.66	2.45	—
Poly(ethylene glycol adipate)**	3.43	5.46	4.52	6.81	6.00
Poly(ethylene glycol succinate)**	4.51	7.06	5.67	8.24	7.69
Poly(neopentyl glycol succinate)**	2.69	4.88	3.87	6.13	5.21

* The number in the name of the sample denotes the percentage by mass of glycidyl methacrylate in the copolymer.
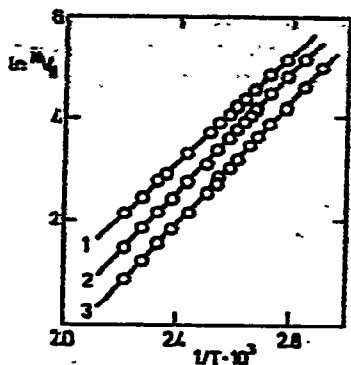
** Values taken from ref. 11.

Fig. 1. Retention diagrams of sorbates on a column (120 × 0.3 cm I.D.) packed with poly(glycidyl methacrylate–ethylene dimethacrylate) copolymer (55:45% by mass). Sorbates: 1 = methyl ethyl ketone; 2 = ethanol; 3 = n-hexane.

retention volumes of compounds on $1/T$ was linear (Fig. 1). Hence, for these cross-linked copolymers prepared by suspension copolymerization, the glass transition temperature (T_g) in this range is not reflected in a break, which is usually very distinct for homopolymers prepared by bulk polymerization and sharply delimits the transition from adsorption to absorption. Similarly, differential scanning calorimetric (DSC) analyses of the copolymers under study in this range do not exhibit any endothermic deviations (Fig. 2).
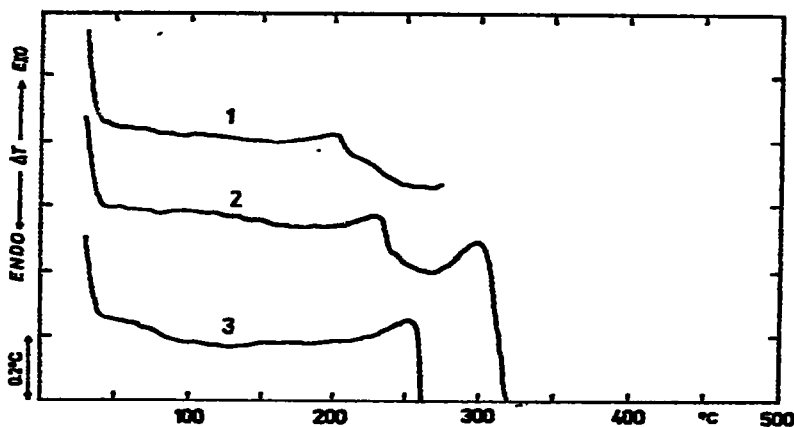

Fig. 2. DSC analyses of glycidyl methacrylate (GMA) copolymers. Heating rate, 10°/min. Copoly-mers: 1 = 44% by mass GMA (8.2 mg); 2 = 55% by mass GMA (8.4 mg); 3 = 71% by mass GMA (8.1 mg).

Similarly to Johnson and Barrall[25], who investigated Porapak Q, R, S and T, other workers found an obvious influence of porosity and of specific surface area on the retention of non-polar compounds, while in the retention of polar compounds the chemical composition of the copolymer also has an effect[21]. For styrene–divinyl-benzene copolymers, Sakodynskij and Moseva[17] pointed out an analogy in the

elution of sorbates on Porapack Q, Polysorb 1 and graphitized carbon black, which allows qualitatively identical interactions to be assumed in this instance. All of these findings justify the assumption that the main separation process occurring in chromatographic columns packed with glycidyl methacrylate–ethylene dimethacrylate, and probably also styrene–divinylbenzene, copolymers is physical adsorption.

The specific retention volumes, as basic chromatographic quantities providing information on interactions of chromatographically separated compounds with the active component of the packing (stationary phase or adsorbent surface), strongly depend on the experimental conditions and the parameters of the column. With higher requirements of accuracy, the measurement of the absolute values of these quantities becomes exacting[26]. Relative retention data may be obtained in a much simpler way, because under constant experimental conditions the effects of the apparatus, and to a considerable extent also the effects of the experimental conditions used, are obviated by expressing the ratio of two retention quantities. The ratio of the specific retention volumes then becomes equal to that of the actual retention times of the compounds concerned. For this reason, the Kováts retention indices, which are interpolated logarithms of the retentions of compounds relative to the homologous series of n-alkanes, can be determined by a simple measurement of the retention times under constant experimental conditions. In addition to very good reproducibility ($\pm$ 0.5%), the Kováts retention indices are almost independent of the column length, flow-rate of the carrier gas, pressure gradient in column and other factors affecting the V_g values[26].

The heat of sorption is the thermodynamic quantity most commonly used if intermolecular adsorbent–adsorbate interactions are to be expressed. The isosteric heats of sorption of ethanol were determined on five polymeric sorbents of the methacrylate type by employing the chromatographic procedure[22]. Fig. 3 shows, in spite of some scattering, a linear dependence between the Kováts retention indices of ethanol and its isosteric heats of sorption measured on these copolymers. The possibility of correlating the Kováts retention indices and the heats of sorption (Fig. 3) proves that the values of these empirical chromatographic quantities are determined by all types of forces involved in the interactions of sorbates with the surfaces of polymeric sorbents, and may therefore become a source of information on such systems.
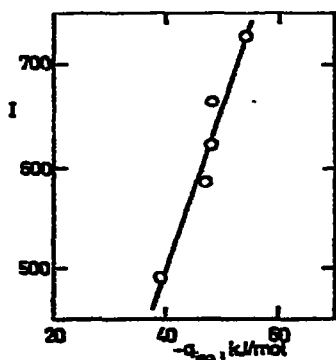

Fig. 3. Dependence between Kováts retention indices of ethanol and its isosteric heats of sorption determined on five macroporous copolymers of the methacrylate type.

The Rohrschneider method of expressing the polarity of stationary phases eliminates the non-specific interactions by subtracting values of the Kováts retention indices of the sorbate on non-polar squalane from the retention index obtained on the given stationary phase. The utilization of this procedure with adsorbents consists in the replacement of squalane with a non-polar adsorbent, Carbopack B. Such a modification of the Rohrschneider method allowed us to extend its application and to include the evaluation of the polarities of polymeric sorbents[19,20]. Smith *et al.*[27] modified the McReynolds constants in a similar way in order to describe the selectivity of polyaromatic copolymers.

By using the non-polar adsorbent Carbopack B as the standard in the Rohrschneider method, objections concerning the inadequacy of squalane are eliminated. Carbopack B was selected as a standard because its specific surface area and porosity are close to those of the samples of macroporous copolymers used.

Using the isosteric heats of sorption and the heat of evaporation of ethanol, the excess enthalpies of sorption (ΔH_a) of ethanol on the individual types of copolymers were calculated. This chromatographic quantity can be correlated with the modified Rohrschneider constants (Fig. 4). The high ΔH_a values (33–52%) from the overall heat of sorption indicate that not only non-specific, but also specific interactions play a role in the sorption of polar sorbates on the copolymers under study, and it is because of these specific interactions that a higher energy is needed in desorption than in mere evaporation. Because under the conditions of chromatographic measurements (*i.e.*, at a relatively high working temperature and a low concentration of the sorbate) no interactions between molecules of the sorbates can be assumed, the ΔH_a values may be regarded as a measure of specific interactions between molecules of the sorbate and the surface of the copolymers. A general dependence relating the excess enthalpy of sorption and the modified Rohrschneider constants of ethanol (Fig. 4) proves that these empirical chromatographic quantities express the sum of all of the specific interactions between sorbates and polymeric sorbents. Thus, by employing the modified Rohrschneider method, it is possible to classify in a simple way and with very good accuracy the polarity of macroporous copolymers of the methacrylate type.
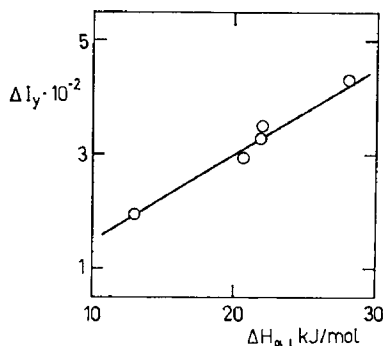

Fig. 4. Dependence between modified Rohrschneider constants of ethanol and its excess enthalpies of sorption determined on five macroporous copolymers of the methacrylate type.

ACKNOWLEDGEMENTS

REFERENCES

1 L. Rohrschneider, *J. Chromatogr.*, 22 (1966) 6.
2 W. O. McReynolds, *J. Chromatogr. Sci.*, 8 (1970) 685.
3 J. R. Ashes, J. K. Haken and P. Souter, *J. Chromatogr.*, 92 (1974) 237.
4 M. B. Evans and J. F. Smith, *J. Chromatogr.*, 28 (1967) 277.
5 M. B. Evans and J. F. Smith, *J. Chromatogr.*, 30 (1967) 325.
6 Z. Szentirmay, G. Tarjan and J. Takacs, *J. Chromatogr.*, 73 (1972) 11.
7 J. Takács, Zs. Tálas, I. Bernáth, G. Czakó and A. Fischer, *J. Chromatogr.*, 67 (1972) 203.
8 F. Riedo, D. Fritz, G. Tarján and E. Kováts, *J. Chromatogr.*, 126 (1976) 63.
9 F. Vernon and C. O. E. Ogundipe, *J. Chromatogr.*, 132 (1977) 181.
10 M. B. Evans, *Chromatographia*, 11 (1978) 183.
11 R. Kaiser, *Chromatographie in der Gasphase, Band III, Teil 1, Tabellen zur Gas-Chromatographie*, Hochschultaschenbücher-Verlag, Bibliographisches Institut, Mannheim/Zürich, 1969.
12 A. V. Kiselev and Ya. I. Yashin, *Gazoadsorptsionnaya Khromatographia*, Nauka, Moscow, 1967.
13 T. N. Gvozdovitsch, A. V. Kiselev and Ya. I. Yashin, *Chromatographia*, 2 (1969) 234.
14 T. N. Gvozdovitsch and Ya. I. Yashin, *J. Chromatogr.*, 49 (1970) 36.
15 H. L. Gearhart and M. F. Burke, *J. Chromatogr. Sci.*, 11 (1973) 411.
16 M. Gassiot-Matas and B. Monrabal-Bas, *Chromatographia*, 3 (1970) 547.
17 K. I. Sakodynskij and L. Moseva, *Chromatographia*, 1 (1968) 483.
18 O. Dufka, J. Malinský and J. Vladyka, *Chem. Prum.*, 21 (1971) 459.
19 J. Lukáš, F. Švec and J. Kálal, *J. Chromatogr.*, 153 (1978) 15.
20 J. Lukáš, F. Švec, E. Votavová and J. Kálal, *J. Chromatogr.*, 153 (1978) 373.
21 Z. Pelzbauer, J. Lukáš, F. Švec and J. Kálal, *J. Chromatogr.*, 171 (1979) 101.
22 J. Lukáš, *Chem. Listy*, 72 (1978) 267.
23 T. E. Jordan, *Vapor Pressure of Organic Compounds*, Interscience, New York, 1954.
24 O. L. Hollis, *Anal. Chem.*, 38 (1966) 309.
25 J. F. Johnson and E. M. Barrall, II, *J. Chromatogr.*, 31 (1967) 547.
26 J. Klein and H. Widdecke, *Angew. Makromol. Chem.*, 53 (1976) 145.
27 J. R. Lindsay Smith, A. H. H. Tameesh and D. J. Waddington, *J. Chromatogr.*, 151 (1978) 21.