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METHACRYLATE RESINS FOR THE GAS CHROMATOGRAPHIC SEPARATION OF STRONGLY POLAR COMPOUNDS*

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SUMMARY

Polymerized 2-cyanoethyl methacrylate (KEM) has been tested as a stationary phase for gas–solid chromatography. Its thermal stability has been investigated and the usable range defined. The specific retention volumes, V_g, of the C_1–C_5 fatty acids and water have been measured and some thermodynamic quantities (ΔH) have been calculated, providing information on the nature and the magnitude of the sorbate–sorbent interactions. The optimum conditions for the separation of the C_1–C_5 acids and water have been determined.

INTRODUCTION

The separation of fatty acids by gas chromatography has always suffered from considerable difficulties. These difficulties arise mainly from the high polarity of the acid molecules and therefore from their excessive affinity for the column packing, resulting in tailing of the elution curves. This effect is probably due to the strong sorption of the polar molecules of acids by solid supports. Therefore, new separation procedures were sought in order to eliminate the disturbing effect and provide a satisfactory analysis. The older method of determination of fatty acids required their conversion into volatile esters before their gas chromatographic analysis. However, the esterification reaction renders the whole determination a more time-consuming procedure and, moreover, the result can be subject to errors. Efforts have been made to suppress the tailing of the elution peaks, *i.e.*, to eliminate the active sites of the support, by four different methods. The first method was based on the use of a strongly polar liquid phase, *e.g.* some polyglycols[1,2], polymeric polyhydric alcohols (*e.g.*, Tween[3,4] and polyethylene glycol[5]), esters of higher dicarboxylic acids[6,8] or phases specially synthesized for this purpose (*e.g.*, FFAP[9,10]). In the second method, a small amount of a non-volatile acid was added to the liquid phase in order to deactivate the active sites of the support. Of inorganic acids, the use of phosphoric acid[11–17] has

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been described in the literature and some organic acids, mainly higher monocarbox-ylic[11,18], dicarboxylic[11,20] and other acids[21], have been used alone or in admixture[22] with phosphoric acid. The third method for suppressing the distortion of elution curves consists in the saturation of the carrier gas by the vapour of an acidic or gen-erally polar compound. Formic acid[23,24] or steam[24] have been found to be suitable for this purpose. In the fourth and simplest method, solid supports were used that pos-sessed virtually no undesirable properties, *i.e.*, minimum adsorption for the analyzed compounds, such as glass beads[25-27], Teflon[28], Fluoropak 80[28] and also terephthalic acid[29] coated with a liquid phase. According to some workers[30-33], very good results were achieved with porous styrene–divinylbenzene copolymers (Porapak, Synachrom), which can be involved in this group.

In the present work, we have investigated the separation of C_1–C_5 free fatty acids and water using resins with cyanoethyl groups as the stationary phase. Our objective was to obtain quantitative information concerning the magnitude of the sorbate–sorbent interactions in gas–solid chromatography and to develop a method for the analysis of the above compounds.

EXPERIMENTAL

Materials

Formic, acetic, propionic, *n*-butyric, isobutyric, *n*-valeric and isovaleric acids (all reagent grade, Lachema, Brno, Czechoslovakia) were dried over molecular sieve 5A and purified by rectification. Acetic acid was rectified with acetic anhydride for 8 h. The content of water was about of $10^{-4}\%$ (w/w) and was determined by the Karl Fischer method. The purity of the acids treated in this manner was checked by gas chromatography. A macroporous copolymer of 2-cyanoethyl methacrylate and ethyl-ene methacrylate (KEM) was synthesized[34] in this Institute. It is a white resin of mechanical strength which retained its porosity after drying. The B.E.T. surface area measured with nitrogen was 24 m^2/g and the average pore diameter was 450 Å.

The measurements of thermal stability were performed gravimetrically using the simplified quartz fibre sorption balance of McBain and Bakr[35]. The thickness of the quartz fibre was 0.3 mm and the sensitivity of the string was 10 mg/mm. Steadily flowing nitrogen was used instead of evacuation. The changes in the weight of the resin were followed with a catharometer.

The retention data of the C_1–C_5 fatty acids were measured with a Chrom 3 instrument (Laboratorní Přístroje, Prague, Czechoslovakia) equipped with a flame ionization detector. The retention data of water and the C_1–C_5 acids were measured with an apparatus constructed in the Development Department of the Czechoslovak Academy of Sciences, Prague, equipped with a catharometer (Zimmermann, Leipzig, G.D.R.). Stainless-steel columns were employed in both instances. For measuring the retention data of the compounds in question, a 100 × 0.4 cm I.D. column was used, while a 100 × 0.3 cm I.D. column was used for investigating the dependence of the height equivalent to a theoretical plate (HETP) on the linear velocity of the carrier gas. For the separation of the actual mixtures under optimum conditions, a 180 × 0.3 cm I.D. column was used. Nitrogen was employed as the carrier gas. The samples were introduced with a 10-μl Hamilton microsyringe. The retention curves of the C_1 and C_2 acids and water obtained by the apparatus equipped with a catharometer showed

not only some tailing, which deteriorated with the amount of sample used and with a decrease in temperature, but also a dependence of the position of the peak maximum on the amount of sample. Therefore, the method described by Purnell[36] was used for determining the retention curve maxima expressed as the retention time, t_R, and its correct value was obtained by the graphical extrapolation of the sample concentration to infinite dilution. With sample volumes of 0.2–0.8 μl, the change in the position of the retention maximum was negligible for the investigated acids and water.

Calculations

The extrapolated value of the retention time of acetic acid was chosen as the standard and used for the calculation[37] of the specific retention volumes, which were 114.1, 61.58, 30.29 and 22.26 ml/g at 112, 129, 146 and 161°, respectively. The values corresponding to the other compounds are summarized in Table I. From these data,

TABLE I

CHROMATOGRAPHIC PARAMETERS OF THE FATTY ACIDS AND THEIR COMPARISON WITH SOME PHYSICAL PROPERTIES

Property	Acid							Water
	Formic	Acetic	Propionic	Butyric	Isobutyric	Valeric	Isovaleric	
B.p. (°C)	100.7	118.5	141.1	163.5	154.3	186	176.6	100
Dielectric constant[38] (D)	58.5	6.1	3.3	3.0	2.7	2.7	2.6	—
$r_{1,2}$: 112°	1.03	1.00	1.46	2.16	1.54	2.59	2.49	0.17
129°	1.11	1.00	1.36	1.89	1.37	2.87	2.05	0.23
146°	1.13	1.00	1.25	1.57	1.25	2.25	1.78	0.29
161°	1.21	1.00	1.23	1.58	1.21	2.19	1.64	0.32
$-\Delta H_S$ (kcal/mole)	10.89	11.80	13.16	14.27	13.52	15.49	14.69	8.03
$-\Delta H_E$ (kcal/mole)	5.54	5.64	10.12	11.55	11.04	13.29	—	9.73

the differential molar enthalpies of sorption, ΔH, were calculated according to the equation

$$\log V_g = -\Delta H_S/2.303\ RT + \text{constant} \qquad (1)$$

where T is the column temperature. The results are also given in Table I.

Separation efficiency

In order to determine the region of maximum column efficiency, the dependence of HETP on the linear gas velocity, $\bar{u}$, was investigated for acetic and valeric acids and water. The HETP values were calculated as a fraction of the column length and the number of the theoretical plate. The values of $\bar{u}$ were calculated from the relationship

$$\bar{u} = V/\pi r^2 \varepsilon \qquad (2)$$

where V is the volume flow-rate of the carrier gas, r is the column radius and ε is the packing porosity, the value of which is assumed to be 0.38 (see, *e.g.*, ref. 39). The de-

pendence was interpreted according to the standard form of the Van Deemter· equation:

$$\text{HETP} = A + B/\bar{u} + C\bar{u} \tag{3}$$

where A, B and C are constants. A Tesla 200 computer was employed for calculating their numerical values. The results are given in Table II. From the plots of HETP

TABLE II

A, B AND C CONSTANTS OF THE VAN DEEMTER EQUATION AT 146°

Compound	A	B	C
Acetic acid	−0.247	2.467	0.030
Valeric acid	−0.008	0.299	0.030
Water	−0.165	3.207	0.037

versus $\bar{u}$ (Fig. 1), the optimum velocities, u_0, of the carrier gas were read off at the maxima of the hyperbolic curves. The values corresponding to acetic and valeric acids were used for the calculation of the average linear velocity of nitrogen in the actual separation of the C_1–C_5 acids and water.
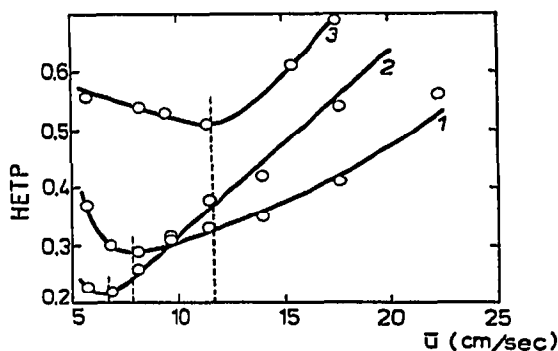

Fig. 1. Plots of the height equivalent to a theoretical plate (HETP) versus the linear velocity of the carrier gas ($\bar{u}$) at 146°. KEM, 0.2–0.4 mm. 1 = Acetic acid; 2 = n-valeric acid; 3 = water.

RESULTS AND DISCUSSION

In studies of the sorption properties of the polymerized 2-cyanoethyl methacrylate resin (KEM), we found[40] that the surface possesses a significant porous structure down to a pore size of 450 Å, whereas it is negligible for the micropore fraction, i.e., in the region of about 20 Å. Therefore, the molecules of the C_1–C_5 acids and water adsorbed on this solid surface during the gas chromatographic process were expected to be easily desorbed again, giving symmetrical retention peaks. Using thermogravimetry we found that the highest temperature at which the resin remained sufficiently stable was 165°. Within the range 20–165°, only water and some gases were desorbed. Above 165°, a gradual decay of the resin took place. The lower limit of the temperature range was determined by the separation efficiency of the compounds investigated

and was found experimentally to be 112°. Temperatures below this value could not be used because of the considerably high V_g and the excessive tailing of some retention peaks.

The retention volumes of the C_1–C_5 acids and water were measured at temperatures of 112, 129, 146 and 161°. The thermodynamic quantities calculated from the retention data served for evaluating the interactions of the investigated compounds with the solid stationary phase. From the magnitude of the differential molar enthalpies of sorption, ΔH, for example, the nature of forces between the sorbate molecules and the sorbent surface can be judged. In this work, the experimental ΔH_S values (Table I) are in the range 11–16 kcal/mole, which indicates that not only physical forces but also chemical interactions are effective to a certain extent between the polar groups of the measured substrates and the cyanoethyl groups of the stationary phase. The increase in ΔH_S depending on the increasing molecular weight is consistent with general observations on the sorption of organic compounds. We found that ΔH_S increases by 1 kcal/mole on average between adjacent members of the homologous series and that the ΔH_S values of the n-acids are always higher than those of the corresponding *iso*-acids. The ΔH_S values of the compounds investigated were compared with the corresponding heats of evaporation, ΔH_E (Table I), calculated according to the equation[41]

$$\Delta H_E = e - dT \qquad (4)$$

where e and d are empirical constants and T is the temperature (°C). A temperature of 136°, representing the mean value of the operating temperature range, was used in the calculation. The values obtained for the sorption enthalpies are higher than those corresponding to the heats of evaporation. This increase can again be explained by the existence of the interaction forces. Therefore, owing to the effect of these forces, it can be stated that the desorption is a more energy-consuming process than is evaporation. The differences between the ΔH_S and ΔH_E values of the C_3–C_5 acids and water were found to be about 20% (relative), while the ΔH_S values of the formic and acetic acids were approximately double. The most likely explanation of this apparently anomalous behaviour is based on the structural differences of the C_1 and C_2 acids predominantly forming dimeric molecules[42] under the conditions used. This property, however, gradually disappears with the higher homologues of the series.

By plotting HETP *versus* the increased linear velocity of the carrier gas, $\bar{u}$, for acetic and valeric acids and water, the hyperbolic curves in Fig. 1 are obtained, which correspond to the Van Deemter equation. If these curves are compared with each other, differences are found both in the positions of the minima with regard to the co-ordinates and in the slopes of the increasing curve branches. In order to demonstrate the optimum properties of the column packing, the mean value of $\bar{u}_0$ was used calculated from the optimum linear velocities of acetic and valeric acids. The $\bar{u}_0$ value of water need not be taken into account because its V_g value is significantly lower than those of the two acids. Thus, the mean value of $\bar{u}_0$ can be considered to be the optimum value for all of the compounds investigated because the hyperbolic curve minima of the C_3 and C_4 acids lie between the $\bar{u}_0$ values of acetic and valeric acids. In the range of higher linear velocities, the comparison of the slopes of the increasing curve branches for the C_2 and C_5 acids shows that with regard to increasing $\bar{u}$, the HETP value of valeric acid

increases much more significantly than that of acetic acid. Therefore, the dependence of the optimum separation efficiency on the change in the linear velocity, $\bar{u}$, is not so important with the lower homologues of the series of acids as it is with the higher members.
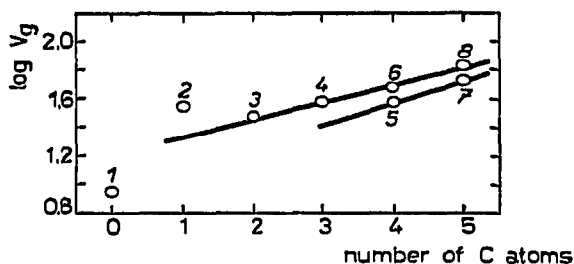

Fig. 2. Plots of log V_g *versus* number of the carbon atoms (n) at 146°. 1 = Water; 2 = formic acid; 3 = acetic acid; 4 = propionic acid; 5 = isobutyric acid; 6 = n-butyric acid; 7 = isovaleric acid; 8 = n-valeric acid.

In order to judge easily the regularity of the separation of the liquid mixtures from the analytical point of view, we plotted log V_g *versus* the boiling points and log V_g *versus* the number of carbon atoms for the compounds investigated (Fig. 2). With the exception of formic acid, the former plot is linear for all n- and *iso*-acids, while the latter plot yields two almost parallel straight lines individually corresponding to n- and *iso*-acids except for formic acid. As is evident from the n-acids correlation, the separation is basically controlled by the boiling points of the compounds. However, the second correlation indicates that the V_g values of the *iso*-acids are generally lower than those of the corresponding n-acids. Therefore, in the chromatogram they partially overlap with the n-acids that possess one carbon atom less.

It may be of interest to consider the apparently anomalous behaviour of formic acid. Although it possesses the lowest boiling point, it is eluted from the column only after acetic acid. This fact can be explained on the basis of the stronger polarity of formic acid compared with the other acids, as shown by the dielectric constants given in Table I. The effect of the polarity on the total value of V_g is supported by the presence of the polar cyanoethyl functional groups contained in the polymerized methacrylate. As is known from the literature, substances of a similar type are used in gas chromatography as liquid phases with considerably strong polarities.

Finally, it should be mentioned that the cyanoethyl methacrylate resin was used successfully for the separation of mixtures containing water, acetic acid, acrylic acid and isopropyl acetate, and esters of the C_1–C_5 acids with the reaction products of their catalytic hydrogenolysis.

ACKNOWLEDGEMENTS

REFERENCES

1 A. I. Gorshunova, O. L. Gorshunov, A. S. Barkov and O. A. Sukhorukov, *Zavod. Lab.*, 32 (1966) 1206.
2 A. Pribela, *Biologia*, 22 (1967) 96.
3 B. Smith, *Acta Chem. Scand.*, 13 (1959) 480.
4 E. M. Emery and W. E. Koerner, *Anal. Chem.*, 34 (1962) 1196.
5 W. R. Mayberry and G. J. Prochazka, *J. Gas Chromatogr.*, 3 (1965) 232.
6 I. R. Hunter, V. H. Ortegren and J. W. Pence, *Anal. Chem.*, 32 (1960) 682.
7 R. W. McKinney, *J. Gas Chromatogr.*, 2 (1964) 108.
8 S. B. Dave, *J. Gas Chromatogr.*, 39 (1969) 389.
9 R. A. Baker, *J. Gas Chromatogr.*, 4 (1966) 418.
10 H. Frauendorf, *Z. Anal. Chem.*, 221 (1966) 305.
11 L. V. Packett and R. W. McCune, *Appl. Microbiol.*, 13 (1965) 22.
12 L. I. Nemtseva, T. S. Kishkinova and A. D. Semionov, *Gidrokhim. Mater.*, 41 (1966) 129.
13 G. Ewald and H. Zech, *Z. Anal. Chem.*, 226 (1967) 331.
14 F. Medzihradsky and W. Lamprecht, *Hoppe-Seyler's Z. Physiol. Chem.*, 343 (1965) 35.
15 J. Hrivňák and V. Palo, *J. Gas Chromatogr.*, 5 (1967) 325.
16 J. Hrivňák, L. Soják, E. Beska and J. Janák, *J. Chromatogr.*, 68 (1972) 55.
17 D. H. Ottenstein and D. A. Bartley, *Anal. Chem.*, 43 (1971) 952.
18 A. P. Martin and A. T. James, *Biochem. J.*, 50 (1952) 679.
19 R. W. McKinney and R. L. Jordan, *J. Gas Chromatogr.*, 3 (1965) 317.
20 A. J. Appleby and J. E. O. Mayne, *J. Gas Chromatogr.*, 5 (1967) 11.
21 B. Kaplanová and J. Janák, *Mikrochim. Acta*, (1966) 119.
22 B. H. Priscott, *Analyst (London)*, 92 (1967) 57.
23 H. S. Knight, *Anal. Chem.*, 30 (1958) 2030.
24 R. G. Ackman and R. D. Burgher, *Anal. Chem.*, 35 (1963) 647.
25 P. Jowett and B. J. Horrocks, *Nature (London)*, 192 (1961) 966.
26 J. G. Nikelly, *Anal. Chem.*, 36 (1964) 2244.
27 M. Maruyama and H. Sakaguchi, *Bunseki Kagaku (Jap. Anal.)*, 15 (1966) 56.
28 J. J. Kirkland, *Anal. Chem.*, 35 (1963) 2003.
29 H. Miyake, M. Mitooka and T. Matsumoto, *Anal. Chem.*, 40 (1968) 113.
30 V. Mahadevan and L. Stenroos, *Anal. Chem.*, 39 (1967) 1652.
31 H. Hoffmann, M. Henke, K. Häupke and G. Schwachula, *Z. Chem.*, 11 (1971) 184.
32 B. Bartoniček and S. Lukáč, *Chromatographia*, 3 (1970) 108.
33 O. Dufa, J. Malinský and J. Vladyka, *Chem. Prům.*, 21 (1971) 459.
34 I. Gavrilová and M. Kraus, *Czech. Pat.*, P.V. 8685-70.
35 J. W. McBain and A. M. Bakr, *J. Amer. Chem. Soc.*, 48 (1926) 690.
36 J. H. Purnell, *Gas Chromatography*, Wiley, New York, London, 1962, p. 105.
37 D. Ambrose, A. I. M. Keulemans and J. H. Purnell, *Anal. Chem.*, 30 (1958) 1582.
38 R. C. Weast (Editor), *Handbook of Chemistry and Physics*, The Chemical Rubber Co., Cleveland, Ohio, 1967, p. D86.
39 J. H. Purnell, *Gas Chromatography*, Wiley, New York, London, 1962, p. 62.
40 R. Komers and D. Tomanová, *Chem. Prům.*, 21 (1971) 559.
41 R. R. Dreisbach, *Physical Properties of Chemical Compounds*, Vol. III, No. 29, American Chemical Society, Washington, D.C., 1961, pp. 437–441.
42 J. H. Purnell, *Gas Chromatography*, Wiley, New York, London, 1962, p. 13.