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Alkali metal salts of benzenesulphonic acid as stationary phases in gas chromatography

Gas chromatography (GC) on clathrate-forming stationary phases has been reported by previous workers[1-5]. As a result of their ability to distinguish between molecular structures, these stationary phases have been widely used. Potassium, rubidium and caesium benzenesulphonates have been used for a long time for sorbing gases and vapours. The sorption of vapours by potassium benzenesulphonate has been explained[6] by the phenomenon of clathration. In particular, the sorption has been found to be maximal for alcohols and, in general, polar compounds are sorbed to a greater extent than non-polar compounds. Metal salts[7,8], on the other hand, because of their higher thermal stabilities, have been used successfully for the separation of isomers and compounds of high-molecular-weight. As such sulphonates act both as clathrate-forming compounds and metal salts, the present study was carried out in order to investigate their selectivity as GC stationary phases for polar compounds and to gain an insight into the mechanism of the sorbate–sorbent interactions.

Experimental

Chemicals. The following three benzenesulphonates were synthesised in this laboratory with authentic reagents and recrystallised from an ethanol–water mixture: (1) potassium benzenesulphonate (BK); (2) sodium benzenesulphonate (BS); (3) rubidium benzenesulphonate (BR).

The sorbates were, in general, of pure grade. For slightly impure samples, the retention of the peak with the greatest area was reported.

Columns. Stainless-steel columns (6 ft. × $\frac{1}{8}$ in. O.D.) were used. Packing materials were prepared by slurrying 40% w/w of the freshly prepared salts in water with Chromosorb P (−60 to +80 mesh), removing the water by heating. Experiments were carried out with a Perkin-Elmer Model 810 gas chromatograph fitted with a flame ionization detector and a 1 mV Honeywell recorder, using nitrogen as the carrier gas (flow-rate 30 ml/min). The BS and BK columns were pre-conditioned by keeping them at 160° for 2 h under nitrogen at a flow-rate of 30 ml/min. The BR column was pre-conditioned at 120° for 3 h. The sample size was 0.2–0.3 μl.

Results and discussion

The retentions of compounds on the benzenesulphonate columns were found to be governed by three important factors, namely, hydrogen bonding, clathration and interactions with the lone pair of electrons on the metal ion.

Alcohols, ethers and hydrocarbons. Table I illustrates the relative retentions of alcohols, ethers and hydrocarbons. Unlike other inclusion compounds where clathration is stabilised by Van der Waals forces[5] or by charge-transfer interaction[9,10], the clathration of alcohols on these phases is governed primarily by hydrogen-bonding. Thus the retention of methanol is high compared with the other alcohols on BK and BR phases, but not on BS, showing the deficiency in the sorption properties of the BS phase[6]. The retentions of normal alcohols decreased with an increase in chain length, except for *n*-butanol. For isomeric alcohols, the retention decreased in the

TABLE I

RELATIVE RETENTION TIMES OF ALCOHOLS, ETHERS AND HYDROCARBONS ON BENZENESULPHONATE COLUMNS

Compound	*Boiling point (°C)*	*Column*		
		BS	*BK*	*BR*
Alcohols		(70°)	(110°)	(80°)
Methanol	64.7	1.00	1.00	1.00
Ethanol	78.3	1.04	0.67	0.60
Isopropanol	82.3	0.70	0.18	0.39
tert.-Butanol	82.5	0.96	0.13	0.25
Allyl alcohol	97.0	1.32	0.56	0.90
n-Propanol	97.2	1.80	0.37	0.60
sec.-Butanol	99.5	1.50	0.18	0.45
Isobutanol	107.9	1.40	0.19	0.49
n-Butanol	117.7	2.52	0.40	0.90
Isopentanol	131.5	4.20	0.25	0.90
Ethers		(46°)	(40°)	(43°)
Diethyl ether	34.7	1.00	1.00	1.00
Diisopropyl ether	69.0	1.25	0.50	0.70
Hydrocarbons		(53°)	(50°)	(52°)
Benzene	80.1	1.00	1.00	1.00
Cyclohexane	80.8	0.83	0.40	0.36

order primary > secondary > tertiary. The lower retention of isoalcohols is due to their molecular shape. Owing to the presence of the more electronegative sp^2-hybridised carbon atom in allyl alcohol, the hydrogen atom of the hydroxyl group acquires a greater electropositive character than that of *n*-propanol, resulting in hydrogen-bonding with allyl alcohol being greater and therefore producing a later elution than with *n*-propanol.

The elution of two ethers from columns of BR and BK clearly indicates the presence of holes in the crystal lattices of the sulphonates. Diisopropyl ether (b.p. 69°) has a bulky structure and cannot enter the holes, so it is eluted earlier than diethyl ether (b.p. 34°). The order of elution of *n*-hexane, *n*-heptane, *n*-octane, isooctane and cyclohexane followed the order of their boiling points on all the columns, and the same result was also obtained for aromatic hydrocarbons. The higher retention of benzene compared with that of cyclohexane is obviously due to the metal ion–π-electron interaction.

Regarding the stability of the BR column, it was observed that on keeping the column at 160° for 1 h and then lowering the temperature to the corresponding temperature for the elution of alcohols and ethers, the retentions followed the order of the boiling points, contrary to previous observations, thereby indicating the collapse of the holes or channels inside the crystal lattice.

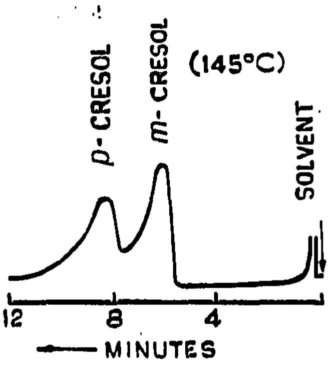
Phenols. The columns used in the present work have excellent possibilities for phenols. Table II presents the relative retention results for some phenols, from which it appears that the elution is governed by two factors. One factor is hydrogen-bonding, and the other is the interaction of the metal ion with the lone pairs of electrons on the oxygen atom of the phenolic group. The retention of a compound is probably due to the combined effects of these two interactions. That the elution does not occur through clathration holes or channels is obvious from the fact that even

TABLE II

RELATIVE RETENTION TIMES OF PHENOLS ON BENZENE SULPHONATE COLUMNS

Compound	*Boiling point (°C)*	*Column*		
		BS (150°)	*BK (160)°*	*BR (160°)*
Phenol	181.7	1.00	1.00	1.00
m-Cresol	202.1	1.00	1.00	1.27
p-Cresol	201.5	1.00	1.10	1.76
o-Cresol	190.8	1.00	0.60	0.83
o-Ethylphenol	207.5	1.00	0.53	0.76
o-*n*-Propylphenol	219.4	1.00	0.50	0.68
o-Isopropylphenol	214.5	1.00	0.33	0.52
o-*tert*.-Butylphenol	221.0	0.90	0.33	0.44
2,6-Xylenol	200.6	0.64	0.30	0.54
2,4-Xylenol	211.3	1.10	1.00	1.59
2,5-Xylenol	211.5	1.00	0.90	0.98
2,3-Xylenol	217.1	1.30	1.00	1.20
3,5-Xylenol	221.7	1.80	1.17	1.84
3,4-Xylenol	227.0	1.55	1.30	1.92
2,6-di-*tert*.-Butylphenol	—	0.60	0.29	0.18
2,4,6-Trimethylphenol	220.6	0.80	0.47	1.13
2,3,5-Trimethylphenol	236.0	3.20	1.30	1.62
2,4,5-Trimethylphenol	235.2	—	1.40	1.78
3,4,5-Trimethylphenol	252.0	4.30	1.90	2.89
2,3,4-Trimethylphenol	237.0	—	—	2.13
Anisole	154.0	0.35	0.17	0.14

after the collapse of the channels, the order of elution of the phenols remains the same. The BS column was found not to behave normally, as the peaks obtained were highly tailed. In *ortho*-substituted phenols, the higher the molecular volume of the alkyl group, the lower is the retention, owing to the steric hindrance by the alkyl group of hydrogen-bonding and metal ion–lone pair interactions. In phenols with alkyl



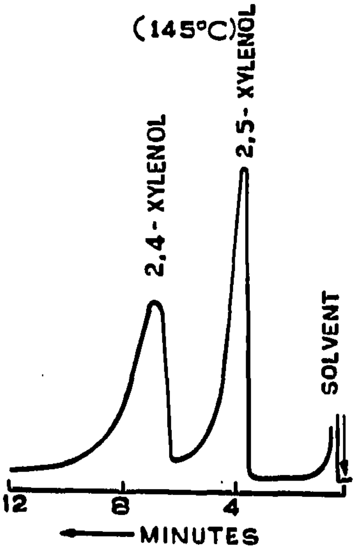


Fig. 1. Separation of *m*-cresol and *p*-cresol on a rubidium benzenesulphonate column.

Fig. 2. Separation of 2,4- and 2,5-xylenol on a rubidium benzenesulphonate column.

groups in *meta-* and *para*-positions, the decrease in the hydrogen-bonding and the increase in the lone pair–metal ion interaction can be attributed to electronic effects. On these phases, the most significant effect is the metal ion–lone pair interaction, which is a maximum with the BR column, on which excellent separations of mixtures that are usually difficult to separate, such as 2,4 and 2,5-xylenols and *m*- and *p*-cresols, have been achieved (Figs. 1 and 2). The separation of the two xylenols ($\alpha = 1.83$) as obtained on such a short column and within such a short time has not been reported elsewhere. In these two pairs of compounds, the higher retentions of *p*-cresol and 2-4 xylenol are due to the higher electron density on the phenolic oxygen atom, which again is due to the presence of a methyl group in the 4-position with consequently higher interaction. The retention ratios of *p*-cresol/*m*-cresol show that the interaction decreases in the order BR $>$ BK $>$ BS. This may be due to the fact that the ionic radii of the metals also decrease in the order Rb $>$ K $>$ Na. The presence of hydrogen-bonding of the solutes with the stationary phases is once again confirmed by the fact that when the phenols are O-methylated[11] the interaction decreases abruptly. The retention of anisole is given in Table II.

In general, the peaks of alcohols and phenols are tailed. Tailing is minimal on the BR column and maximal on the BS column. Finally, regarding the stabilities of the columns for phenols, the BR and BK columns were used for 2 months without any deterioration. Further work on the analytical applications of this technique is in progress.

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