Letter to the Editor

снком. 6114

Sub-classification of hydrocarbons by the temperature coefficient of retention index

Dear Sir,

Recently, VERNON¹ has compared the suitability of gas-solid chromatography (GSC) and gas-liquid chromatography (GLC) for the sub-classification of aromatic hydrocarbons with the help of our method² involving the temperature coefficient of the retention index (dI/dT). VERNON claimed GSC to be superior for this purpose.

Using sodium chloride-modified alumina, VERNON obtained linear I-T plots, which illustrates the validity of our theory of linearity of I versus T in GSC. For the first time, VERNON has reported negative dI/dT values for aromatic hydrocarbons, which is a phenomenon of considerable significance in analytical and physicochemical studies. Obviously, this needs further investigation with respect to the chemical nature of solutes, adsorbents and stationary liquids. Our experience with various types of stationary liquids has shown that negative dI/dT values might not be possible in GLC for aromatic hydrocarbons^{3,4}.

On the basis of a small variation, viz, from -0.31 to -0.42, in dI/dT for a few aromatic hydrocarbons, VERNON has attempted to carry out their sub-division with respect to number, size, position and nature of alkyl substituents in the benzene ring. Although commendable, we consider this move to be premature. For such a study, the following must be considered:

(i) a high precision in the determination of retention index, preferably of a fractional order;

(*ii*) the standard deviation of dI/dT values;

(*iii*) availability of dI/dT values of a large number of representative compounds;

(iv) a knowledge of the relation between the solute and solvent structure in GLC and between surface properties of adsorbents and retention properties of solutes in GSC.

Regarding another remark made by VERNON as to whether SAHA AND MITRA would classify dodecylbenzene with alkyl paraffins or aromatic hydrocarbons from the consideration of dI/dT values in GLC, we would like to mention the following:

(i) the distinction between the dI/dT values of isoalkanes and aromatic hydrocarbons is very clear, some overlapping being noticed only in non-polar liquids for those isoalkanes having four or more branched chains;

(*ii*) We have studied the dI/dT values of alkylbenzenes with methyl, ethyl, *n*-propyl and *n*-butyl substituents in stationary liquids of various polarities and observed that the dI/dT values. instead of decreasing with the size of the alkyl

instances^{3,4}. If permitted to project on this finding, we would state that dodecy1benzene will definitely be classified with aromatic hydrocarbons from consideration of its dI/dT values in GLC.

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