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Retention Behavior of Alkyl Bonded superficially Porous Silica in the Separation of Alkylbenzenes with High Pressure Liquid Chromatography

The number of methylene groups, log *k'* and solvent composition can be related mathematically to estimate elution conditions and resolution during chromatography on alkyl bonded silica columns. The slope for a plot of log *k'* *vs.* the number of methylene groups is practically identical for various types of benzene homologs and is a linear function of the composition of methanol in an aqueous methanol eluent.

Keywords——high pressure liquid chromatography; Permaphase ODS; alkylbenzene; alkylphenone; benzoic acid esters

Reversed phase liquid chromatography is a most widely applied mode of high pressure liquid chromatography. In most cases, the separation is made on a column of octadecyl silica. However, there is little quantitative information available concerning the nature of selectivity or the elution strength of the moving phase.[1] Recently, we have studied the retention behavior of porous styrene divinylbenzene copolymer on the separation of fatty acids and their analogs, and found i) there is a common and quantitative relationship between the capacity factor and the number of methylene groups in a molecule, and ii) there is a well defined relationship between the composition of the moving phase of aqueous methanol and the capacity factor equivalent to one methylene group.[2] In the present communication, essentially the same relationship has been found on the separation of several benzene derivatives with alkyl bonded superficially porous silica.

A chromatograph (type 830 du Pont) equipped with a Pyrex glass column (3×500 mm) of Permaphase ODS was used. The concentration of methanol in the aqueous methanol was by volume. Elution was made at ambient temperature (18—19°) with a flow rate of 0.5 ml/min. Sample compounds were obtained from Tokyo Kasei Kogyo Co., Ltd. Picric acid was assumed

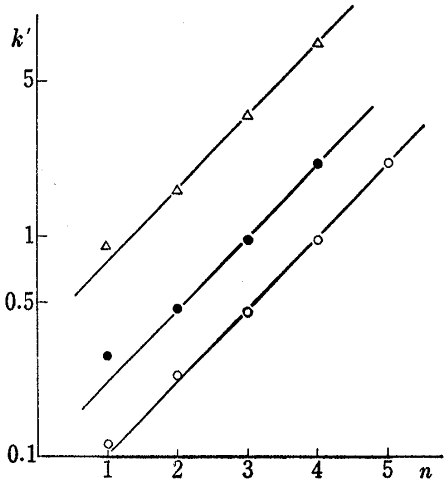

Fig. 1. Linear Relationship between log *k'* and Methylene Numbers

moving phase; 50% (v/v)MeOH
—△—: alkylbenzene $C_6H_5(CH_2)_nH$
—●—: benzoic acid esters $C_6H_5COO(CH_2)_nH$
—○—: alkylphenones $C_6H_5CO(CH_2)_nH$

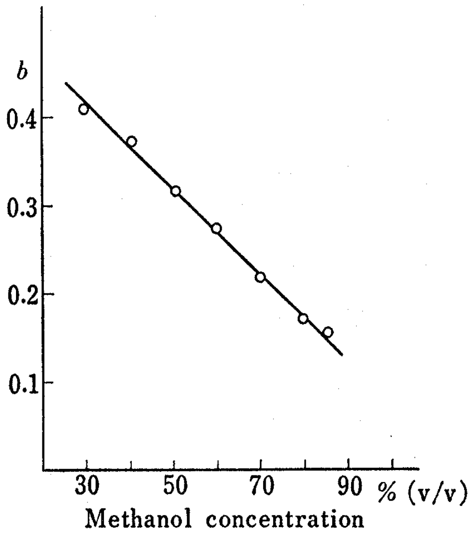

Fig. 2. Relationship between *b* Value and Methanol Concentration

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2) M. Uchida and T. Tanimura, *J. Chromatogr.*, in press.

to be not retained and its retention time was used as t_0 in calculating the capacity factors. The coefficient of variation of t_0 was 1.8% for constant elution conditions and no steady increase was observed on elution with lower methanol concentration.

The number of methylene groups in alkylbenzenes, alkylphenones and benzoic acid esters were plotted *vs.* log k' in Fig. 1. The result is consistent with Martin's equation for partition chromatography,

$$\log k' = a + bn$$

in which a and b are constants and n is the number of methylene groups in a molecule.³⁾ Similar linearities are found for various compositions of an aqueous methanol eluent, although the slope of the lines decreases with increasing methanol concentration. In Fig. 2, b is plotted *vs* the concentration of methanol in the moving phase. The linearity indicates that the relationship previously observed in partition between solutions⁴⁾ is applicable for reversed phase column chromatography on alkyl bonded superficially porous silica. One remarkable observation from Fig. 1 is that, the slopes of the lines for the different types of compounds with a given eluent, seem to be constant within experimental error. These observations imply that the increment of a methylene group to retention volume is similar for the various types of compounds. Consequently, b in the equation should have a specific value independent of types of compounds.

From these relationships, it is possible to estimate the elution conditions of compounds in a homolog from the data experimentally obtained for one member of the homologous series, and the number of theoretical plates required to obtain necessary resolution between neighboring compounds of the homologous series.

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