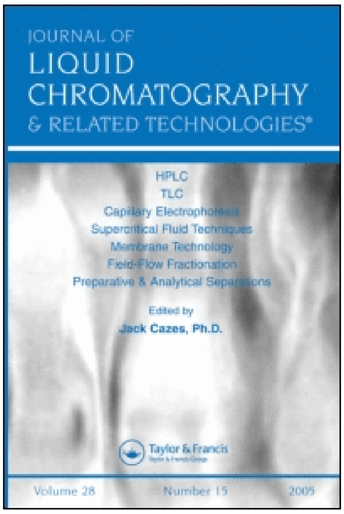

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Toshio Ogawa[a]; Masakazu Sakai[a]
[a] Hirakata Plastics Laboratory, Ube Industries, Ltd., Hirakata Osaka, Japan

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SOLVATION AND ADSORPTION EFFECTS IN GEL PERMEATION CHROMATOGRAPHY

Toshio Ogawa and Masakazu Sakai

Hirakata Plastics Laboratory
Ube Industries, Ltd.
3-10, Nakamiyakita-machi, Hirakata
Osaka 573, Japan

ABSTRACT

Saturated hydrocarbons are generally eluted according to molecular volumes in gel permeation chromatography(GPC). Other compounds, containing polar groups such as hydroxyl and carbonyl groups, deviate from the molecular volume/elution count relationship which is prepared using saturated hydrocarbons. The deviation is more or less observed regardless of the kinds of eluents. In this paper, this problem is investigated in detail with respect to infrared(IR) and proton magnetic resonance(NMR) spectra, and concentration dependences of peak heights and elution volumes in GPC. IR and NMR spectra reveal that alcohols, ketones and esters are strongly solvated by eluent molecules such as chloroform and tetrahydrofuran(THF). The solvation effect leads to faster elution for these compounds than expected for aliphatic hydrocarbons. On the other hand, the concentration dependences of elution counts and peak heights prove the adsorption of amines on polystyrene gel in chloroform. In fact, the elution rates of amines and polychlorides are retarded. In the case of aliphatic carboxylic acids, the elution mechanism is more complicated: association and adsorption effects would be overlapped.

INTRODUCTION

Many organic compounds such as ketones and alcohols are eluted at lower elution counts than expected from data for aliphatic hydrocarbons, as reported previously.1) The phenomenon is assumed to be due to solvation by eluent molecules. On the other hand, some other organic compounds such as amines and polychlorides are eluted at higher elution counts. This case is assumed to be due to adsorp-

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tion of solute molecules on polystyrene gel. However, no evidence other than deviation of elution volume has been presented yet. The solvation phenomenon is detectable by observing the wavenumbers of absorption bands due to polar groups in IR spectra, or by the δ values of peaks in NMR spectra. For example, the stretching vibration band of hydroxyl groups should appear from 3200 to 3600 cm^{-1}. If solvation occurs, the band will appear at a lower wavenumber. If adsorption of solute molecules occurs, the peak height or the area under the peak will not be proportional to the concentration, because some amount of solute molecules will stay longer in columns than remaining molecules. Some other anomalous behavior would be expected.

EXPERIMENTAL

GPC

A Shimadzu Model 1-A gel permeation chromatograph was used, equipped with the two columns which were packed with cross-linked polystyrene gel. One column had a nominal exclusion limit of 10Å and the other 10^2Å. Each column was 4ft in length and 0.305in. in inner diameter. The instrument was operated using o-dichlorobenzene(ODCB) as eluent with a flow rate of 1.0ml/min at ambient temperature and 80°C. One milliliter of a 1.0% ODCB solution of sample was injected into the columns. One count corresponded to 5ml of eluent, which was measured by a siphon.

Another instrument was used for investigating concentration dependences of peak heights and elution counts in chloroform. A Toyosoda HLC-807 high speed liquid chromatograph was used euipped with the two columns($G2000H_8$) which were packed with cross-linked polystyrene gel. The columns had a nominal exclusion limit of 250Å. Each column was 2ft in length and 0.305in. in inner diameter. The instrument was operated with a flow rate of 1.0ml/min at ambient temperature. One hundred microliter of a 0.5% chloroform solution of sample was injected into the columns.1) In this case, one count corresponded to 128 drops of eluent coming out from a special nozzle which forms a part of an eluent volume detector. This count also corresponded to nearly 0.74ml of eluent.

IR spectroscopy

A Hitachi Model EPI-G3 infrared spectrophotometer was used with liquid NaCl cells of 0.5mm thickness. Measurements were done at a concentration 1 to 2g/dl in chloroform, or in Nujol for solid compounds. Infrared spectra of neat samples were measured by spreading on NaCl plates or as a Nujol mull. Calibration was accomplished by referring the spectra to that of a thin film of polystyrene.

NMR spectroscopy

A Nihondenshi Model JNM4H-100 high resolution NMR spectrometer was used to determine the chemical shifts in ^{1}H-NMR. NMR spectra should be measured at 1% concentration, that is, the same concentration as in GPC. However, at such low concentrations, NMR spectra are not readily obtainable. A concentration of 5% was usually provided for the measurement. Tetramethylsilane($Si(CH_3)_4$) was used as an internal standard.

Samples and solvents

Aliphatic and aromatic hydrocarbons were supplied by various chemical producers. Esters and alcohols were supplied by Applied Science Laboratories Inc.,(State College, Pa., U.S.A.), and ketones by Polyscience Corp.,(Niles, IL, U.S.A.). ODCB is a special grade purchased from Kishida Chemical Co.,(Higashi-ku, Osaka, Japan).

RESULTS AND DISCUSSION

Elution behavior in ODCB

The elution behavior in chloroform was shown in the previous paper.1) To understand the elution behavior it is very valuable that measurements are done in different eluents. Logarithmic molecular volumes log V_M were plotted against elution counts by the same way as in the previous paper,1) where V_M equals M/d (M: molecular weight, d: density) in this discussion. The result at ambient temperature is shown in Figure 1. The extent of deviation of the elution volumes is much smaller in ODCB than was previously reported in chloroform.1) The elution behavior at 80°C is shown in Fig-

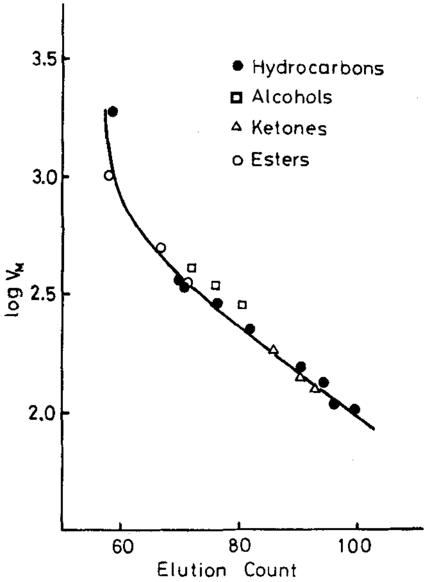

FIGURE 1. Logarithmic molecular volumes vs. elution counts in ODCB at ambient temperature. Two columns having nominal exclusion limits of 10^1 and 10^2Å were used.

ure 2. Experimental points seem to fall on the same curve as obtained for aliphatic hydrocarbons. However, this apparent agreement comes from the decrease of resolution, because only one column having a nominal exclusion limit of 10Å was used at 80°C. It is difficult to compare exactly the result shown in Figure 1 with that in Figure 2. In that sense, these results do not involve so detailed information on the temperature dependence of elution counts as presented by Cantow et al.[2)] At any rate, it is sure that there is no substantial change of experimental results at high temperature. If solvation was the major factor, the deviation should disappear or decrease at high temperature. We conclude that the deviation is caused by solvation, but by adsorption of solute molecules.

Elution behavior depends upon the kind of eluent. Moreover, we cannot expect to prepare a universal calibration for low molecular weight compounds even if any eluents were carefully selected.

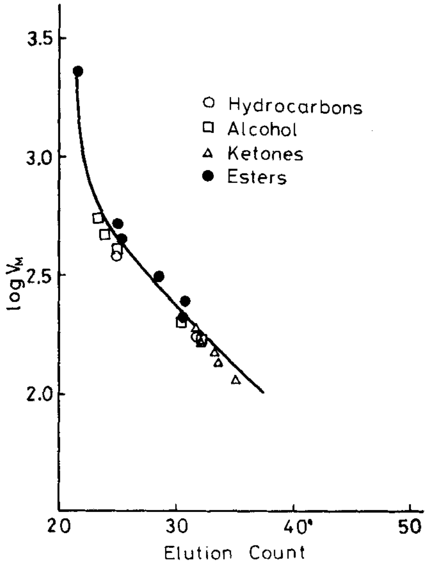

FIGURE 2. Logarithmic molecular volumes vs. elution counts in ODCB at 80°C. One column having a nominal exclusion limit of 10^{10} Å was used. This column was different in history from that used for experiment of Figure 1.

Solvation

In the previous paper, we suggested that solvation and adsorption are the major factors by which the deviation occurs in GPC elution behavior. Concerning solvation, NMR and IR spectra reveal directly the presence of hydrogen bonding between solutes and eluent molecules. Various cases are demonstrated in Table 1. For example, stearyl alcohol has an absorption band at 3323.5cm^{-1} due to hydroxyl group, when the spectrum is measured for neat sample. This low frequency is the result of intermolecular hydrogen bonding. The same compound in a 1% solution shows the absorption band at 3445.9cm^{-1} in chloroform, at 3465.2cm^{-1} in THF and 3607.0cm^{-1} in ODCB. These wavenumbers reveal that stearyl alcohol is solvated strongly by chloroform and THF. NMR spectra also clearly show this tendency. The signals of hydroxyl group lie at lower magnetic field in chloroform and THF than in ODCB. Solute/solute interaction may be taken into account. However, the fraction of eluent in the solution is almost 100%. Solute/eluent interaction is more predominant than solute/solute interaction in their probabilities if we assume that interaction forces are similar.

In Table 1, the estimated results from IR and NMR spectra are shown in the column, "solvation." The extent of the deviation observed in GPC is shown in the column, "deviation." In most cases, the agreement between the estimated deviation, i.e., "solvation," and the observed deviation, i.e., "deviation," is good. This fact clearly proves that elution volumes are largely influenced by solvation between solute and eluent molecules. Large discrepancies between the estimated and observed deviation are, however, present for amines and carboxylic acids, especially when chloroform is used as eluent. In the former, the elution volumes are smaller than in hydrocarbons. This behavior is completely different from that expected from IR and NMR spectra. This fact suggests that the adsorption effect is more predominant than solvation in this system.

Free carboxylic acids generally do not exist in solution. Even in fairly diluted solution, carboxylic acids exist as dimers.3) IR and NMR spectra do not simply reflect the phenomenon of solvation by eluent molecules in this case. Carboxylic acids should be eluted at considerably lower counts than expected from hydrocarbons, since the dimer is the most probable structure in solution. However, these compounds are eluted at almost the same elution counts as corresponding hydrocarbons, as compared with amines and esters.1) This abnormal phenomenon would be due to the adsorption of solute molecules on the gel surface.

Adsorption

To confirm the adsorption effect, the following experiments were carried out in amine/chloroform system. If adsorption of solute molecules takes place on the gel surface, the peak heights in GPC will not be proportional to the concentration of solutes because of retardation of some amount of solute molecules. The concentration dependence of peak heights was measured for various compounds. Figures 3 and 4 show these results. In n-octadecane and toluene,

TABLE 1 Comparison of NMR and IR Data with Elution Behavior

Compound		Solvent			Neat sample
		$CHCl_3$	C_4H_8O**	C_6H_4Cl	
Stearyl Alcohol	$\nu_{OH}(cm^{-1})$	3445.9	3465.2	3607.0	3323.5
	δ(ppm)	3.72	...	3.64	
	Solvation*	M	M	S	
	Deviation*	M	L	M	
Stearic Acid	$\nu_{C=O}(cm^{-1})$	1706.7	1736.3	1710.2	1702.3
	δ(ppm)	2.36	2.10	2.28	
	Solvation*	L	S	M	
	Deviation*	S	L	M	
Stearyl Amine	$\nu_{NH}(cm^{-1})$	3375.0	3561.0	3375.0	3323.5
	δ(ppm)	1.58	1.46	1.64	
	Solvation*	M	S	M	
	Deviation*	-L	S	S	
2-Octanone	$\nu_{C=O}(cm^{-1})$	1709.4	1718.4	1714.5	1718.9
	δ(ppm)	2.16	2.04	2.04	
	Solvation*	L	S	M	
	Deviation*	L	S	M	
Methyl Arachidate	$\nu_{C=O}(cm^{-1})$	1727.6	1740.0	1730.5	1742.8
	δ(ppm)	2.34	2.55	2.26	
	Solvation*	L	S	M	
	Deviation*	L	S	M	

*: L > M > S, **: the data on "deviation" is quoted from reference (4).

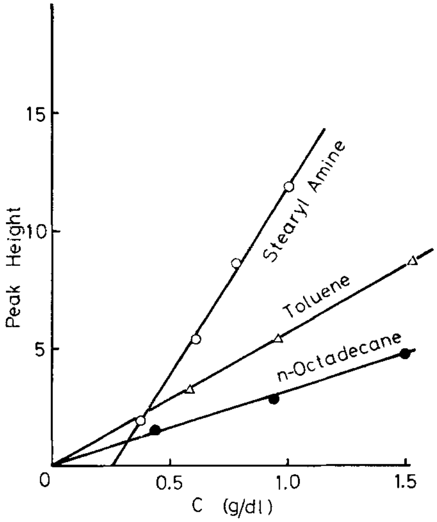

FIGURE 3. Concentration dpendence of peak heights in chloroform.

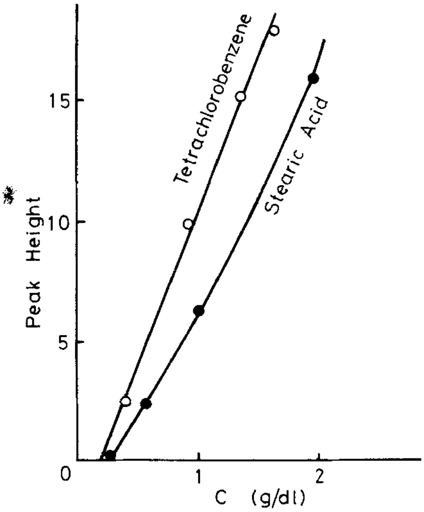

FIGURE 4. Concentration dependence of peak heights in chloroform.

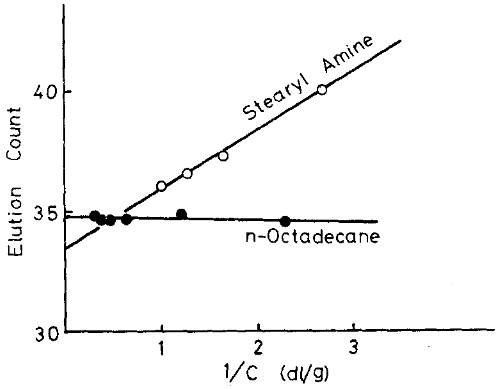

FIGURE 5. Concentration dependence of elution counts in chloroform.

the peak heights are completely proportional to the concentration. These straight lines pass through the origin. In stearyl amine, 1,2,4,5-tetrachlorobenzene and stearic acid, the peak heights vs. concentration curves, however, do not pass through the origin. These figures demonstrate that the peak of the compounds disappears at a certain concentration. The solute molecules are completely adsorbed on the gel surface at the concentration where the peak disappears.

As shown in Figure 5, the elution counts in stearyl amine decreased with increasing concentration: the elution volume is considerably increased by adsorption at low concentration. On the other hand, the behavior in octadecane is contrary to that of stearyl amine and is rather normal for GPC.[5)] The concentration dependence of elution counts also proves the occurence of adsorption in stearyl amine.

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