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A HPLC Study of Adsorption of Organic Solutes on Cellulose Acetate

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Synopsis. The liquid chromatographic technique was useful for the measurement of adsorption of some nonionic organic solutes on cellulose acetate. It was recognized that there were linear correlations between logarithmic capacity factors measured by HPLC, log k', and logarithmic 1-octanol: water partition coefficients, log P.

In the reverse osmosis process, the adsorption of organic solutes on a cellulose acetate membrane is assumed to be important for the permeabilities of the solutes and the membrane fouling.[1–3] The interaction between cellulose acetate (CA) and some organic or inorganic solutes has been investigated with the high performance liquid chromatograhy (HPLC).[4,5] Y. Taketani *et al.*[4] estimated the distribution coefficients for solutes between the stationary phase around CA and the bulk phase, K_A'. The values of K_A' for some organic solutes were more than unity. These results rather suggested that the organic solutes were adsorbed on the CA surface. However, the factors affecting the adsorption of organic solutes on the CA surface were known little. The objects of this work are to confirm the usefulness of liquid chromatography for the measurement of adsorption characteristics and to examine the effects of molecular structures on adsorption.

Experimental

The HPLC column was prepared by packing cellulose acetate (acetyl content 39.8%, Kodak 4644, 200/325 mesh) into a stainless steal column (I. D.=4.6 mm, L=250 mm). The moving phase was water and a solvent velocity was 0.5 ml min^{-1}. The HPLC apparatus used was a Toyosoda HLC-803A connected with a RI detector. The solutes used for this study were listed in Table 1. The concentrations of organic solutes in sample solution were less than 1%. The capacity factor for each solute, k', was calculated by the following equation;

$$k' = (t_i - t_0)/t_0, \qquad (1)$$

where t_i and t_0 are the retention times of solute i and D_2O, respectively.

Results and Discussion

The capacity factors of all alcohols and ketones in Table 1 were positive and these solutes seemed to be adsorbed on CA. It was also recognized that more hydrophobic solutes were adsorbed more. However, more hydrophobic compounds such as benzene, nitrobenzene or acetophenone did not elute and seemed to be adsorbed strongly on CA. These facts suggested that these HPLC conditions were useful for the measurement of relatively weak interaction between CA and organic solutes. From these results, it was attempted to correlate log k', with logarithmic 1-octanol: water partition coefficients,[6] log P, logarithmic activity coefficients at infinite dilution calculated by the UNIFAC method,[7] $\ln \gamma^{\infty}$, or the connectivity index,[8] $^1\chi^v$. These results were shown in Figs. 1, 2, and 3.

In the cases of ketones except acetyl acetone and aliphatic alcohols except 2-methyl-2-propanol, it was recognized that log k' was related linearly to log P as follows:

$$\text{1-alkanols; } \log k' = 0.675 \log P - 0.914 \quad (N = 9,\ r = 0.9961) \qquad (2)$$

$$\text{2-alkanols; } \log k' = 0.699 \log P - 1.048 \quad (N = 5,\ r = 0.9986) \qquad (3)$$

$$\text{ketones; } \log k' = 0.613 \log P - 0.451 \quad (N = 9,\ r = 0.9901) \qquad (4)$$

Table 1. Organic solutes

No.	Solute	log $P^{a)}$	$\ln\gamma^{\infty b)}$	$^1\chi^{v c)}$	No.	Solute	log $P^{a)}$	$\ln\gamma^{\infty b)}$	$^1\chi^{v c)}$
1	Methanol	−0.77	—	0.447	16	2-Hexanol	1.76$^{d)}$	10.326	2.951
2	Ethanol	−0.31	1.637	1.023	17	2-Methyl-2-propanol	0.35	—	1.724
3	1-Propanol	0.25	3.397	1.523	18	2-Ethyl-2-propanol	0.89	—	2.284
4	1-Butanol	0.88	5.176	2.023					
5	1-Pentanol	1.56	6.954	2.523	20	Acetone	−0.24	2.984	1.204
6	1-Hexanol	2.03	8.735	3.023	21	2-Butanone	0.29	4.738	1.765
7	2-Methyl-1-propanol	0.65	5.173	1.879	22	2-Hexanone	1.38	8.224	2.765
8	2-Ethyl-1-propanol	1.42	6.954	2.379	23	3-Methyl-2-butanone	0.71$^{d)}$	6.481	2.148
9	2-Methyl-1-hexanol	2.44$^{d)}$	10.505	3.417	24	4-Methyl-2-pentanone	1.15$^{d)}$	8.221	2.621
10	Benzyl alcohol	1.10	5.374	2.841	25	3-Pentanone	0.83$^{d)}$	6.484	2.325
11	*dl*-1-Phenylethanol	1.36	7.605	3.195	26	Cyclopentanone	0.37	5.311	2.411
12	Cyclohexanol	1.23	9.077	3.117	27	Cyclohexanone	0.81	7.054	2.911
13	2-Propanol	0.05	4.866	1.413	28	4-Methylcyclohexanone	1.35$^{d)}$	8.790	3.305
14	2-Butanol	0.61	6.701	1.951	29	Acetophenone	1.58	7.189	2.865
15	2-Pentanol	1.29$^{d)}$	8.520	2.451	30	Acetyl acetone	0.34	1.886	1.911

a) 1-Octanol: water partition coefficient.[6] b) Logarithmic activity coefficient at infinit dilution calculated by the UNIFAC method.[7] c) Connectivity Index.[8] d) Calculated value.

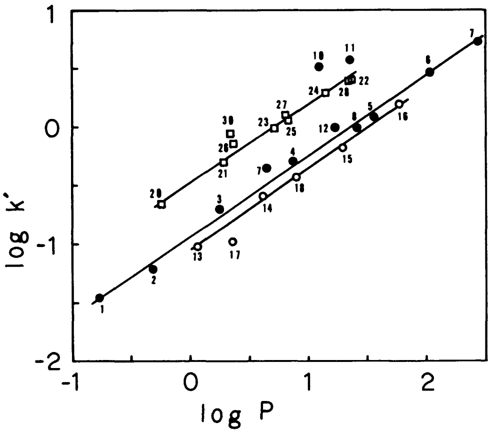

Fig. 1. The relationship between log P and log k' (numbers in figure mean the solute numbers). ●; 1-alkanol, ○; 2-alkanol, □; ketone.

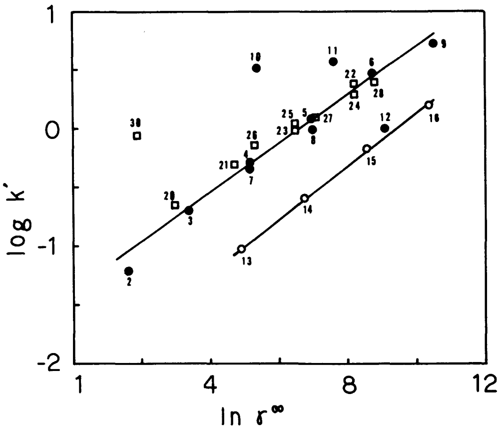

Fig. 2. The relationship between ln γ^{∞} and log k'.

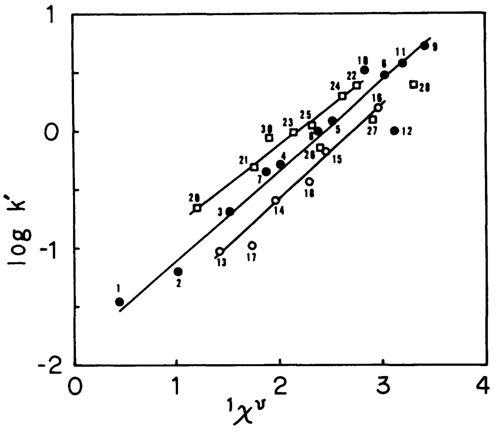

Fig. 3. The relationship between connectivity index $^1\chi^v$ and log k'.

These results indicated that the adsorption of organic solutes was controlled by the hydrophobicity of solutes and that the effect of hydrophobicity in these solutes was equivalent because the slopes in these equations were almost equal. These results showed that the functional group affected the adsorption, because the intercept of ketones was larger than that of alcohols and acetyl acetone was above the line of ketones in Fig. 1. It was assumed that the steric factors also influenced the adsorption from the following results; (a) the intercept of 2-alkanols was a little less than 1-alkanols, and (b) the log k' value of 2-methyl-2-propanol was less than the value estimated by Eq. 3.

Table 2. Solutes eluted earlier than D_2O

Solute	Retention time/min
D_2O	6.27
NaCl	5.57
Glucose	5.65
Lactose	5.57
Tween-20	5.51
PEG(#6000)	5.35
PVP(K-90))	4.35

The log k' values of benzyl alcohol and dl-1-phenylethanol were larger than those estimated by using Eq. 2. Acetophenone, nitrobenzene and benzene, whose log P values were 1.58, 1.85, and 2.15 respectively, did not elute under these conditions. These results suggested that the phenyl group was adsorbed more easily than the aliphatic group. Considering the results of aromatic compounds and ketones, it was assumed that unsaturated bonds in solutes also affected the adsorption on CA.

The relationship between log k' and ln γ^{∞} or $^1\chi^v$ was also linear as shown in Figs. 2 or 3, and these tendencies were similar to those in Fig. 1. From these results, it was assumed that the adsorption of organic solutes on CA was able to be correlated with some free energy parameters or some structure parameters.

The results for solutes whose retention time was less than that of D_2O are shown in Table 2. Glucose and lactose, the most hydrophilic solutes, were not adsorbed on CA. Polymer solutes (PEG and PVP) and Tween-20, which caused the membrane fouling,[3] were not adsorbed on CA and it seems that the retention time of these solutes decreased as molecular weight increased. Y. Taketani *et al.*[4] showed a similar tendency by using PEG. These facts seem to be caused by the size exclusion effect, because the large specific area of CA[4] suggested that there are many micro pores on the surface of cellulose acetate particles.

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