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LIQUID CRYSTALS AS STATIONARY PHASES IN GAS CHROMATOGRAPHY

V. ADSORPTION BEHAVIOUR OF ALIPHATIC ALCOHOLS AND THEIR ESTERS ON AN ELECTRIC FIELD LIQUID CRYSTAL COLUMN

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SUMMARY

Previously various aspects of adsorption phenomena in electric field liquid crystal (EF–LC) columns were investigated. In this study, to establish the mechanism of the phenomenon, the amounts of C_4 and C_5 aliphatic alcohols and esters adsorbed were measured on three types of EF–LC columns, and the effects of the dielectric constants and the carbon skeleton structures of the solutes on the amounts adsorbed were determined. It was found that the amounts of isomers such as pentanols and butanols adsorbed were different from each other, although these isomers have similar dielectric constants. It was concluded that the adsorption was influenced not only by the dielectric constant, but also by the structure of the carbon skeleton. The equation proposed previously for the relationship between the field strength and the extent of adsorption was modified by introducing a structural term, f_s. Subsequently, the dielectric constants of esters were calculated from the equation by using the f_s values of the corresponding alcohols, and were compared with those found in the literature. The differences were within 10 %.

INTRODUCTION

In our investigations[1-4] on liquid crystal stationary phases in gas chromatography, it was found that highly polar compounds were selectively adsorbed in the column when a d.c. electric field was applied and that when the adsorption occurred, the liquid crystals were changed to nematic mesophases by the d.c. electric field. The dielectric constants of adsorbed compounds were shown to have a close relationship with this phenomenon.

This phenomenon was utilized for the selective determination of aromatic hydrocarbons co-existing with large amounts of oxygen-containing compounds. Interfering oxygen-containing compounds were completely eliminated by application of the d.c. electric field to the liquid crystal column.

In this study, in order to clarify the mechanism of this phenomenon further, the

adsorption of butanols and pentanols was investigated. By measuring the amounts of alcohols adsorbed in three kinds of electric field–liquid crystal (EF–LC) column, it was found that the amount adsorbed was affected not only by the dielectric constant, but also by the structure of carbon skeleton and the position of the functional group of the adsorbed compound. Therefore, the previously described equation which expressed the relationship between the field strength and the amount adsorbed was modified by introducing a structural term, f_s. By using the modified equation, the dielectric constants of corresponding esters were successfully calculated.

EXPERIMENTAL

Materials

Three nematic liquid crystals, 4′-ethoxybenzylidene-4-cyanoaniline (EBCA), 4′-anisal-4-acetoxyaniline (APAPA) and 4,4′-azoxydianisole (ADA), as stationary phases for the EF–LC column were obtained from Tokyo Chemical Industry (Tokyo, Japan), and were used without further purification. Butanols, pentanols, butyl acetates and amyl acetates and butyrates were of analytical-reagent grade. Diethylene glycol succinate (DEGS) polyester was obtained from Nishio Industry (Tokyo, Japan). Fine nickel wire (0.15 mm in diameter) for the inner electrode of the EF–LC column was purchased from Nippon Denkyu (Tokyo, Japan), and Sealbest P-246, an electroconductive resin, for the outer electrode from Tokuriki Kagaku (Kanagawa, Japan).

Gas chromatograph

A modified Shimadzu Model GC 6AM-Pr gas chromatograph equipped with a flame-ionization detector was used, modified as described elsewhere[4].

EF–LC column and separation column

All of the EF–LC columns were 4 m × 0.35 mm I.D. and the configuration and method of preparation were described previously[1].

A whisker-walled open-tubular glass capillary column, coated with DEGS by passing 5% methylene chloride solution through it, was employed as the separation column.

The separation column and EF–LC column were connected in series by shrinkable PTFE tubing.

d.c. generator

A high-voltage power supply for the photomultiplier (Hamamatsu TV, 1.5k-M; Hamamatsu, Shizuoka, Japan) was used.

GC conditions

Pure nitrogen gas (99.999%) was used as the carrier gas at a flow-rate of *ca.* 1 ml/min. The temperatures of the injection port and the flame-ionization detector were 150°C. The oven temperatures for DESG–ADA, DEGS–EBCA and DEGS–APAPA were 120, 120 and 90°C, respectively.

Under these conditions, an appropriate d.c. voltage was applied. Before injection, these columns must be allowed to stand for 3–4 h.

RESULTS AND DISCUSSION

Adsorption in EF–LC column

For the EF–LC column which was connected behind the separation column, three different liquid crystal stationary phases were used. The extent of adsorption in the EF–LC columns was measured by injecting ethereal solutions of the sample compounds.

The effect of the different liquid crystals on the extent of adsorption amount of each compound was studied. The amounts adsorbed and also amounts of each compound adsorbed relative to 1-pentanol are shown in Table I. The extent of adsorption of a compound varied from column to column, but the relative values were similar in all three columns. Therefore, it might be concluded that the relative amount of each compound adsorbed is independent of the liquid crystal phase used for the EF–LC column.

TABLE I

EFFECT OF LIQUID CRYSTAL IN EF–LC COLUMN ON ADSORPTION

Separation column, DEGS (30 m × 0.35 mm I.D.); EF–LC column, 4 m × 0.35 mm I.D.; applied potential, 250 V d.c. Results given are amounts adsorbed (nmol) and relative amounts adsorbed (R) (relative to 1.00 for 1-pentanol).

Compound	ADA		EBCA		APAPA	
	$[A_s]$ (nmol)	R	$[A_s]$ (nmol)	R	$[A_s]$ (nmol)	R
1-Pentanol	3.64	1.00	2.58	1.00	1.86	1.00
1-Butanol	4.11	1.13	2.93	1.14	2.06	1.11
n-Butyl acetate	0.764	0.210	0.559	0.217	0.424	0.228
n-Amyl acetate	0.749	0.206	0.463	0.179	0.392	0.211
Ethyl n-butyrate	0.668	0.183	0.442	0.171	0.349	0.187
Column temperature (°C)	120		120		90	

Adsorption of butanols and pentanols

The amounts of butanols and pentanols adsorbed were measured in EBCA, ADA and APAPA EF–LC columns under applied voltages of 150, 100 and 150 V d.c., respectively. The results are presented in Table II. It was found that, when the number of side-chains increased, the amount of isomers adsorbed decreased, and also that the nearer the side-chain was located to the OH group the smaller was the amount adsorbed. In addition, the position of the OH group influences the amount adsorbed; Thus, 1-pentanol was adsorbed more than 2-pentanol, and 2-pentanol more than 3-pentanol. Further, it was observed that, even though these isomers had similar dielectric constants, the amounts adsorbed were different.

Amounts of the adsorbed butanol isomers decreased in the order *n- > iso- > sec.- > tert.-butanol.* These results obviously indicate that adsorption in the EF–LC column is influenced not only by the dielectric constant, but also by the carbon skeleton structure of the compound adsorbed.

TABLE II

AMOUNTS OF ALIPHATIC ALCOHOLS ADSORBED

Applied potential: 100 V d.c. on ADA column, 150 V d.c. on EBCA column, 150 V d.c. on APAPA column. Other conditions as in Table I.

Compound	Amount adsorbed (nmol)		
	ADA	EBCA	APAPA
1-Pentanol	1.46	1.53	1.09
2-Pentanol	1.02	1.00	0.733
3-Pentanol	0.765	0.867	0.550
3-Methyl-1-butanol	1.31	1.39	0.928
3-Methyl-2-butanol	0.978	0.957	0.699
2-Methyl-2-butanol	0.750	0.947	0.579
1-Butanol	1.63	1.73	1.21
2-Butanol	1.08	1.01	0.762
2-Methyl-1-propanol	1.37	1.33	0.921
2-Methyl-2-propanol	0.405	0.747	0.447

Expression of degree of adsorption

From the above results, the influence of the carbon skeleton structure on the adsorption was explained as follows. When the polar molecules were exposed to an electric field, the coulombic force between the polar molecule and the electrode played an important role in the adsorption process. This force increased as the polarization distance of the molecule increased.

Eqn. 1 was proposed previously[2] for the calculation of the dielectric constant of a solute:

$$[A_s] = k(\varepsilon - 1)E \tag{1}$$

where $[A_s]$ is the amount adsorbed (mol), E is the applied potential (V d.c.), ε is the dielectric constant of the adsorbed compound and k is a constant. As k could be considered to have a structural contribution, it was divided into a structural term of the adsorbed compound, f_s, and k'. Here, f_s could be assumed, for a straight-chain compound, to be the distance from the functional group to the terminal carbon. In this study, f_s values were expressed by the C–C bond and C–O bond numbers. Then, the resulting equation is

$$[A_s] = k(\varepsilon - 1)f_s E \tag{2}$$

The k' and f_s values of pentanols and butanols were calculated by the following procedure. For reference 1-pentanol in the DEGS–ADA EF–LC column mode, the f_s value was *ca.* 5. This value and its amount adsorbed were put into eqn. 2, and then $k' = 2.25 \cdot 10^{-4}$ was obtained. The f_s values of other isomers were calculated from eqn. 2 by substituting this k' value and using the individual amount of the isomers absorbed, $[A_s]$. By the same procedure, f_s values of butanols could be calculated. The k' and f_s values obtained are given in Table III.

TABLE III

k' AND f_s VALUES FOR ALCOHOLS CALCULATED FROM EQN. 2

Compound	ADA		EBCA		APAPA	
	k'	f_s	k'	f_s	k'	f_s
1-Pentanol	$2.25 \cdot 10^{-4}$	5*	$1.61 \cdot 10^{-4}$	5*	$1.14 \cdot 10^{-4}$	5*
2-Pentanol		3.45		3.23		3.55
3-Pentanol		2.84		2.99		2.85
3-Methyl-1-butanol		4.25		4.21		3.97
3-Methyl-2-butanol		3.17		2.91		2.98
2-Methyl-2-butanol		6.19		6.42		7.02
1-Butanol	$2.45 \cdot 10^{-4}$	4*	$1.65 \cdot 10^{-4}$	4*	$1.22 \cdot 10^{-4}$	4*
2-Butanol		2.89		2.64		2.69
2-Methyl-1-propanol		3.37		3.35		3.18
2-Methyl-2-propanol		1.47		1.97		2.28

* The assumed f_s values used for calculating the k' values.

The f_s values were closely, related to the chain length from the functional group to the terminal carbon, except for 2-methyl-2-butanol and 2-methyl-2-propanol, which had much larger values than expected. It was presumed that a structural interaction between the solute molecule and the long molecule of the nematic liquid existed. The k' values of the alcohols examined were similar to each other provided that the same EF–LC column was used.

Adsorption of esters

The amounts of amyl and butyl acetates, methyl and ethyl n-butyrates and ethyl isobutyrate adsorbed were measured under the same conditions as for alcohols in EBCA, ADA and APAPA EF–LC columns. The results are given in Table IV. The adsorption behaviour of butyl acetate isomers was similar to that of butanols, *i.e.*, n-butyl acetate was the most strongly adsorbed and whereas *tert.*-butyl acetate the most weakly. The amounts of butyrates adsorbed were comparable to those of *sec.-* and

TABLE IV

AMOUNTS OF ALIPHATIC ESTERS ADSORBED

Conditions as in Table II.

Compound	$[A_s]$ (nmol)		
	ADA	EBCA	APAPA
n-Butyl acetate	0.302	0.319	0.248
Isobutyl acetate	0.279	0.272	0.207
sec.-Butyl acetate	0.236	0.251	0.190
tert.-Butyl acetate	0.156	0.192	0.146
n-Amyl acetate	0.302	0.333	0.283
Isoamyl acetate	0.295	0.276	0.247
Ethyl isobutyrate	0.173	0.164	0.126
Methyl n-butyrate	0.243	0.210	0.159
Ethyl n-butyrate	0.254	0.233	0.176

TABLE V

COMPARISON OF CALCULATED AND LITERATURE VALUES OF DIELECTRIC CONSTANTS ON THREE EF–LC COLUMNS

ε_{calc} is the value calculated from eqn. 2; ε_{lit} is the value found in the literature.

Compound	ADA			EBCA			APAPA			ε_{lit}
	k'	f_s	ε_{calc}	k'	f_s	ε_{calc}	k'	f_s	v_{calc}	
n-Butyl acetate*	$1.88 \cdot 10^{-4}$	4.00		$1.32 \cdot 10^{-4}$	4.00		$1.03 \cdot 10^{-4}$	4.00		5.01
Isobutyl acetate		3.37	5.33		3.35	5.08		3.18	5.21	5.29
sec.-Butyl acetate		2.89	5.34		2.64	5.64		2.69	5.56	–
tert.-Butyl acetate		1.47	5.65		1.97	5.86		1.28	5.14	–
n-Amyl acetate		5.00	5.42		5.00	4.36		5.00	4.66	4.75
Isoamyl acetate		4.25	4.67		4.21	4.31		3.97	5.01	4.63

* Used for calculating the k' value. The f_s values are from corresponding alcohols and were used for calculating the dielectric constant of each compound.

tert.-butyl acetates. The adsorption behaviour of these butyrates is explained by the position of the functional group, which was located in the middle of the carbon skeleton, as in *sec.*- and *tert.*-butyl acetates.

It is concluded that an almost identical structural effect of alcohols on the adsorption to that of esters exists. In order to justify this conclusion, the dielectric constants of the corresponding esters were calculated by using the f_s values of the alcohols. Thus, the k' value of *n*-butyl acetate was obtained by putting $f_s = 5$, the amount adsorbed and the dielectric constant into eqn. 2. Then, the dielectric constants of other esters were calculated by using this k' value, the amounts adsorbed and the f_s values of the corresponding alcohols. In Table V these dielectric constants calculatd are compared with those found in the literature[5,6]. Good agreement between the two values was observed each compound.

CONCLUSIONS

The adsorp.ion behaviour of C_4 and C_5 alcohols was shown to be closely related to the structure of the carbon skeleton. When the number of side-chains in the carbon skeleton was increased the amount adsorbed decreased, and the nearer the side-chain was located to the OH group the smaller was the amount adsorbed. A compound that had the OH group at the end of the carbon skeleton was more adsorbed than one with the OH group nearer the middle.

The results indicate that the adsorption was influenced not only by the dielectric constant, but also by the structure of a compound. The equation expressing the relationship between the field strength and the amount adsorbed was modified by introducing the structural term f_s. The f_s values of alcohols calculated from this equation were shown to be closely correlated with structure, except for 2-methyl-2-butanol.

The adsorption of butyl and amyl acetates was similar to that of the corresponding alcohols. Therefore, the f_s values for alcohols were applicable to esters, and the dielectric constants of the corresponding esters were calculated. These values were compared with those found in the literature, and good agreement between the values was observed for each compound.

Additionaly, the k' values of pentanols and butanols were similar. It was found that the k' terms contained the effect of the functional group on adsorption.

Further work concerning the prediction of the amounts of ketones and aldehydes adsorbed is in progress.

REFERENCES

1 K. Watabe, S. Suziki and S. Araki, *J. Chromatogr.*, 192 (1980) 89.
2 K. Watabe, S. Suzuki and S. Araki, *Nippon Kagaku Kaishi (J. Chem. Soc. Jap.)*, (1980) 582.
3 K. Watabe, S. Suzuki and S. Araki, *Bunseki Kagaku (Jap. Anal.)*, 29 (1980) 585.
4 K. Watabe, T. Hobo and S. Suzuki, *J. Chromatogr.*, 206 (1981) 223.
5 J. A. Riddick and W. B. Bunger, *Organic Solvents*, Wiley-Interscience, New York, 1970.
6 *Kagaku Binran (Handbook of Chemistry)*, Chemical Society of Japan, Maruzen, Tokyo, 1966, p. 1163.