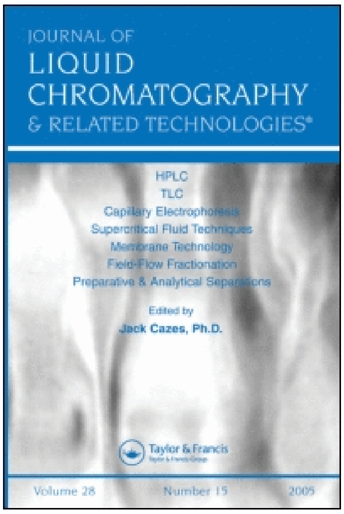

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EFFECT OF DILUENT ON THE STRUCTURE OF THE ADSORPTION LAYER IN SYSTEMS OF THE TYPE DILUENT + POLAR SOLVENT-SILICA

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ABSTRACT

The adsorption behaviour of solvents whose molecules differ in polarity, functional groups and shape and the effect of the less polar diluent was investigated. The surface excess was determined for various combinations of diluents and polar solvents using the modified thin-layer frontal chromatography technique.

INTRODUCTION

Adsorption in liquid-solid systems is important not only from the viewpoint of the phenomenon itself, but also owing to its fundamental role in the description of disperse systems /1/. Differences in the opinions about the orientation of molecules in the adsorption layer and

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its structure are reflected by the use of various models in the theory of retention mechanism in liquid chromatography /2-4/. Recently, Ościk et al./5/ concluded that ketones form multilayers when adsorbed from heptane solutions and monomolecular layers in benzene solutions. Therefore, it seemed worthwhile to investigate the adsorption behaviour of other solvents whose molecules differ in polarity, functional groups and shape; the effect of the less polar diluent was also investigated. For this purpose, the surface excess $\Gamma_i^{/n/}$ was determined for various combinations of diluents and polar solvents, using the modified thin-layer frontal chromatography technique /6/.

EXPERIMENTAL

The chromatographic experiments were carried out according to the procedure described in an earlier paper /6/ with a recently introduced modification /7/.

RESULTS AND DISCUSSION

Four polar solvent of class B and AB according to Pimentel and McClellan and belonging to various homologous series were chosen: diethyl ether, diethyl ketone, methyl ethyl ketone and n-pentanol-1. The four solvents have similar molar volumes. As diluent, both nonpolar /heptane, hexane, cyclohexane, decalin/ as well as weakly polar solvents were chosen /benzene, chloroform, methylene chloride/. The point of the excess isotherm was determined for 1 M concentration of the polar solvent which should correspond in most cases to monomolecular coverage. If the monomolecular adsorption model is correct /t = 1/, then the molar fraction of the solvent in the adsorption layer should not exceed unity /$X_i \leqslant 1$/. The value of X_i was calculated from Everett's equation:

Assuming t = 1 we have

$$X_i^{\sigma} = \frac{x_i^l + a_j^o \Gamma_i^{/n/}}{1 - /a_i^o - a_j^o/\Gamma_i^{/n/}} \qquad /1/$$

where $a_{i,j}^o$ are the areas covered by the given molecules in the monolayer

$\Gamma_i^{/n/}$ - surface excess concentration

t - number of layers

x_i^l - molar fraction of "i" in the bulk phase.

If the calculations for given values of $a_{i,j}^o$ result in $X_i^{\sigma} > 1$ then the assumption of monomolecular adsorption was false. For many simple systems the condition t = 1 is fulfilled, however, for others t > 1 is required.

The surface excess values obtained are given in Table 1.

TABLE 1

Values of the surface excess $n_1^{\sigma/v/}$ for some solvent systems at C_1^1= 1 ML^{-1}. Adsorbent: silica gel, a_s=500 m^{2}g^{-1}

Diluent	Di-ethyl ether	Di-ethyl ketone	Methyl-propyl ketone	n-pentanol-1
Heptane	0.94	1.59	1.95	0.83
Hexane	0.82	0.99	1.33	0.80
Cyclohexane	0.66	1.10	1.16	0.71
Benzene	0.46	0.76	0.94	0.64
Decalin	1.00	1.14	1.32	0.81
Carbon tetrachloride	0.51	0.67	0.81	0.55
Dichloromethane	0.31	0.33	0.49	0.57
Chloroform	0.27	0.32	0.42	0.53

The calculations according to eq.1 should be preceded by the choice of the values of the molecular areas $a^0_{i,j}$. Two methods were applied in the present study. In the first the calculation were based on the formula proposed by McClellan and Harnsberg /8/

$$\omega_{ads} = 2.567 . V^{0,687} - 10.336$$

To calculate the molecular area from this formula it is sufficient to know the molar volume of the component: ω_{liq} denotes the area of the molecule assuming spherical shape and dense hexagonal packing. In the second method the molecules were considered as cylinders of cross-section area equal to 0.22 nm^2 /calculated from molecular parameters; Van der Waals radii etc./ and length proportional to the chain length, in accordance with the equation

$$0.22 \times H \times N_A = \bar{V} \qquad /3/$$

where N is the length of the cylinder, N_A - Avogadro number and $\bar{V}$ - molar volume.

The areas of 1 mole of adsorbate calculated by the two methods are given in Table 2 for flat and perpendicular orientation relative to the adsorbent surface.

From the molecular excess values $n_i^{\sigma/v/}$ /assuming that $n_i^{\sigma/v/} = n_i^{\sigma/n/}$ and specific surface area of silica equal to 500 m^2g^{-1}/ the molar fraction of the polar component in the adsorption layer was calculated for various possible values of $a_{i,j}^o$, /relative to 1 mole/.

TABLE 2

Areas occupied by one mole of molecules in the monolayer $a_{i,j}^o$, $\times 10^5\ m^2mol^{-1}$

Solvent	a_i^o, a_j^o calculated		
	from /eq.2/	for cylindrical shape	
		flat orientation	vertical orientation
Heptane	3.73	3.29	1.27
Hexane	3.29	2.82	1.27
Cyclohexane	2.93	2.05	1.40
Benzene	2.49	2.05	1.40
Decalin	3.88	4.10	2.80
Carbon tetra-chloride	2.67		
Dichloromethane	1.89		
Chloroform	2.29		
Di-ethyl ether	2.84	2.35	1.48
Di-ethyl ketone	2.88	2.46	1.48
Methyl-propyl ketone	2.89	2.69	1.48
n-Pentanol-1	2.95	2.67	1.27

TABLE 3

a. Molar fraction X_i^{σ} of polar solvents in the adsorption layer /calculated for a_i^o, a_j^o from eq./2// assuming monolayer adsorption /t = 1/

Diluent	Di-ethyl ether	Di-ethyl ketone	Methyl-propyl ketone	n-pentanol-1
Heptane	0.72	1.04	1.20	0.67
Hexane	0.62	0.72	0.91	0.62
Cyclohexane	0.49	0.74	0.78	0.53
Benzene	0.33	0.50	0.60	0.43
Decalin	0.76	0.84	0.93	0.67
Carbon tetrachloride	0.38	0.47	0.55	0.40
Dichloromethane	0.20	0.21	0.28	0.32
Chloroform	0.21	0.24	0.29	0.35

b. Molar fraction X_1^{σ} of polar solvent in the adsorption layer /calculated for cyllindrical molecular shape and flat adsorption of polar solvent and vertical adsorption the diluent/

Diluent	Di-ethyl ether	Di-ethyl ketone	Methyl propyl ketone	n-pentanol-1
Heptane	0.73	1.50	2.66	0.76
Hexane	0.62	0.80	1.35	0.71
Cyclohexane	0.48	0.85	1.04	0.59
Benzene	0.33	0.55	0.79	0.51
Decalin	0.57	0.66	0.83	0.57

c. As in b/ calculated for cyllindrical molecule shape and flat adsorption of polar solvent and flat adsorption the diluent

Diluent	Di-ethyl ether	Di-ethyl ketone	Methyl-propyl ketone	n-pentanol-1
Heptane	0.49	0.73	0.96	0.53
Hexane	0.48	0.57	0.81	0.54
Cyclohexane	0.44	0.49	0.86	0.53
Benzene	0.31	0.49	0.68	0.47
Dekaline	0.46	0.52	0.62	0.42

The molar fractions calculated for various assumptions are given in Table 3 a,b,c.

The simplified procedure /various geometrical models of molecules/ is commonly used when no general solution is available; it may provide approximate information about the role of the investigated parameters in the phenomena studied.

It follows from the calculations /Table 3a/ that the use of molecular areas based on eq.2 results in molar fractions larger than unity for methyl-n-propyl ketone and in same cases also for diethyl ketone. This seems to indicate that the monomolecular model of adsorption is not valid in these cases. On the other hand, the molar fraction of ether is smaller than unity for all diluents which is in accordance with the monomolecular adsorption model.

In the second model cylindrical shape of the molecules was assumed. In the case of polar solvents flat adsorption was assumed while for diluents /hexane, heptane, benzene, cyclohexane, dekaline/ two extreme cases i.e., vertical or flat adsorption were considered. The results are presented in Table 3b,c. Flat adsorption of polar solvent and vertical adsorption of the diluent results in data which can be interpreted by multilayer adsorption /mole fraction smaller than unity is obtained for $t > 1$/. On the other hand, assumption of flat configurations for both polar and nonpolar molecules leads to calculated values of X_i^{σ} which are in agreement with the monomolecular adsorption model.

The conclusions emphasize the role of estimated sitting areas of adsorbed molecules. For instance, the results indicating bilayer adsorption in ketone solutions and monolayer adsorption in ether solutions may lead to explication of some anomalies in the behaviour of ethers in comparison to ketones when used as eluents in liquid-solid adsorption chromatography. Owing to the limited number of experimental data analysed, only general conclusions could be formulated.

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