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ADSORPTION OF METHANOL FROM THE LIQUID MOBILE PHASE ON THE COLUMN PACKING SURFACE

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Abstract

The adsorption isotherms of methanol in water solutions which were used as mobile phase in RP HPLC on adsorbents modified with dimethyloctadecylchlorosilane were measured. On the basis of these isotherms the chemical composition of the stationary phase as a function of the mobile phase concentration was determined. The influence of both those phases on retention factors k' of alkyl derivatives of benzene was discussed. It was stated that k' of benzene and its derivatives decreases with the various rate together with the increase of the methanol concentration in both phases. Quotient of volume coefficient corresponding to a unit of adsorbed methanol ($\log k'/n^{s}_{Me}$) decreases linearly.

Keywords: adsorption of benzene derivatives from mobile phase, LC packing with bonded phase, retention factors optimization

Introduction

Nowadays chromatography is the most often used analytic method. Over 80 percent of the methods used in analysis of chemical compounds are chromatographic methods, which in turn, in 90 per cent cases are performed on adsorbents with stationary phases bonded with the packing surface [1, 2]. The reason for using adsorbents with bonded phases is the need to adjust molecular interactions between phases of chromatographic systems and components of mixtures separated [3–11]. In liquid chromatography it is commonly assumed that chemical composition of stationary phase does not change, irrespective of the change of chemical composition of the mobile phase [12, 13]. According to this assumption upon chromatographic separation of mixtures have an effect on main physicochemical properties of invariable stationary phase and the kind and chemical composition of the mobile phase. Chromatographic systems with a liquid mobile phase and fixed stationary phase should be treated as dynamic, equilibrium adsorption systems. Thus, the composition of the stationary phase that occurs during the flow of mobile phase of a given concentration is determined by the real adsorption (n^{s}_{1} *vs.* x^{1}_{Me}) which are counted on the basis of excess adsorption (n^{σ}_{i} *vs.* x^{1}_{Me}) [14–20].

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The chemical composition of modified with octadecylchlorosilane silica gel surface, arising in the process of methanol adsorption during the flow through chromatographic column of methanol–water mobile phase with increasing concentration of methanol in this phase was described in paper [21]. It was observed that in RP HPLC systems the value of retention factor k' of polycyclic aromatic hydrocarbons decreases with the increase of methanol concentration in both phases, mobile as well as stationary one. The phenomenon was explained by the increase of hydrophobization of silanized silica support surface with the increase of methanol adsorption.

The aim of this paper is to show that the changing methanol concentration in liquid mixtures which were used as mobile phase causes the increasing methanol adsorption on the surface of column packing with chemically bonded dimethyloctadecylchlorosilane (DMODS) phase. Moreover, we want to present the influence of change in chemical composition of both phases upon retention factor (k') of alkyl derivatives of benzene in chromatographic system of reversed phases HPLC. Benzene; toluene; ethyl, propyl and butyl benzenes were used as a model adsorbates.

Experimental

Materials

Benzene, toluene, ethyl-, *n*-propyl- and *n*-butyl- benzenes, methanol, dimethyloctadecylchlorosilane for analysis grade of POCH of Poland and silica gel Si-100 Merck were used.

Preparation of the Si-100 DMODS and chromatographic measurements

Silica gel Si-100 of specific surface area S=235 m^2 g^{-1} and grain fraction 10 μm was silanized with dimethyloctadecylchlorosilane, in boiling toluene with morpholine used as catalyst. Adsorbent (Si-100 DMODS), containing 4 μmol m^{-2} of chemically bonded dimethyloctadecylsilyl groups on the silica gel surface was obtained.

The process of silanization and chromatographic method of measuring of methanol adsorption isotherm on column packing, as well as retention of analytes used were described in [21, 22]. The methanol in water mixtures with the concentration (x^1_{Me}): 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, and 0.9 of mole fraction of methanol were used as mobile phase. Using the same concentrations of solutions, the excess isotherm of methanol adsorption (n^{σ}_{Me} *vs.* x^1_{Me}) from water solutions on silanized silica gel Si-100 DMODS was determined. This isotherm was the basis to count the real methanol adsorption isotherm ($n^{\mathrm{s}}_{\mathrm{Me}}$ *vs.* x^1_{Me}) on obtained packing Si-100 DMODS by means of Everett method [14, 16].

Results and discussion

Both methanol adsorption isotherms (excess n^{σ}_{Me} and real $n^{\mathrm{s}}_{\mathrm{Me}}$) as functions of methanol concentration in the mobile phase (x^1_{Me}) are presented in Fig. l. The excess adsorption isotherm of methanol (n^{σ}_{Me} *vs.* x^{1}_{Me}) was measured by chromatography. The same figure contains also the mole fraction of methanol (x^{s}_{Me}) in the adsorption layer as a function of its concentration in the volume phase (x^{1}_{Me}). As seen in Fig. 1 the concentration of methanol (x^{s}_{Me}) in the surface layer is much greater than in equilibrium volume phase (x^{1}_{Me}), $x^{s}_{Me} >> x^{1}_{Me}$. We deal with the similar phenomenon in the chromatographic system RP HPLC with the methanol–water mobile phase. During the flow of methanol–water mobile phase through the chromatographic column in RP HPLC preferential adsorption of methanol on silanized column packing takes place. The amount of adsorbed methanol on this surface is the function of methanol concentration in the mobile phase. Due to the above phenomenon the surface of the silanized column packing undergoes further hydrophobization compared to its hydrophobization obtained during silanization process. As a result, there a stationary phase appears composed of 4.0 μmol m^{-2} DMODS+n^{s} (x^{1}_{Me}) μmol m^{-2} of methanol+α_{OH} μmol m^{-2} OH groups on the surface.

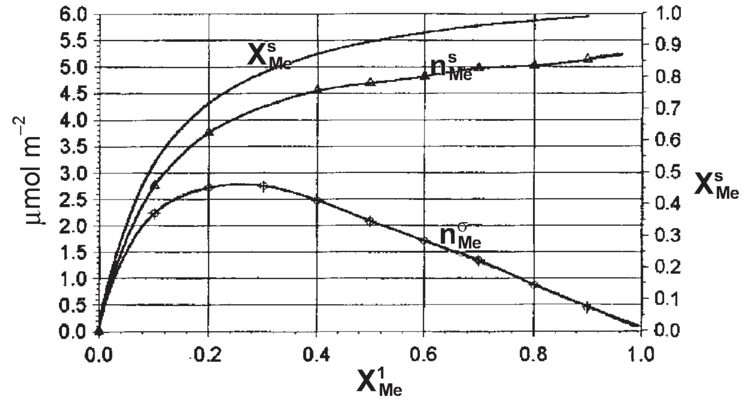

Fig. 1 Isotherms: of real adsorption of methanol n^{s}_{Me} *vs.* x^{1}_{Me}; excess adsorption n^{σ}_{Me} *vs.* x^{1}_{Me} and its mole fraction in the surface phases x^{s}_{Me} *vs.* x^{1}_{Me} on Si-100 DMODS silica gel

The distribution of alkyl benzenes takes place between the above-mentioned stationary phase and equilibrium mobile phase (x^{1}_{Me}). As the concentration of the bonded DMODS phase is fixed throughout the whole range of concentrations of mobile phase, its influence upon retention should also be fixed irrespectively of the mobile phase concentration. Thus, the changes of retention of alkyl benzenes should depend mainly on the change of methanol concentration in the mobile phase and on the amount of adsorbed methanol and water in the stationary phase. Because of numerous difficulties in determining the amount of water in the stationary phase (due to association) at a given concentration in the mobile phase, the retention of alkyl benzenes will be discussed as a function of methanol concentration in both phases.

The influence of methanol concentration in the mobile phase upon the retention of alkyl benzenes is presented in Fig. 2. As will readily be observed, linear dependencies logk' *vs.* x^{1}_{Me} of alkyl benzenes examined decrease much faster in the range $x^{1}_{\mathrm{Me}}\approx 0.0\sim 0.4$ than in the range $x^{1}_{\mathrm{Me}}\approx 0.4\sim 1$ of mole fraction of methanol in the mobile phase. Figure 1 shows that in this range a rapid growth of real methanol adsorption takes place (x^{s}_{Me}). Due to this, quicker hydrophobization of packing surface in the range $x^{1}_{\mathrm{Me}}\approx 0.0\sim 0.4$ than in the range $x^{1}_{\mathrm{Me}}\approx 0.4\sim 1$ follows. A rapid loss of surface OH groups of packing with alkyl benzenes interact much stronger than with the hydrocarbon chains bonded with the surface of the silica support [23–26] is the reason for quicker decreasing of retention (Fig. 2). Moreover, the growth of hydrophobization of packing surface causes a decrease in the amount of water in the stationary phase. Dependencies logk' *vs.* x^{1}_{Me} however, decreasing more slowly in range of methanol mole fraction in water $x^{1}_{\mathrm{Me}}=0.4$–1 result from the slower growth of methanol concentration in the stationary phase (Fig. 1).

The above conclusion is proved also by linearly decreasing dependencies of $\log k'/(n^{s}_{\mathrm{Me}})x^{1}_{\mathrm{Me}}$ *vs.* n^{s}_{Me} within the whole range of methanol concentrations in the mobile phase. Figure 3 shows the change in quotient $\log k'/(n^{s}_{\mathrm{Me}})x^{1}_{\mathrm{Me}}$ *vs.* (n^{s}_{Me}) which characterizes the values of logk' referring to the unit of adsorbing methanol at its given concentration in the mobile phase compared with the real amount of methanol adsorbed (n^{s}_{Me}). As it is seen, these functions do not undergo the break characteristic of the function logk' *vs.* x^{1}_{Me} (Fig. 2). Dependencies in Fig. 3 are convergent in the point corresponding to the maximum amount of methanol adsorbed on the surface of obtained adsorbents.

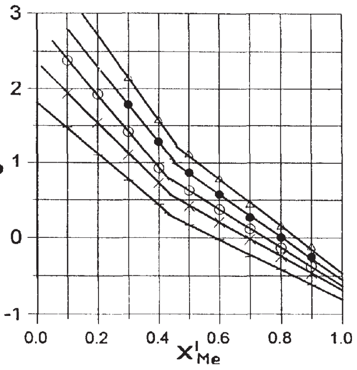

Fig. 2 Plots of capacity factor log k' *vs.* concentration of methanol in the liquid mobile phase x^{1}_{Me} for *n*-alkylbenzene derivatives (here and in Figs 3 and 4: + – benzene, x – toluene, – ethylbenzene, • – *n*-propylbenzene, Δ – *n*-butylbenzene) on Si-100 DMODS silica gel

The convergence of these dependencies can be explained by decreasing selectivity of the surface of chemically modified packings with the increase of their hydrophobization. Moreover, it is perceived that in the range of smaller concentrations of adsorbed methanol ($n^{s}_{\mathrm{Me}}=2.7\sim 4$ μmol m^{-2}) the differences of quotient $\log k'/n^{s}_{\mathrm{Me}}$ for particular alkyl benzenes are greater. Thus, the conclusion may be drawn that this range of concentration of the bonded phase on the support surface is the most useful

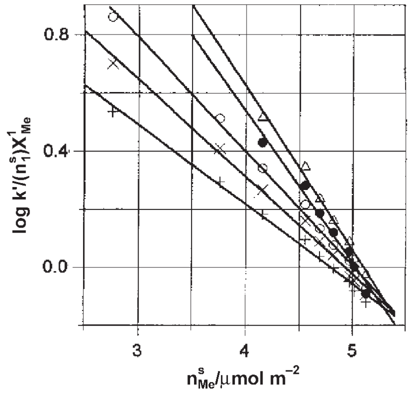

Fig. 3 Plots of quotients log$k'/(n^s_{Me})x^1_{Me}$ *vs.* n^s_{Me} ((n^s_{Me})x^1_{Me} is adsorption date as a function x^1_{Me}) for alkylbenzene derivatives on Si 100 DMODS silica gel

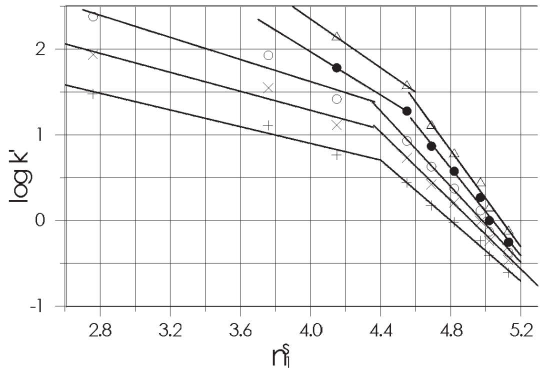

Fig. 4 Plots of logk' *vs.* n^s_{Me} (n^s_{Me} is the number of μmole of methanol in the stationary phase) of *n*-alkylbenzene derivatives on Si 100 DMODS column packings

for the chromatographic analysis. Retention of alkyl benzenes depending on the amount of methanol adsorbed (n^s_{Me} μmol m^{-2}) on the surface of column packing Si-100 DMODS (in the stationary phase) is illustrated in Fig. 4. Functions logk' *vs.* n^s_{Me} undergo a break similarly to the dependencies logk' *vs.* x^1_{Me} (Fig. 2). The difference is that those dependencies decrease more slowly within the range of smaller amount of methanol adsorbed (n^s_{Me}≅2.8÷4.5 μmol m^{-2}) than within the range (n^s_{Me}≅4.5 ÷5.13 μmol m^{-2}). Assuming that on fully hydroxylated silica gel surface there are 8.5 μmol m^{-2} OH groups [27, 28], out of which 4.0 μmol m^{-2} reacted with modifier (DMODS) in the process of silanization. About 4.5 μmol m^{-2} of methanol may be adsorbed on the remaining groups. In the point, in which, according to the counting, all OH groups are eliminated, dependencies logk' *vs.* n^s_{Me} break. It may be suggested that faster decrease in retention of alkyl benzenes within the concentration range n^s_{Me}≅4.4÷5.13 μmol m^{-2} of the bonded phase is connected with their distribution on the created hydrocarbon surface covering of the column packing (Fig. 4). Functions of retention of mole fraction of methanol in the stationary phase log*k*′ (x^s_{Me}) go similarly with the course of the dependencies log*k*′ *vs.* n^s_{Me}. That is why their figure is not included in the paper.

Figure 5 shows the change log*k*′ depending on the number of carbon atoms in the molecules of analyzed alkyl benzenes (n_c) on the adsorbents with given concentrations of the bonded phase. This can be graphically seen that on particular adsorbents containing different concentration of the bonded phase dependencies (log*k*′ *vs.* n_c) n^s_{Me} increase linearly with the increase of n_c. Distances between curves decrease with the increase of concentration of the methanol adsorbed (n^s_{Me}). Such a phenomenon proves the earlier conclusion that increasing concentration of the bonded hydrocarbon phase on the surface of the silica support decreases selectivity of adsorbents. Moreover, it is

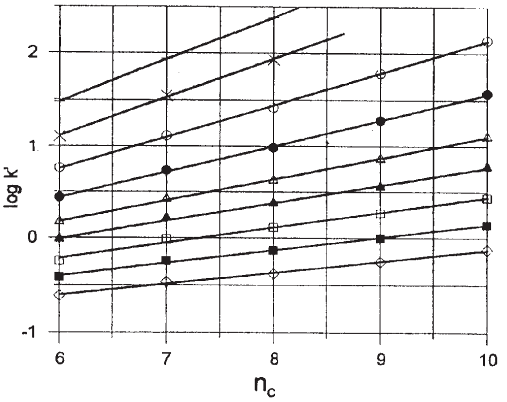

Fig. 5 Plots of log*k*′ *vs.* number carbon atoms in molecules (n_c) at constant amount of methanol adsorbed in the stationary phase (n^s_{Me}), here and in Fig. 6: 2.76 (+), 3.76 (×), 4.14 (o), 4.55 (•), 4.69 (Δ), 4.82 (▲), 4.97(□), 5.02 (■), and – 5.13 (◊) μmol m^{-2}

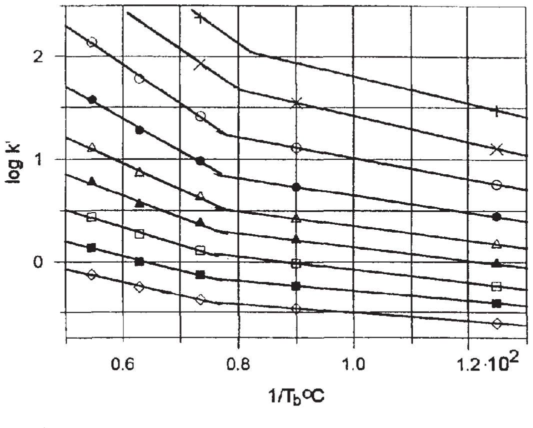

Fig. 6 Plots of log*k*′ *vs.* 1/T_b (T_b is boiling temperature of alkylbenzene derivatives, °C) at constant surface concentrations of methanol in the stationary phase (n^s_{Me})

seen in Fig. 5 that on adsorbents with fixed methanol concentration in the stationary phase, distances logk' *vs.* n_c of the subsequent alkyl benzenes are equal which enables determining the following unknown alkyl benzene homologues.

Dependencies logk' *vs.* n_c run in a similar way to the dependencies logk' *vs.* T_b where T_b is the boiling temperature of the alkyl benzenes used. It is comprehensible because the boiling temperature is connected with the number of carbon atoms in molecules of homologous series. Due to that, the figure presenting those dependencies is not included in the paper.

Linear functions logk' $(1/T_b)$ of alkyl benzenes examined, however, undergo a break in the point corresponding with the boiling temperature of ethyl benzene (Fig. 6). Possibly, it is connected with the difference in boiling temperatures of alkyl benzenes $(T_b(n_c+1)–T_b(n_c))$, out of which the boiling temperature of ethyl benzene is the smallest. Starting from ethyl benzene this difference increases both for lower as well as for higher alkyl benzenes.

* * *

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