# Studies of the interfacial properties of chemically bonded phases by sorption and liquid chromatography

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## Abstract

The interfacial composition of chemically bonded phases, which controls the solute's retention under reversed-phase conditions, was evaluated by using sorption and retention data. Previous studies showed that the composition of the solvents in the stationary phase significantly influences the solute's retention even in the case of conventional bonded phases, and this effect is much stronger for silica-based packings with chemically bonded phases of specific properties. The composition can be evaluated from the sorption excess data, which for chemically bonded phases are difficult to measure and analyze. An alternative way to estimate the composition of solvents in the stationary phase is based on liquid chromatographic measurements. It was shown that both methods provide similar information on the competitive sorption of solvents into the chemically bonded phase.

## 1. Introduction

Study of the interfacial properties of chemically bonded phases is extremely important in understanding chromatographic separations under reversed-phase conditions. Reversed-phase liquid chromatography (RPLC) comprises systems with a non-polar stationary phase and a polar mobile phase (e.g., water–methanol, water–acetonitrile and water–tetrahydrofuran). Although different non-polar materials have been used in RPLC as column packing (e.g., solid supports coated with non-polar compounds, carbon-based packings, etc.), several packings with chemically bonded phases (e.g., silica-based alkyl bonded phases) became the most popular packings in RPLC applications [1]. Chemical modification of silicas via attachment of various functionalities onto its surface is a powerful method for preparing novel packing materials with specific interfacial properties. Thus, RPLC is currently one of the most frequently used techniques in analytical laboratories.

In general, the retention of a solute can be represented by a two-step process: (i) formation of a mixed stationary phase, and (ii) distribution of the solute between the stationary and mobile phases [2,3]. The composition of the solvents in the stationary phase is established via a competitive sorption process and differs from that in the mobile phase. While solute distribution is taken into account in all retention models, intercalation of solvents into the stationary phase is often ignored. In several retention models for RPLC, such as those based on interaction indices, the mobile phase was considered to be a key element that controls the elution while the bonded phase was merely regarded as a passive acceptor of the solute [4]. Recent studies showed that the stationary phase plays an essential role in RPLC separations [5,6]. It has been shown that the solvent composition of the stationary phase sig-

nificantly influences the solute's retention even in the case of conventional bonded phases, and this effect is much stronger in the case of silicas with chemically bonded phases of specific properties, i.e., phases which contain ligands of different functionality.

In a typical RPLC system the stationary phase consists of the chemically bonded ligands (which essentially cannot be removed from the silica surface) and the solvent molecules (e.g., methanol, acetonitrile, water) intercalated into this phase. In analytical RPLC the injected amount of solute is infinitely low and does not perturb the composition of the solvents in the stationary phase. The composition of the solvents in the stationary phase is established according to the thermodynamic equilibrium and usually differs from that in the mobile phase [7–11]. It depends on the mobile phase composition, the chemical nature of the bonded ligands, their surface concentration and conformation. In addition, the thickness of the stationary phase may change with the mobile phase composition because the conformation of the bonded ligands in an aqueous environment is usually different from that in an organic environment [12]. Another important factor that controls the composition and structure of the silica-based chemically bonded phases is the silica, i.e., its porosity, surface properties and the amount of unreacted silanol groups. The "silanophilic" interactions, initially ignored in interpreting the solute's retention under reversed-phase conditions, have been found to play an important role in the RPLC process [13]. It is obvious that the amount of unreacted surface silanol groups controls the concentration of water molecules in the chemically bonded phase and consequently influences significantly the composition of solvent molecules in this phase. Knowledge of this composition is essential for understanding RPLC separations.

The stationary phase composition can be investigated by various methods. In the present work special emphasis was given to sorption and chromatographic measurements, which were utilized to evaluate the amount of solvents intercalated into the chemically bonded phase. A comparative study of the competitive sorption of

solvents for conventional RPLC systems showed that both types of measurements provide similar information on the interfacial properties of chemically bonded phases.

## 2. Experimental

To illustrate the methodology proposed for the characterization of the interfacial composition of solvents in a given chemically bonded phase, the sorption and chromatographic data reported in the literature [14,15] for acetonitrile (MeCN)–water mixtures on octadecyl bonded phases were used. The sorption excess isotherm [5] of acetonitrile from aqueous solutions on alkyl bonded phases was studied extensively by several researchers [14,16–18]. In the present work we utilized the sorption excess data for acetonitrile on the Merck RP-18 (carbon load: 19.8%) octadecyl phase measured by Slaats et al. [14] at 295 K using the minor disturbance method [14]. Shown in Fig. 1 is the sorption excess of acetonitrile, $n_0^{e(n)}$, plotted as a function of the mole fraction of acetonitrile. In Ref. [5] these sorption data were compared with the excess data measured at 303 K by Tani and Suzuki [16]. Both excess isotherms were measured on endcapped polymeric octadecyl phases of very similar carbon loads (i.e., 19.8% and 18.5% C), which were prepared on silica samples with similar specific surface areas (about 300 $m^2/g$) and with similar
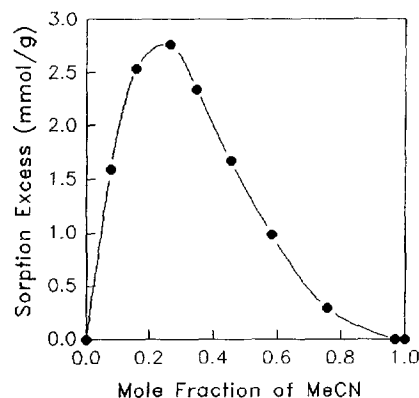


Fig. 1. Sorption excess of acetonitrile on the Merck RP-18 bonded phase at 295 K (data taken from Ref. [14]).

mean pore diameters (about 10 nm). Although the source of both silicas was different and the excess isotherms were measured in different laboratories at slightly different temperatures, the coincidence between these isotherms was surprisingly excellent [5]. Good reproducibility of the sorption excess data on the alkyl-rich bonded phases facilitates their use to characterize the interfacial properties of the RPLC systems.

In addition to the sorption measurements, the methylene selectivity data reported by Colin et al. [15] were used to evaluate the sorption excess of acetonitrile on the Merck RP-18 phase. The methylene selectivity is the ratio of the capacity factors for two adjacent homologs and its logarithm is proportional to the Gibbs free energy of transfer of the methylene group from the mobile phase to the stationary phase. Since the methylene selectivity data reported in Ref. [15] were measured at 298 K (only a three-degree difference with the sorption measurements shown in Fig. 1) on the Merck RP-18 phase over the entire range of acetonitrile concentrations, they are suitable to estimate the sorption excess data for this solvent on the octadecyl phase and compare them with the measurements performed by Slaats et al. [14].

## 3. Results and discussion

The composition of solvents in a given stationary phase can be evaluated on the basis of the sorption excess measured for a given liquid mixture (which is used as a mixed eluent in RPLC separations) on the chromatographic packing studied. There exist extensive literature dealing with the physicochemical interpretation and measurement of the sorption excesses at the liquid–solid interface (e.g., Refs. [19,20] and references therein). A special elaboration was prepared by the Commission on Colloid and Surface Chemistry of the IUPAC on reporting the excess data for adsorption from solutions at liquid–solid interfaces [21]. Although a rigorous thermodynamic description of liquid–solid adsorption was presented by Everett in 1964 [22], its first application to formulate the theory of LC

with mixed mobile phases appeared in the literature only fourteen years later [23]. The sorption excesses of solvents on chemically bonded phases can provide valuable information about the structure and composition of the stationary phase, which is essential for a proper description of the solute's retention in RPLC. The available sorption data for the most popular eluents in RPLC, i.e., for methanol–water and acetonitrile–water on alkyl bonded phases, showed that the preferential sorption of acetonitrile is much stronger than that for methanol [14]. Thus, in the case of acetonitrile its concentration in the stationary bonded phase is much greater than that in the mobile phase. Therefore, in the current work acetonitrile–water chromatographic systems were studied.

The excess sorption data shown in Fig. 1 were used to estimate the composition of solvents in the octadecyl phase studied, which may be defined by the volume fraction of acetonitrile in this phase. The following expressions were used to calculate this volume fraction:

$$\phi_o^s = \frac{x_o^s}{x_o^s + r(1 - x_o^s)} \tag{1}$$

where

$$x_o^s = n_o^{e(n)}/n^s + x_o^l \tag{2}$$

where $\phi_o^s$ and $x_o^s$ are respectively the volume and mole fractions of acetonitrile in the surface (stationary) phase, $r$ is the ratio of the molar volumes of water and acetonitrile, $n_o^{e(n)}$ is the sorption excess of acetonitrile at its equilibrium mole fraction in the bulk (mobile) phase, $x_o^l$, and $n^s$ is the surface phase capacity. In order to convert the sorption excess to the absolute sorption one needs to know the surface phase capacity $n^s$. Shown in Fig. 2 are the phase composition plots obtained for different values of $n^s$. For instance, the plot obtained for $n^s = 5.64$ mmol/g (the value taken from Ref. [14]) does not satisfy the thermodynamic condition (has a minimum) [19]. From the thermodynamic viewpoint the values of $n^s$ between 10 and 14 mmol/g are acceptable and their average was used in further calculations. The surface phase composition ex-
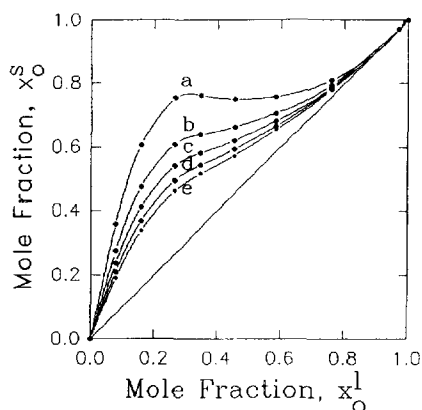
Fig. 2. Phase-composition diagrams for acetonitrile–water mixture on the Merck RP-18 packing calculated from the sorption excess (cf., Fig. 1) according to Eq. 2 by assuming $n^s = 5.64$ (a), 8 (b), 10 (c), 12 (d) and 14 mmol/g (e).

estimate the composition of solvents in the stationary phase. However, the sorption excesses evaluated on the basis of the retention data were not compared with the experimental sorption excesses.

According to the partition–displacement model of the solute's retention the logarithm of the methylene selectivity, $s = \ln k'_{n+1}/k'_n$, can be expressed as follows [24]:

$$s = \phi^l_o s_o + \phi^l_w s_w - s^*(\phi^s_o - \phi^l_o) \qquad (3)$$

where $s_o$ and $s_w$ denote respectively the $s$-values in pure organic and water phases, $\phi^l_o$ and $\phi^l_w$ are respectively the volume fractions of acetonitrile and water in the mobile phase, and $s^*$ is the logarithm of the hypothetical partition coefficient of a given solute between the organic and water phases [24]. Note that the third term in Eq. 3 is proportional to the sorption excess. If this excess equals zero (identical composition of solvents in both phases), then the quantity $s$ is an additive value and depends linearly on the mobile phase composition. For instance, when binary mixtures of methanol–water were used on several alkyl bonded phases the quantity $s$ changed in a nearly linear fashion with the mobile-phase composition over a wide range [15]. This result indicates that for these chromatographic systems the composition of solvents in both phases was similar. However, this linear dependence generally does not hold for other mobile phases [15,25–28], e.g., acetonitrile–water (see open circles in Fig. 4, which show the methylene selectivity data from Ref. [15]). However, presenting these data against the volume fraction of acetonitrile in the surface phase gives an almost linear plot (filled circles in Fig. 4). The excess selectivity data, i.e.,

$$s^e = s - \phi^l_o s_o - \phi^l_w s_w = s^*(\phi^s_o - \phi^l_o) \qquad (4)$$

pressed in terms of the mole fractions (see Fig. 2) can be converted by means of Eq. 1 to the volume fractions (see Fig. 3). Subsequently, these volume fractions (calculated from the excess sorption data shown in Fig. 1), were used to analyze the methylene selectivity data reported in Ref. [15]. It was suggested previously [7–11] that in addition to sorption measurements the methylene selectivity data measured at different compositions of the mobile phase can be used to

obtained from the open-circle plot shown in Fig. 4 were used to calculate the sorption excess according to Eq. 4. A comparison of the sorption excess calculated from the selectivity data with that measured experimentally is shown in Fig. 5. Since sorption and chromatographic measurements were carried out at slightly different con-
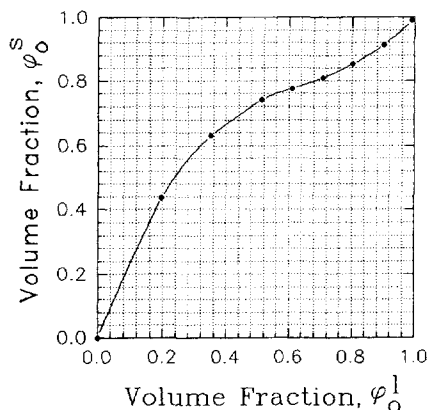


Fig. 3. Phase-composition diagram for acetonitrile–water mixture on the Merck RP-18 phase presented in terms of the volume fractions for $n^s = 12$ mmol/g.
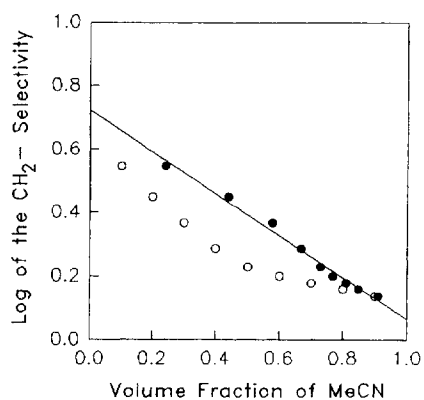
Fig. 4. Dependence of the logarithm of the methylene selectivity data on the volume fraction of acetonitrile in the mobile phase (○) and the surface phase (●) for the acetonitrile–water mixture on the Merck RP-18 packing at 298 K (calculated on the basis of the LC data reported in Ref. [15]).

ditions, the agreement between these excesses is satisfactory.

## 4. Conclusions

It was shown that the composition of solvents in the chemically bonded phase can be evaluated on the basis of the excess sorption data, as well as on the basis of chromatographic measure-

ments. A short discussion of this problem demonstrated that the methylene selectivity data are useful for estimating the composition of solvents in the chemically bonded phases. Both the sorption and chromatographic measurements provided similar information about sorption excesses of solvents in the stationary phase. Further systematic studies are desirable in order to relate these excesses to the solute's retention under RPLC conditions.

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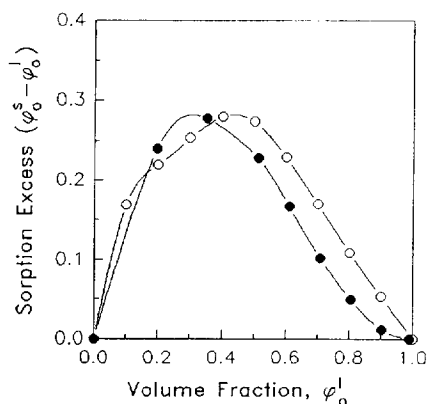[21] D.H. Everett, Pure Appl. Chem., 58 (1986) 967.

Fig. 5. Comparison of the sorption excesses of acetonitrile from aqueous solutions on the Merck RP-18 phase evaluated on the basis of sorption (●) and chromatographic measurements (○).

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