

Liquid Chromatography Problem Solving and Troubleshooting

Question

What is meant by the term sorption excess and how does it influence reversed-phase selectivity?

Answer

In answering this question, it is helpful to point out what is meant by the terms mobile phase and stationary phase, which respectively are: (a) the moving stream of solvent that transports solutes through the column and (b) the fixed surface layer in which solutes are selectively retained. Operationally, in the case of reversed-phase separations, the mobile phase is usually a binary mixture of water and an organic cosolvent such as methanol or acetonitrile, and the stationary phase is a porous silica that has been chemically modified with organic groups (i.e., often either linear C_{18} or C_8 chains). In addition to the attached groups, the surface also contains residual silanol groups that result from an incomplete derivatization of the surface. The extent of modification and the distribution of the attached organic groups are dependent on both the silica substrate and the manufacturing process used. When bonded-phase materials are placed in contact with the mobile phase, they are solvated to varying degrees.

Thus, under reverse-phase conditions, sorption excess refers to the preferential enrichment of one of the components of the mobile phase at the surface (i.e., the intercalated solvent layer). In the case of mobile phases prepared from binary mixtures of methanol and water, the sorption excess is relatively small (i.e., the composition of the intercalated solvents and that of the bulk mobile phase is nearly identical) over the total binary range. However, for other binary mixtures (such as acetonitrile and water), the intercalated solvent composition and the mobile-phase composition may be quite different. Both of these examples of sorption excess for a C_{18} column are illustrated in Figure 1 using mixtures of acetonitrile–water (curve A) and methanol–water (curve B) as the mobile phase (1).

When a mobile phase is prepared using either acetonitrile and water or THF and water there is a significant enrichment of the organic cosolvent (positive sorption excess) compared with water in the intercalated solvent layer. The effect of differences in the sorption excess is an influence on the chromatographic behavior of the bonded phase. Hence, selectivity differences may be observed when different binary solvents are used to carry out a separation even though the overall mobile phase can be adjusted to provide a similar eluent strength. Another important feature of the sorption excesses (comparing curve A with curve B in Figure 1) is that they are not linear over the total composition range, which results in larger or smaller differences in the chromatographic selectivity when using different solvents to prepare the mobile phase.

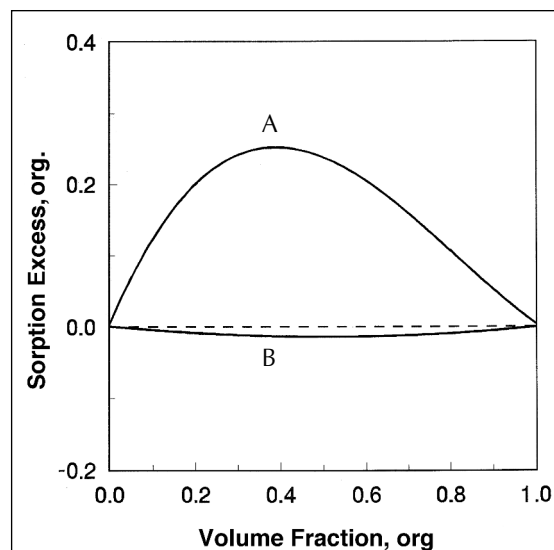


Figure 1. Sorption excess of the organic component of binary mixtures (A) acetonitrile–water and (B) methanol–water for a C_{18} bonded phase.

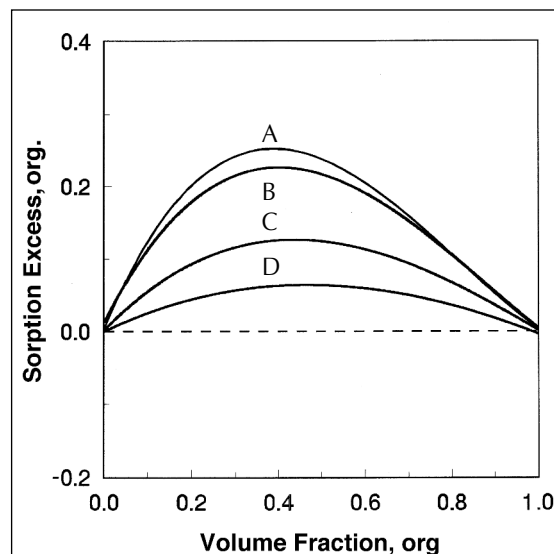


Figure 2. Sorption excess of acetonitrile on a (A) C_{18} , (B) C_8 , (C) phenyl, and (D) cyano bonded phase using acetonitrile–water as the mobile phase.

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Roger K. Gilpin
Associate Editor

In addition to differences arising from the solvent blends used to prepare the mobile phase, the sorption excess is dependent on the particular bonded phase. This is illustrated in Figure 2 for four different column types: octadecyl (curve A), octyl (curve B), phenyl (curve C), and cyano (curve D) (2). To complicate the problem further, the intercalated solvents are also influenced by the concentration and microscopic distribution of the attached groups as well as the residual silanol concentration. The net effect of these differences that arise during the column manufacturing process is a change in the chromatographic selectivity.

A positive advantage of differences in the sorption excess between systems is that although it is not always possible to produce the same separation using different mobile-phase blends of equivalent eluent strength, these same effects can provide subtle enough changes in the solute retention to obtain better resolution between analytes that are difficult to separate.

References

1. M. Jaroniec, S. Lin, and R.K. Gilpin. Use of a displacement model for solvent sorption to study non-specific selectivity in reversed-phase liquid chromatography. *Chromatographia* **32(1/2)**: 13–18 (1991).
2. M. Jaroniec and R.K. Gilpin. Partition-sorption model for describing non-specific selectivity in reversed-phase liquid chromatography. *J. Liq. Chromatogr.* **15(9)**: 1431–42 (1992).