

Characterization of RP Sorbents by Linear Solvation Energy Relationships (LSER)

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Introduction

LSER can be used to characterize stationary phases in chromatography. The logarithm of the retention factor k' of a compound can be described by the addition of a constant c and five different types of interaction forces (eq. 1) [1,2].

$$(1) \log k' = c + eE + sS + aA + bB + vV$$

In this equation, the capital letters describe the properties of the respective analyte. E being the excess molar refraction, S the absolute dipolarity / polarizability, A and B the solute effective hydrogen bond acidity and basicity, and V the McGowan characteristic volume. Values for many compounds are available in the literature [3]. The lowercase letters describe the corresponding values of the chromatographic system. If the chromatographic conditions are kept constant, these values depend only on the properties of the stationary phase. Table 1 explains the meaning of the different coefficients. In this method interactions between analyte / stationary phase and analyte / mobile phase are always compared. Positive valued coefficients are obtained when the interaction with the stationary phase is stronger, at negative values the interaction between analyte and mobile phase is stronger.

Table 1: Description of the different LSER coefficients

LSER coefficients	Interaction
c	Intercept
e	Interactions of the phase with n and π electrons of the analyte
s	Dipolarity / polarizability of the phase
a	Hydrogen bonding acceptor properties of the phase
b	Hydrogen bonding donor properties of the phase
v	Strength of hydrophobic interactions

Experimental

The investigated stationary phases were made from silica gels NUCLEODUR® (totally porous) and NUCLEOSHELL® (core shell silica). The stainless steel columns (100 mm x 3 mm ID) are commercially available (MACHEREY-NAGEL). For the chromatographic investigations, a Nexera HPLC system (Shimadzu) was used. All solvents were of HPLC grade. The analytes were chemically pure or of higher quality and were used in methanolic solution (1 mg/mL). Chromatographic conditions: acetonitrile / water 50:50 (v/v), 0.6 mL/min, 40 °C, DAD 220–300 nm. To determine the LSER coefficients of the stationary phase, Excel was used with the extension Real Statistics [4].

Figure 2: Determined values for coefficients c and e

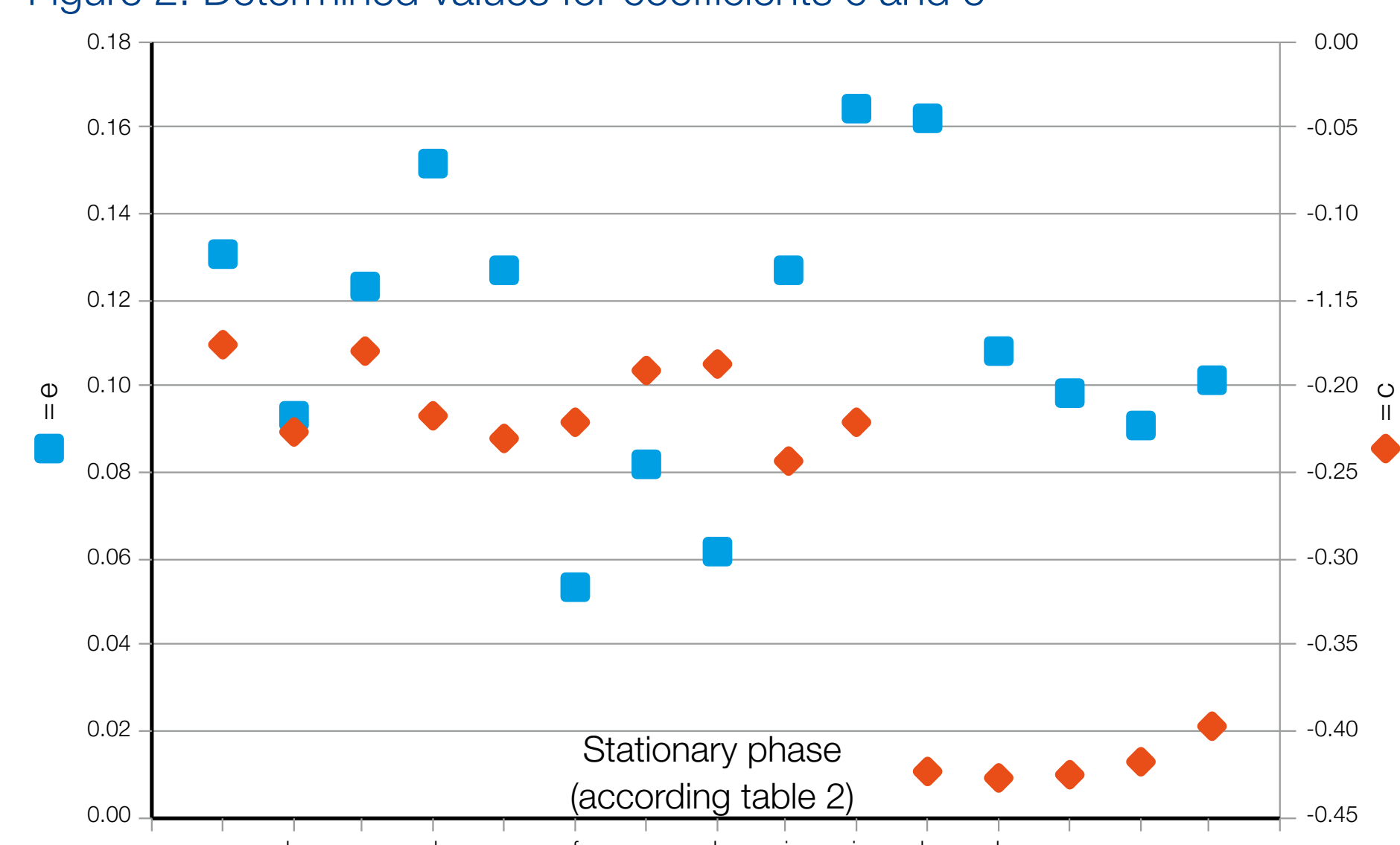


Figure 3: Determined values for coefficients a and b

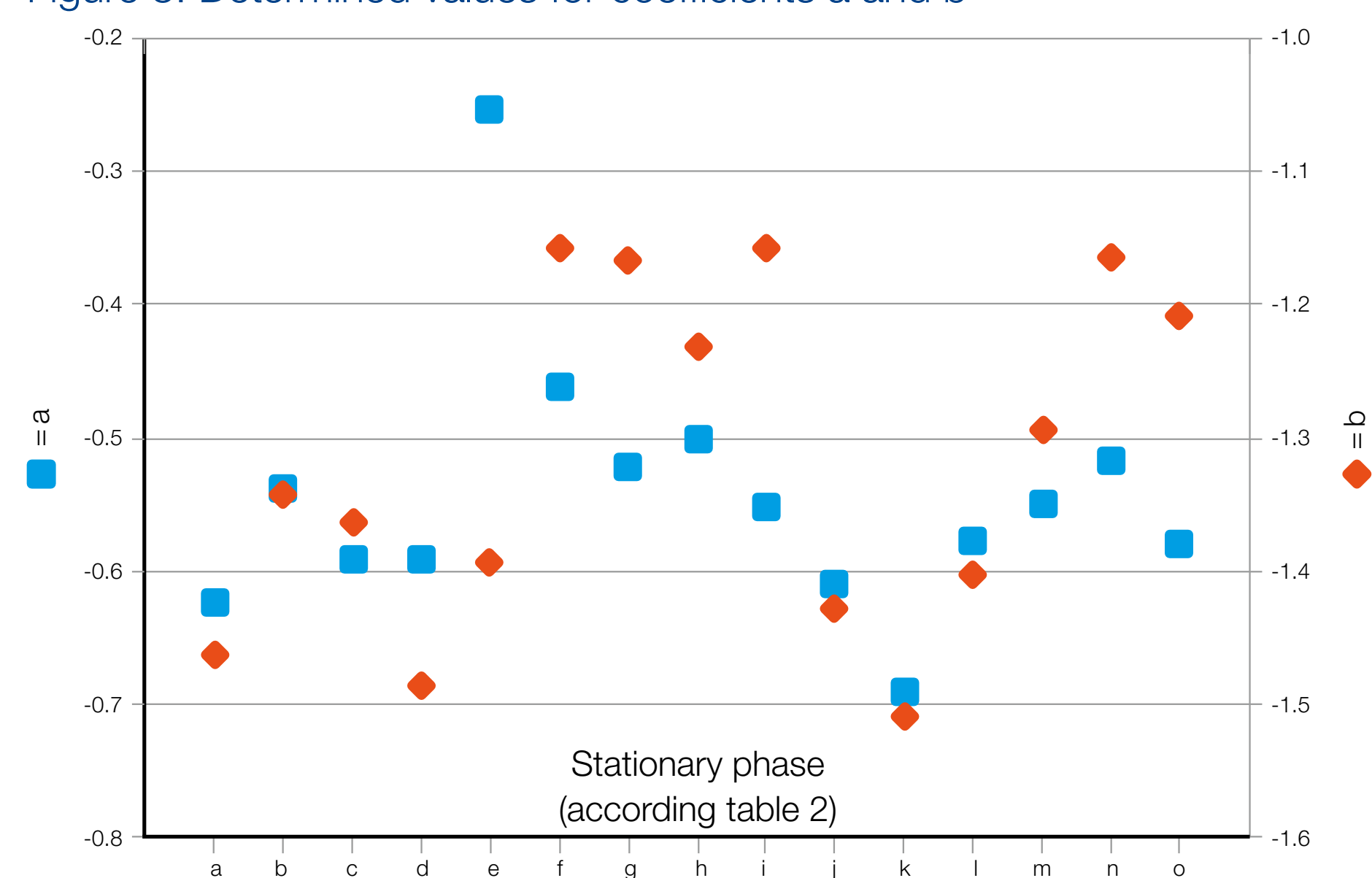


Figure 4: Determined values for coefficients s and v

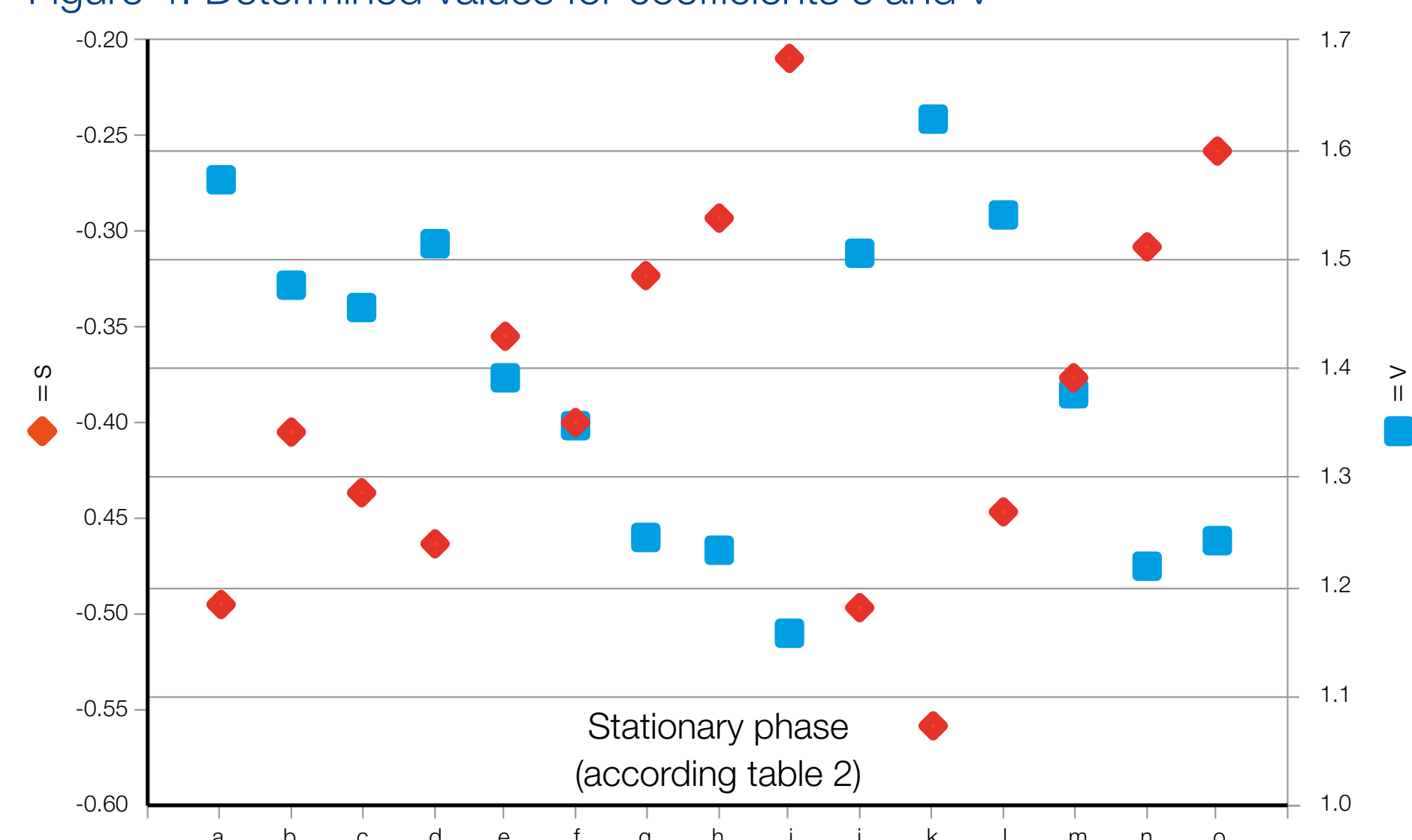


Table 2: Description of the phases studied

Stationary phase	Surface modification	Structures of surface modification	Stationary phase	Surface modification	Structures of surface modification
a NUCLEODUR® C ₁₈ Gravity	Brush type, dense C ₁₈ layer, cross-linked		i NUCLEODUR® π ²	Brush type, biphenyl modification	
b NUCLEODUR® C ₁₈ Gravity-SB	C ₁₈ modification with bulky substituents		j NUCLEODUR® PFP	Brush type, pentafluorophenyl phase	
c NUCLEODUR® C ₁₈ Pyramid	Brush type, dense C ₁₈ -layer, hydrophilic endcapping		k NUCLEOSHELL® RP 18	Brush type, dense C ₁₈ layer, crosslinked	
d NUCLEODUR® C ₁₈ Isis	Polymeric C ₁₈ layer		l NUCLEOSHELL® RP 18plus	C ₁₈ modification with bulky substituents at the silicon atom	
e NUCLEODUR® PolarTec	C ₁₈ modification with polar embedded groups		m NUCLEOSHELL® Bluebird	Brush type, dense C ₁₈ -layer, hydrophilic endcapping	
f NUCLEODUR® C ₈ Gravity	Brush type, dense C ₈ layer, cross-linked		n NUCLEOSHELL® Phenyl-Hexyl	Brush type, phenylhexyl modification	
g NUCLEODUR® Sphinx RP	Brush type, dense mixed phase with C ₁₈ und C ₆ H ₅ ligands		o NUCLEOSHELL® Biphenyl Biphenyl	Biphenylpropyl modification with bulky substituents	
h NUCLEODUR® Phenyl-Hexyl	Brush type, phenylhexyl modification				

Results

Figure 1: Plot of $\log(k'_{\text{measured}})$ and $\log(k'_{\text{calculated}})$

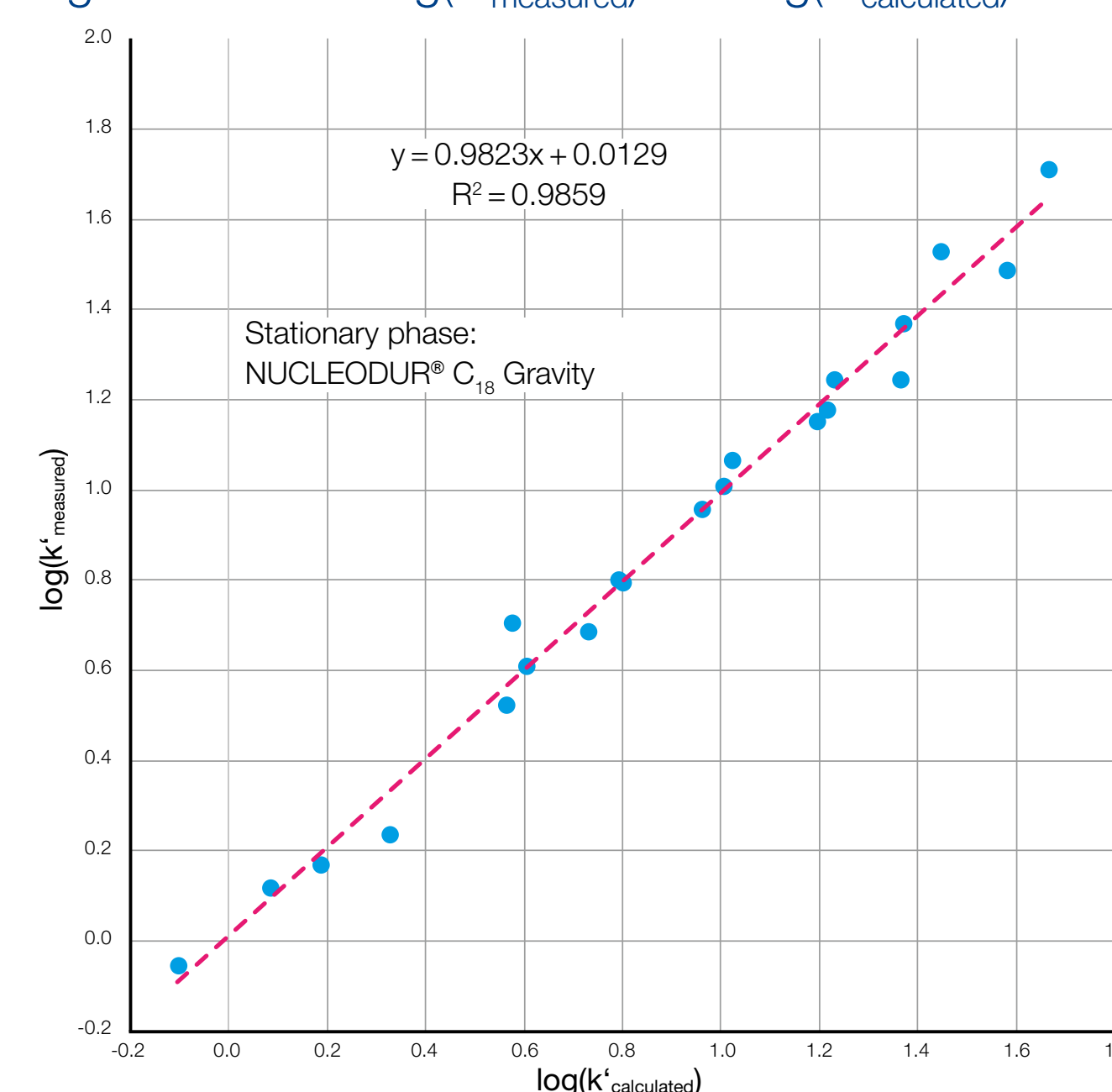


Figure 1 shows the plot of $\log(k'_{\text{measured}})$ versus $\log(k'_{\text{calculated}})$ for NUCLEODUR® C₁₈ Gravity. The determined LSER coefficients were used for the calculation. The diagram shows a good linear correlation between measured and calculated values. The intercept c is primarily influenced by the used silica (figure 2). Highly dense RP18 phases such as NUCLEODUR® C₁₈ Gravity, NUCLEODUR® C₁₈ Isis and NUCLEOSHELL® RP 18 have the largest e values and therefore interact most strongly under the investigated phases with n - and π -electrons of the analytes. Surprisingly, aromatic phases like NUCLEODUR® Phenyl-Hexyl have this property only to a minor extent.

Figure 3 compares the acceptor and donor properties of the sorbent for the formation of sorbent hydrogen bonds. While they play only a minor role in the investigated RP 18 phases, they are important interactions for the polar embedded phase NUCLEODUR® PolarTec and especially for the aromatic phases like NUCLEODUR® π². The values for s and v are in the opposite direction for the ones studied here. While C₁₈ sorbents have high hydrophobicity, they show only low values for s . In contrast, NUCLEODUR® C₈ Gravity has a lower hydrophobicity with barely increased value for s . With the exception of NUCLEODUR® PFP, the phases with aromatic ligands show significantly higher values for s .

Conclusion

The LSER method allows the estimation of chromatographic interactions between analyte and stationary phases under given conditions. Thereby, the selection of a stationary phase for the user can be facilitated.

Literature

- [1] L. Szepes, J. Sep. Sci. 26 (2003) 201 - 214
- [2] M. Reta, P. W. Carr, P. C. Sadek, S. C. Rutan, Anal. Chem. 71 (1999) 3484 - 3496
- [3] C. West, E. Lesellier, J. Chromatogr. A 505 (2008) 21 - 39
- [4] Charles Zaiontz, <http://www.real-statistics.com> (accessed 24.4.2019)

