

Supporting Information

Investigation of Adsorption Thermodynamics at Electrified Liquid-Solid Interfaces by Electrochemically Modulated Liquid Chromatography

Lisa M. Ponton,¹ David W. Keller,² Lorraine M. Siperko,³ Mark A. Hayes,⁴ and Marc D. Porter⁵

¹Chemistry Department, Baldwin Wallace University, Berea, OH 44017

²Charles River Laboratories, Mattawan, MI 49071

³Nano Institute of Utah, University of Utah, Salt Lake City, UT 84112

⁴School of Molecular Sciences, Arizona State University, Tempe, AZ 85287

⁵Department of Chemistry, Department of Chemical Engineering, and Nano Institute of Utah, University of Utah, Salt Lake City, UT 84112

*E-mail: marc.porter@utah.edu

Table of Contents

<i>SI-1. Determination of V_{sp} (stationary phase volume) and analysis of possible errors</i>	S1
<i>SI-2. Determination of V_{mp} (column void volume) and analysis of possible errors</i>	S3
<i>SI-3. Determination of the potential of zero charge (pzc) for the glassy carbon (GC) packing</i>	S4
<i>Table SI-1. Chromatographically Determined Values of the pzc for 1,5-NDS in a 95% water:5% acetonitrile (v/v) Mobile Phase Containing NaF, NaCl, LiClO₄, or NaPF₆, and ΔG_{ads} for NaCl, LiClO₄ or for NaPF₆ relative to NaF</i>	S5
<i>SI-4. References</i>	S5

SI-1. Determination of V_{sp} (stationary phase volume) and analysis of possible errors.

Exact definitions and measurements for determining the volume of the stationary phase (V_{sp}) and the void volume of the mobile phase (V_{mp}) can be problematic.¹⁻⁷ When using bonded-phase packings in reversed-phase LC (RPLC), one of the most challenging issues in assessing V_{sp} rests with the location of the “Gibb’s dividing surface.” The Gibb’s dividing surface is the

theoretical boundary between the mobile and stationary phases.³ In RPLC, the difficulty arises from concerns about how the composition of the mobile phase affects the alkyl chain structure of the coating on the bonded phase, which, in turn, can have an impact on how the solute interacts with the coated surface. Stated differently, it can prove difficult to identify accurately what portion of the bonded-phase coating is involved in the mechanism of retention.

Our experiments do not use a bonded-phase packing or a resin-based ion exchange material. Glassy carbon (GC) is an uncoated, nonporous solid. We have, therefore, made the reasonable assumption that the V_{sp} is defined by the position of the Gibb's dividing surface, which coincides with the outer boundary of the compact layer in the electrical double layer,⁸ and the surface area of the GC packing. We have also assumed that the location of the Gibb's dividing layer is invariant over the range of conditions (*i.e.*, temperature and E_{app}) used in our experiments.

The first of the three assumptions is supported by our recent work,⁹ which provided strong evidence that the compact layer, and not the diffuse layer, controls the interactions of aromatic sulfonates with the carbonaceous stationary phases used in EMLC. The latter two assumptions reflect the fact that the potential of zero charge (pzc) for the GC packing is controlled by the specific adsorption of PF_6^- for the values of E_{app} (from -200 to +200 mV vs. AgCl (sat'd NaCl)) used in our experiments. PF_6^- is the anionic component of the supporting electrolyte in the mobile phase and has a potential of zero (pzc) due to specific adsorption to carbon electrode surface of -400 mV (see *Section SI-3* for details on pzc determination).

As such, the value of V_{sp} can be found as the product of the total surface area of the stationary phase and the thickness of the compact layer. The actual surface area ($1.17 \pm 0.03 \times 10^4 \text{ cm}^2$) can be calculated from the mass of GC loaded in the column (*i.e.*, $0.49 \pm 0.01 \text{ g}$), and its surface area determined by measurements of Brunauer–Emmett–Teller (BET) isotherms ($2.39 \pm$

$0.10 \times 10^4 \text{ cm}^2/\text{g}$). The thickness of the compact layer,^{8, 10} calculated using the dehydrated radius¹⁰ for PF_6^- , equals 0.49 nm. Based on this model, V_{sp} equals 0.57 μL . For comparison, the thickness of the compact layer for fully hydrated PF_6^- is 0.54 nm,¹⁰ which translates to a V_{sp} of $0.62 \pm 0.02 \mu\text{L}$ that is 9% larger than the value when using the dehydrated size for the anion.

SI-2. Determination of V_{mp} (void volume or volume of the mobile phase) and analysis of possible errors.

The value of V_{mp} can be determined in several ways, including the minor disturbance method, which uses a non-retained component of the mobile phase as a void marker.¹¹ Other methods (e.g., pycnometry)¹¹ were ruled out as possibilities because the uptake of liquid by the Nafion membrane and porous stainless steel used as components in the EMLC column would compromise the measurement. As a result, we determined V_{mp} by using the pseudo peak for water, which constitutes 95% (v/v) of the mixed mobile phase. From 194 replicate injections, the elution time for the pseudo peak equaled $0.570 \pm 0.004 \text{ min}$. This value, when multiplied by the flow rate of the mobile phase ($0.499 \pm 0.002 \text{ mL/min}$), yields a V_{mp} of $0.284 \pm 0.003 \text{ mL}$.

As a check on the validity of this approach, measurements of the pseudo peak for water were carried out in which the solutes were dissolved in acetonitrile:water mixtures of varied composition (0-5% acetonitrile (v/v)) that also varied values of E_{app} . The pseudo peak for water was also measured in a 95:5% water:acetonitrile mobile phase devoid of supporting electrolyte. These experiments showed no detectable changes in the elution time for the void marker and its utility in the determination of V_{mp} . Coupled with the value of V_{sp} (0.57 μL), ϕ was calculated to be $2.0 \pm 0.1 \times 10^{-3}$.

An evaluation of the impact of an error in V_{sp} indicates that possible differences in the most likely source of error - the thickness of the compact layer - have a small effect on ΔS_{trans}^0 . For example, a 0.1-nm increase in the thickness of the compact layer translates to an increase in ΔS_{trans}^0 of 1.4 J/mol-K and $T\Delta S_{trans}^0$ of 0.3 kJ/mol (25°C), and a decrease in ΔG_{trans}^0 of 0.3 kJ/mol. A doubling of the thickness of the compact layer from 0.54 to 1.08 yields increases of 5.8 J/mol-K for ΔS_{trans}^0 and 1.7 kJ/mol for $T\Delta S_{trans}^0$, and a decrease of 1.7 kJ/mol for ΔG_{trans}^0 . These values, which assume a V_{mp} of 0.284 mL, are ~10% smaller than those reported in this paper, and represent a well-known limitation with this methodology when examining the calculated values of ΔS_{trans}^0 and ΔG_{trans}^0 . An analysis of a doubling of V_{mp} , which approximates water uptake in a Nafion membrane,¹² also translates to differences in ΔS_{trans}^0 , $T\Delta S_{trans}^0$, and ΔG_{trans}^0 that are 10% smaller than the values reported herein.

SI-3. Determination of the potential of zero charge (pzc) for the glassy carbon packing.

EMLC differs from conventional LC methodologies because of the ability to manipulate solute retention by changes in E_{app} . Therefore, EMLC requires the presence of a supporting electrolyte in the mobile phase, which serves the same three purposes found in electrochemistry. The supporting electrolyte: (1) increases the conductivity of the mobile phase; (2) minimizes contributions of migration to mass transport; and (3) enables the reproducible formation of the electrical double layer. Moreover, the supporting electrolyte can alter solute retention by competing for sorption on the stationary phase. This competition is comparable to how the differences in the strength of the interactions for a charged solute and an eluting electrolyte can be used to manipulate separations in ion exchange chromatography.

One of the most effective measures to compare the sorption strength of supporting electrolytes is the pzc .⁸ At the pzc , the charge of an electrode surface is zero, meaning that the electrostatic driving force for the adsorption of a species solely based on charge is zero. In other words, a solute that interacts with a stationary phase at the pzc will elute with the injection band. It follows that the pzc corresponds to the applied potential in which the retention of a solute is invariant with respect to electrolyte concentration.¹³ These determinations are often made when using solid electrodes by identifying the minimum in a set of differential capacity-applied potential curves. As we have recently shown,¹⁴ the pzc can be determined by EMLC through measurements of solute retention (*e.g.*, the capacity factor, k') at different values of E_{app} and concentrations of supporting electrolyte. In this case, the point of intersection in the collected plots of $\ln k'$ vs. E_{app} corresponds to the pzc . Using this approach, we previously determined the pzc for the EMLC packing when using NaF, KCl, or LiClO₄ as supporting electrolytes.¹⁴ We have applied that same approach to determining the pzc for the NaPF₆-containing mobile phase in the work herein,¹⁵ which is listed as part of **Table SI-1**.

Table S1. Chromatographically Determined Values of the pzc for 1,5-NDS in a 95% water:5% acetonitrile (v/v) Mobile Phase Containing NaF, NaCl, LiClO₄, or NaPF₆, and ΔG_{ads} for NaCl, LiClO₄ or for NaPF₆ relative to NaF.

Supporting Electrolyte	NaF ^a	KCl ^a	LiClO ₄ ^a	NaPF ₆ ^b
pzc (mV) ^c	-25 ± 13	-280 ± 13	-325 ± 24	-400 ± 30
Δpzc (mV) ^d	--	-255	-300	-375
ΔG_{ads} (kJ/mol) ^d	--	-50	-58	-72

a) From Table 2 in D. W. Keller and M. D. Porter, Anal. Chem. 2005, 77, 7399-7407.

b) J. A. Williams and M. D. Porter, University of Utah, unpublished results.

c) Applied potentials are reported with respect to Ag/AgCl (sat'd NaCl).

d) $\Delta pzc = pzc \text{ of } ion_i - pzc_{NaCl}$, where i is either NaCl, LiClO₄, or NaPF₆ (*e.g.*, $pzc_{KCl} - pzc_{NaF}$) as differences of averages.

e) $\Delta G_{ads} = zF\Delta pzc$, where z is the charge with sign on the supporting electrolyte ion and F is the Faraday.

SI-4. References

1. Riedo, F.; Kovats, E. S., Adsorption from liquid mixtures and liquid chromatography, *J. Chromatogr. A* **1982**, 239, 1-28.
2. Shibukawa, M.; Ohta, N., A new method for the determination of mobile phase volume in normal and reversed-phase liquid chromatography, *Chromatographia* **1988**, 25, 288-294.
3. Yun, K. S.; Zhu, C.; Parcher, J. F., Theoretical relationships between the void volume, mobile phase volume, retention volume, adsorption, and gibbs free energy in chromatographic processes, *Anal. Chem.* **1995**, 67, 613-619.
4. Poole, C. F., *The essence of chromatography*. Elsevier: Boston, 2003.
5. Chester, T. L.; Coym, J. W., Effect of phase ratio on van't Hoff analysis in reversed-phase liquid chromatography, and phase-ratio-independent estimation of transfer enthalpy, *J. Chromatogr. A* **2003**, 1003, 101-111.
6. Sentell, K. B.; Dorsey, J. G., On the calculation of the stationary phase volume in reversed phase chromatography, *J. Liq. Chromatogr.* **1988**, 11, 1875-1885.
7. Moldoveanu, S.; David, V., Estimation of the phase ratio in reversed-phase high-performance liquid chromatography, *J. Chromatogr. A* **2015**, 2015, 194-201.
8. Bard, A. J.; Faulkner, L. R., *Electrochemical methods: Fundamentals and applications*. 2nd ed.; John Wiley & Sons: New York, 2001; p 534-579.
9. Keller, D.; Ponton, L.; Porter, M. D., Assessment of supporting electrolyte contributions in electrochemically modulated liquid chromatography, *J. Chromatogr. A* **2005**, 1089, 72-81.
10. Marcus, Y., *Ion properties*. Marcel Dekker, Inc.: New York, 1997; p 34.
11. Rimmer, C. A.; Simmons, C. R.; Dorsey, J. G., The measurement and meaning of void volumes in reversed-phase liquid chromatography, *J. Chromatogr. A* **2002**, 965, 219-232.
12. Majsztrik, P. W.; Satterfield, M. B.; Bocarsly, A. B.; Benziger, J. B., Water sorption, desorption and transport in nafion membranes, *J. Membr. Sci.* **2007**, 301, 93-106, and references therein.
13. Valette, G., Double layer on silver single-crystal electrodes in contact with electrolytes having anions which present a slight specific adsorption: Part i. The (110) face, *J. Electroanal. Chem.* **1981**, 122, 285-297.
14. Keller, D. W.; Porter, M. D., Electrochemically modulated liquid chromatography and the Gibbs adsorption equation, *Anal. Chem.* **2005**, 77, 7399-7407.
15. Williams, J. A.; Porter, M. D., Unpublished results, University of Utah.