

# Supporting Information

## A Molecular Dynamics Study of the Relation Between Analyte Retention and Surface Diffusion in Reversed-Phase Liquid Chromatography

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**Table S1.** Number of W ( $N_W$ ) and ACN ( $N_{ACN}$ ) molecules in productive simulations.

| W/ACN<br>(v/v) | $N_W$ | $N_{ACN}$ |
|----------------|-------|-----------|
| 80/20          | 27493 | 3689      |
| 70/30          | 23975 | 4902      |
| 60/40          | 20433 | 6227      |
| 50/50          | 16979 | 7440      |
| 40/60          | 13604 | 8568      |
| 30/70          | 10169 | 9741      |
| 20/80          | 6647  | 10842     |
| 10/90          | 3368  | 11832     |

**Table S2.** Locations of 10% and 90% total solvent density ( $z_{I/II}$  and  $z_{II/III}$ , respectively), width of interfacial region ( $w_{II}$ ), and location of the ACN density maximum ( $z(\rho_{ACN,max})$ ).

| W/ACN<br>(v/v) | $z_{I/II}$<br>(nm) | $z_{II/III}$<br>(nm) | $w_{II}$<br>(nm) | $z(\rho_{ACN,max})$<br>(nm) |
|----------------|--------------------|----------------------|------------------|-----------------------------|
| 80/20          | 1.29               | 2.13                 | 0.84             | 1.65                        |
| 70/30          | 1.26               | 2.19                 | 0.93             | 1.75                        |
| 60/40          | 1.23               | 2.23                 | 1.00             | 1.85                        |
| 50/50          | 1.19               | 2.24                 | 1.05             | 1.95                        |
| 40/60          | 1.12               | 2.26                 | 1.14             | 1.95                        |
| 30/70          | 1.08               | 2.25                 | 1.17             | 2.05                        |
| 20/80          | 1.03               | 2.23                 | 1.20             | 2.15                        |
| 10/90          | 0.93               | 2.13                 | 1.20             | 2.45                        |

**Table S3.** Local solvent ratios at the ACN density maximum and the analyte lateral mobility maximum in the interfacial region.

| Bulk (III) | W/ACN (v/v)                   |                           |
|------------|-------------------------------|---------------------------|
|            | Interfacial region (II)       |                           |
|            | at $z(\rho_{\text{ACN,max}})$ | at $z(D_{  ,\text{max}})$ |
| 80/20      | 32/68                         | 53/47                     |
| 70/30      | 29/71                         | 40/60                     |
| 60/40      | 27/73                         | 35/65                     |
| 50/50      | 26/74                         | 29/71                     |
| 40/60      | 22/78                         | 28/72                     |
| 30/70      | 18/82                         | 24/76                     |
| 20/80      | 14/86                         | 16/84                     |
| 10/90      | 8/92                          | 9/91                      |

**Table S4.** Relative contributions from partitioning and adsorption to analyte retention.

| W/ACN<br>(v/v) | Ethylbenzene |      | Benzene |      | Acetophenone |      | Benzyl alcohol |      |
|----------------|--------------|------|---------|------|--------------|------|----------------|------|
|                | part.        | ads. | part.   | ads. | part.        | ads. | part.          | ads. |
| 80/20          | 0.30         | 0.70 | 0.29    | 0.71 | 0.09         | 0.91 | 0.05           | 0.95 |
| 70/30          | 0.33         | 0.67 | 0.29    | 0.71 | 0.13         | 0.87 | 0.06           | 0.94 |
| 60/40          | 0.33         | 0.67 | 0.29    | 0.71 | 0.13         | 0.87 | 0.06           | 0.94 |
| 50/50          | 0.32         | 0.68 | 0.28    | 0.72 | 0.14         | 0.86 | 0.06           | 0.94 |
| 40/60          | 0.31         | 0.69 | 0.28    | 0.72 | 0.19         | 0.81 | 0.07           | 0.93 |
| 30/70          | 0.30         | 0.70 | 0.24    | 0.76 | 0.17         | 0.83 | 0.07           | 0.93 |
| 20/80          | 0.28         | 0.72 | 0.24    | 0.76 | 0.14         | 0.86 | 0.07           | 0.93 |
| 10/90          | 0.28         | 0.72 | 0.23    | 0.77 | 0.13         | 0.87 | 0.07           | 0.93 |

**Table S5.** Locations of the stationary-phase limit ( $z_{\text{SP}}$ ) and of the analyte lateral mobility maximum ( $z(D_{||,\text{max}})$ ).

| W/ACN<br>(v/v) | Ethylbenzene    |                        | Benzene         |                        | Acetophenone    |                        | Benzyl alcohol  |                        |
|----------------|-----------------|------------------------|-----------------|------------------------|-----------------|------------------------|-----------------|------------------------|
|                | $z_{\text{SP}}$ | $z(D_{  ,\text{max}})$ | $z_{\text{SP}}$ | $z(D_{  ,\text{max}})$ | $z_{\text{SP}}$ | $z(D_{  ,\text{max}})$ | $z_{\text{SP}}$ | $z(D_{  ,\text{max}})$ |
| 80/20          | 2.59            | 1.9                    | 2.49            | 1.9                    | 2.41            | 1.9                    | 2.31            | 1.9                    |
| 70/30          | 2.51            | 1.9                    | 2.43            | 1.9                    | 2.43            | 1.9                    | 2.37            | 1.9                    |
| 60/40          | 2.55            | 2.1                    | 2.47            | 1.9                    | 2.43            | 1.9                    | 2.37            | 1.9                    |
| 50/50          | 2.47            | 2.1                    | 2.39            | 1.9                    | 2.43            | 1.9                    | 2.41            | 1.9                    |
| 40/60          | 2.47            | 2.1                    | 2.41            | 2.1                    | 2.49            | 1.9                    | 2.45            | 2.1                    |
| 30/70          | 2.51            | 2.1                    | 2.39            | 2.1                    | 2.45            | 2.1                    | 2.45            | 2.1                    |
| 20/80          | 2.61            | 2.3                    | 2.49            | 2.3                    | 2.45            | 2.1                    | 2.43            | 2.3                    |
| 10/90          | 2.67            | 2.3                    | 2.53            | 2.5                    | 2.55            | 2.5                    | 2.43            | 2.5                    |

**Table S6.** Distribution coefficients  $K$  (cf. Figure 4 in the main text) calculated from the simulated analyte density profiles (cf. Figure 3 in the main text) using individual  $z_{\text{sp}}$ -values (Table S5).

| W/ACN | Ethylbenzene | Benzene | Acetophenone | Benzyl alcohol |
|-------|--------------|---------|--------------|----------------|
| (v/v) | <i>K</i>     |         |              |                |
| 80/20 | 860.87       | 91.33   | 33.36        | 22.18          |
| 70/30 | 300.91       | 60.57   | 19.84        | 9.61           |
| 60/40 | 136.36       | 27.84   | 8.46         | 5.80           |
| 50/50 | 46.93        | 14.23   | 4.97         | 3.84           |
| 40/60 | 25.86        | 7.49    | 2.77         | 2.03           |
| 30/70 | 10.58        | 4.40    | 1.72         | 1.41           |
| 20/80 | 4.83         | 2.69    | 1.13         | 0.85           |
| 10/90 | 2.59         | 1.67    | 0.90         | 0.59           |

**Table S7.** Experimentally determined retention factors  $k'$  (cf. Figure 5 in the main text).

| W/ACN<br>(v/v) | Ethylbenzene | Benzene | Acetophenone | Benzyl alcohol |
|----------------|--------------|---------|--------------|----------------|
| $k'$           |              |         |              |                |
| 80/20          | 184.91       | 26.58   | 11.85        | 3.21           |
| 70/30          | 63.89        | 13.69   | 5.45         | 1.65           |
| 60/40          | 24.32        | 7.17    | 3.01         | 1.05           |
| 50/50          | 9.67         | 3.66    | 1.71         | 0.69           |
| 40/60          | 4.92         | 2.17    | 1.10         | 0.49           |
| 30/70          | 2.67         | 1.30    | 0.70         | 0.34           |
| 20/80          | 1.52         | 0.80    | 0.46         | 0.24           |
| 10/90          | 0.82         | 0.47    | 0.29         | 0.16           |

**Table S8.** Phase ratio  $\beta$  calculated as the ratio between experimental retention factor  $k'$  and simulated distribution coefficient  $K$ .

| W/ACN<br>(v/v) | Ethylbenzene | Benzene | Acetophenone | Benzyl alcohol |
|----------------|--------------|---------|--------------|----------------|
| $\beta = k'/K$ |              |         |              |                |
| 80/20          | 0.21         | 0.29    | 0.36         | 0.14           |
| 70/30          | 0.21         | 0.23    | 0.27         | 0.17           |
| 60/40          | 0.18         | 0.26    | 0.36         | 0.18           |
| 50/50          | 0.21         | 0.26    | 0.34         | 0.18           |
| 40/60          | 0.19         | 0.29    | 0.40         | 0.24           |
| 30/70          | 0.25         | 0.30    | 0.41         | 0.24           |
| 20/80          | 0.31         | 0.30    | 0.41         | 0.28           |
| 10/90          | 0.32         | 0.28    | 0.32         | 0.27           |

**Table S9.** Parallel diffusion coefficients  $D_{\parallel}$  and contribution to overall bonded-phase presence of bonded-phase groups CH<sub>3</sub>(18) and CH<sub>2</sub>(17) at the analyte lateral mobility maximum.

| W/ACN<br>(v/v) | CH <sub>3</sub> (18)                               |                                       | CH <sub>2</sub> (17)                               |                                       |
|----------------|----------------------------------------------------|---------------------------------------|----------------------------------------------------|---------------------------------------|
|                | $D_{\parallel}$                                    | contrib. to bonded-<br>phase presence | $D_{\parallel}$                                    | contrib. to bonded-<br>phase presence |
|                | (10 <sup>-9</sup> m <sup>2</sup> s <sup>-1</sup> ) | (%)                                   | (10 <sup>-9</sup> m <sup>2</sup> s <sup>-1</sup> ) | (%)                                   |
| 80/20          | 1.58 ± 0.19                                        | 45.6                                  | 1.28 ± 0.13                                        | 28.6                                  |
| 70/30          | 1.64 ± 0.23                                        | 41.4                                  | 1.33 ± 0.17                                        | 29.3                                  |
| 60/40          | 1.71 ± 0.19                                        | 40.6                                  | 1.39 ± 0.13                                        | 28.7                                  |
| 50/50          | 1.75 ± 0.19                                        | 38.3                                  | 1.41 ± 0.13                                        | 28.5                                  |
| 40/60          | 1.79 ± 0.20                                        | 53.6                                  | 1.45 ± 0.17                                        | 29.8                                  |
| 30/70          | 1.84 ± 0.25                                        | 51.3                                  | 1.49 ± 0.17                                        | 30.4                                  |
| 20/80          | 2.01 ± 0.23                                        | 71.7                                  | 1.66 ± 0.20                                        | 24.1                                  |
| 10/90          | 2.17 ± 0.19                                        | 95.8                                  | 1.76 ± 0.16                                        | 4.2                                   |

**Table S10.** Diffusive mobility data for **ethylbenzene**.

| W/ACN<br>(v/v) | $D_{  ,\text{max}}$<br>( $10^{-9} \text{ m}^2 \text{ s}^{-1}$ ) | $D_{  ,\text{bulk}}$<br>( $10^{-9} \text{ m}^2 \text{ s}^{-1}$ ) | $D_{  ,\text{max}}/D_{  ,\text{bulk}}$ | $D_{\text{m,analyte\_max}}$<br>( $10^{-9} \text{ m}^2 \text{ s}^{-1}$ ) |
|----------------|-----------------------------------------------------------------|------------------------------------------------------------------|----------------------------------------|-------------------------------------------------------------------------|
| 80/20          | $1.62 \pm 0.07$                                                 | $1.14 \pm 0.02$                                                  | $1.42 \pm 0.07$                        | 1.34                                                                    |
| 70/30          | $1.64 \pm 0.05$                                                 | $1.20 \pm 0.04$                                                  | $1.37 \pm 0.06$                        | $1.46 \pm 0.10$                                                         |
| 60/40          | $1.66 \pm 0.06$                                                 | $1.28 \pm 0.02$                                                  | $1.30 \pm 0.05$                        | 1.54                                                                    |
| 50/50          | $1.65 \pm 0.03$                                                 | $1.33 \pm 0.02$                                                  | $1.24 \pm 0.03$                        | $1.65 \pm 0.10$                                                         |
| 40/60          | $1.72 \pm 0.05$                                                 | $1.47 \pm 0.02$                                                  | $1.17 \pm 0.04$                        | 1.68                                                                    |
| 30/70          | $1.85 \pm 0.05$                                                 | $1.64 \pm 0.02$                                                  | $1.13 \pm 0.03$                        | 1.81                                                                    |
| 20/80          | $2.09 \pm 0.08$                                                 | $1.91 \pm 0.03$                                                  | $1.09 \pm 0.05$                        | 2.09                                                                    |
| 10/90          | $2.33 \pm 0.12$                                                 | $2.34 \pm 0.02$                                                  | $1.00 \pm 0.05$                        | 2.50                                                                    |

**Table S11.** Diffusive mobility data for **benzene**.

| W/ACN<br>(v/v) | $D_{  ,\text{max}}$<br>( $10^{-9} \text{ m}^2 \text{ s}^{-1}$ ) | $D_{  ,\text{bulk}}$<br>( $10^{-9} \text{ m}^2 \text{ s}^{-1}$ ) | $D_{  ,\text{max}}/D_{  ,\text{bulk}}$ | $D_{\text{m,analyte\_max}}$<br>( $10^{-9} \text{ m}^2 \text{ s}^{-1}$ ) |
|----------------|-----------------------------------------------------------------|------------------------------------------------------------------|----------------------------------------|-------------------------------------------------------------------------|
| 80/20          | $2.04 \pm 0.08$                                                 | $1.39 \pm 0.03$                                                  | $1.47 \pm 0.07$                        | 1.54                                                                    |
| 70/30          | $2.05 \pm 0.07$                                                 | $1.44 \pm 0.02$                                                  | $1.42 \pm 0.05$                        | $1.74 \pm 0.08$                                                         |
| 60/40          | $1.99 \pm 0.03$                                                 | $1.51 \pm 0.02$                                                  | $1.32 \pm 0.03$                        | 1.86                                                                    |
| 50/50          | $2.04 \pm 0.07$                                                 | $1.59 \pm 0.06$                                                  | $1.28 \pm 0.07$                        | $2.00 \pm 0.10$                                                         |
| 40/60          | $2.14 \pm 0.07$                                                 | $1.73 \pm 0.03$                                                  | $1.24 \pm 0.05$                        | 2.04                                                                    |
| 30/70          | $2.27 \pm 0.08$                                                 | $1.93 \pm 0.02$                                                  | $1.18 \pm 0.04$                        | 2.28                                                                    |
| 20/80          | $2.61 \pm 0.05$                                                 | $2.33 \pm 0.02$                                                  | $1.12 \pm 0.02$                        | 2.58                                                                    |
| 10/90          | $2.91 \pm 0.09$                                                 | $2.86 \pm 0.03$                                                  | $1.02 \pm 0.03$                        | 2.90                                                                    |

**Table S12.** Diffusive mobility data for **acetophenone**.

| W/ACN<br>(v/v) | $D_{  ,\text{max}}$<br>( $10^{-9} \text{ m}^2 \text{ s}^{-1}$ ) | $D_{  ,\text{bulk}}$<br>( $10^{-9} \text{ m}^2 \text{ s}^{-1}$ ) | $D_{  ,\text{max}}/D_{  ,\text{bulk}}$ | $D_{\text{m,analyte\_max}}$<br>( $10^{-9} \text{ m}^2 \text{ s}^{-1}$ ) |
|----------------|-----------------------------------------------------------------|------------------------------------------------------------------|----------------------------------------|-------------------------------------------------------------------------|
| 80/20          | $1.28 \pm 0.03$                                                 | $1.05 \pm 0.02$                                                  | $1.22 \pm 0.04$                        | 1.10                                                                    |
| 70/30          | $1.31 \pm 0.02$                                                 | $1.08 \pm 0.02$                                                  | $1.21 \pm 0.03$                        | $1.20 \pm 0.06$                                                         |
| 60/40          | $1.30 \pm 0.02$                                                 | $1.08 \pm 0.03$                                                  | $1.20 \pm 0.04$                        | 1.26                                                                    |
| 50/50          | $1.32 \pm 0.02$                                                 | $1.11 \pm 0.02$                                                  | $1.19 \pm 0.03$                        | $1.36 \pm 0.05$                                                         |
| 40/60          | $1.35 \pm 0.02$                                                 | $1.15 \pm 0.02$                                                  | $1.17 \pm 0.03$                        | 1.36                                                                    |
| 30/70          | $1.48 \pm 0.02$                                                 | $1.30 \pm 0.02$                                                  | $1.14 \pm 0.02$                        | 1.45                                                                    |
| 20/80          | $1.68 \pm 0.02$                                                 | $1.54 \pm 0.02$                                                  | $1.09 \pm 0.02$                        | 1.71                                                                    |
| 10/90          | $1.96 \pm 0.08$                                                 | $1.91 \pm 0.03$                                                  | $1.03 \pm 0.05$                        | 1.98                                                                    |

**Table S13.** Diffusive mobility data for **benzyl alcohol**.

| W/ACN<br>(v/v) | $D_{  ,\text{max}}$<br>( $10^{-9} \text{ m}^2 \text{ s}^{-1}$ ) | $D_{  ,\text{bulk}}$<br>( $10^{-9} \text{ m}^2 \text{ s}^{-1}$ ) | $D_{  ,\text{max}}/D_{  ,\text{bulk}}$ | $D_{\text{m,analyte\_max}}$<br>( $10^{-9} \text{ m}^2 \text{ s}^{-1}$ ) |
|----------------|-----------------------------------------------------------------|------------------------------------------------------------------|----------------------------------------|-------------------------------------------------------------------------|
| 80/20          | $1.26 \pm 0.03$                                                 | $1.09 \pm 0.02$                                                  | $1.16 \pm 0.03$                        | 1.09                                                                    |
| 70/30          | $1.30 \pm 0.03$                                                 | $1.11 \pm 0.02$                                                  | $1.17 \pm 0.03$                        | $1.15 \pm 0.08$                                                         |
| 60/40          | $1.26 \pm 0.02$                                                 | $1.08 \pm 0.03$                                                  | $1.17 \pm 0.04$                        | 1.19                                                                    |
| 50/50          | $1.28 \pm 0.02$                                                 | $1.10 \pm 0.02$                                                  | $1.16 \pm 0.03$                        | $1.24 \pm 0.07$                                                         |
| 40/60          | $1.36 \pm 0.03$                                                 | $1.18 \pm 0.02$                                                  | $1.15 \pm 0.03$                        | 1.25                                                                    |
| 30/70          | $1.46 \pm 0.02$                                                 | $1.29 \pm 0.03$                                                  | $1.13 \pm 0.03$                        | 1.38                                                                    |
| 20/80          | $1.67 \pm 0.03$                                                 | $1.53 \pm 0.02$                                                  | $1.09 \pm 0.02$                        | 1.61                                                                    |
| 10/90          | $1.98 \pm 0.04$                                                 | $1.93 \pm 0.04$                                                  | $1.03 \pm 0.03$                        | 1.93                                                                    |