Water Resources Research

Supporting Information for

The two-phase flow IPTT method for measurement of nonwetting-wetting liquid interfacial areas at higher nonwetting saturations in natural porous media

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Description of the calculation of the liquid-liquid interfacial partition coefficient
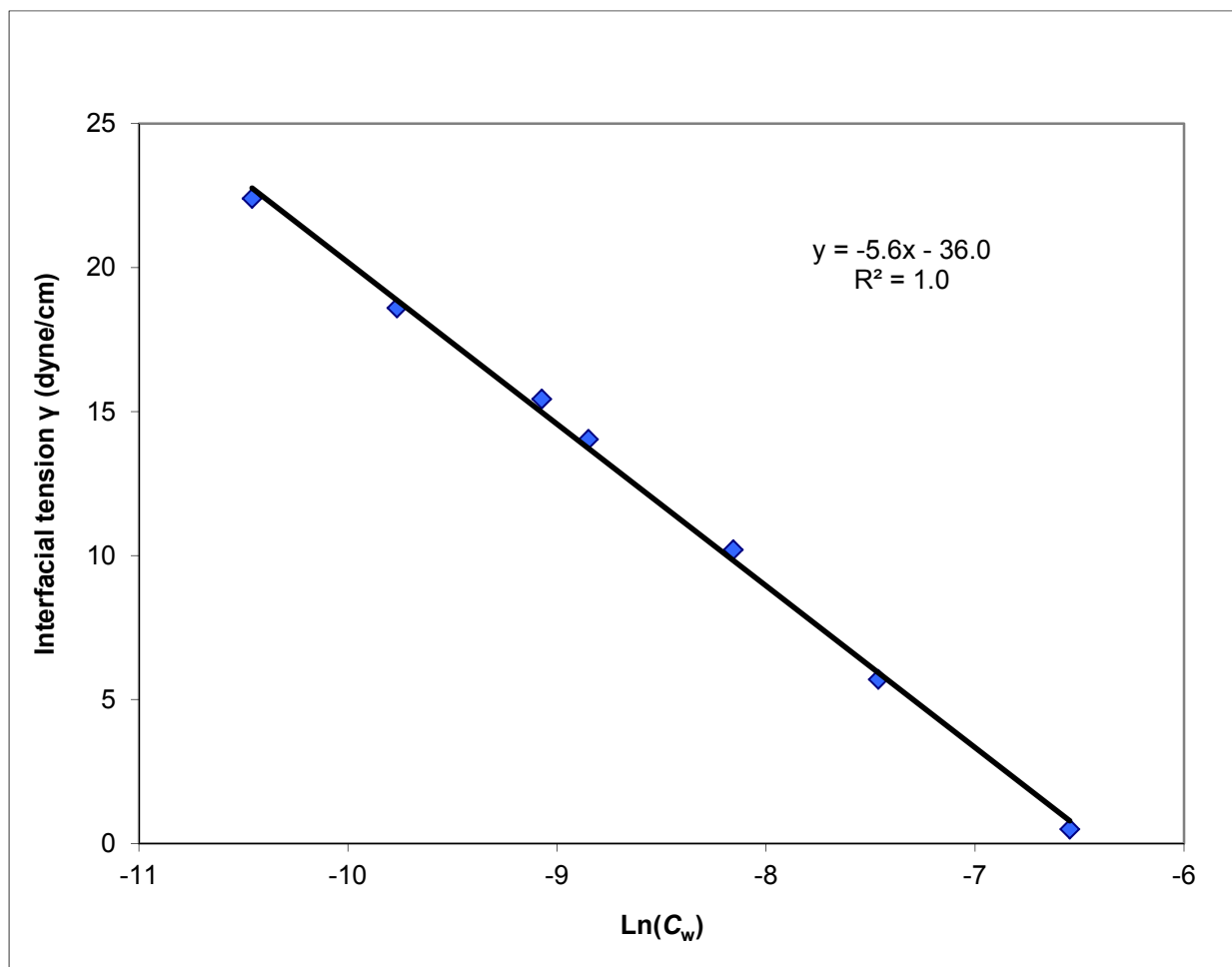
$$y = -5.6x - 36.0$$
$$R^2 = 1.0$$

Figure S1. Relation between PCE-water interfacial tension and SDBS concentration to obtain interfacial partition coefficient K_i. The unit of C_w is mol/L. Temperature for the measurement is 25 °C.

Calculation of liquid-liquid interfacial partition coefficient (K_i) for SDBS

Adsorption of SDBS to the PCE/water interface is related to interfacial tension and surfactant bulk activity as expressed by the Gibbs equation (1):

$$\Gamma = -\frac{a}{2RT}\left(\frac{d\gamma}{da}\right) \times 10^{-3} \qquad (1)$$

where a is the surfactant bulk activity (mol/L); R is the universal gas constant (8.314 J/(mol·K)), T (K) is the absolute temperature; Γ (mol/m^2) is the interface excess of the surfactant; γ (mN/m) is the interfacial tension.

SDBS adsorption at fluid-fluid interfaces is described by the Langmuir equation at concentrations below the critical micelle concentration (CMC):

$$\Gamma = \Gamma_{\max}\frac{Ka}{1+Ka} \qquad (2)$$

where $\Gamma_{\max}$ (mol/m^2) is the maximum interface excess of surfactant and K (L/mol) is the Langmuir constant.

Resolving equation (1) and combining it with equation (2) give the Szyszkowski equation, which describes interfacial tension as a function of SDBS bulk activity at concentrations below CMC:

$$\gamma_0 - \gamma = 2RT\Gamma_{\max}\ln(1 + Ka) \times 10^3 \qquad (3)$$

where γ_0 (mN/m) is the interfacial tension in the absence of surfactant. The relation between a and the concentration, C_w (mol/L), is:

$$a = fC_w \qquad (4)$$

where f is the activity coefficient of SDBS. At very low SDBS concentrations (e.g. 35 mg/L) f is very close to 1 and $a \approx C_w$.

For the range of C_w examined in this test, Ka is orders of magnitude greater than 1, and equation (3) can be simplified to:
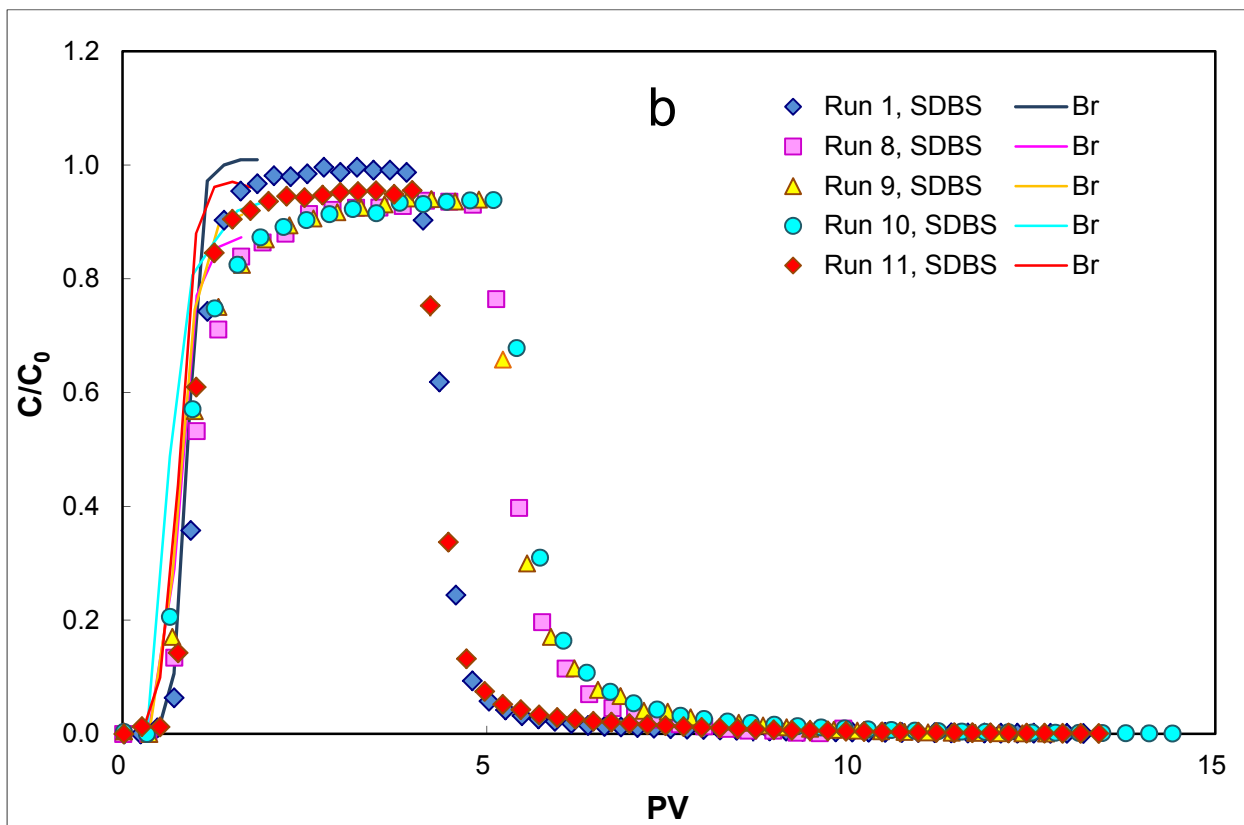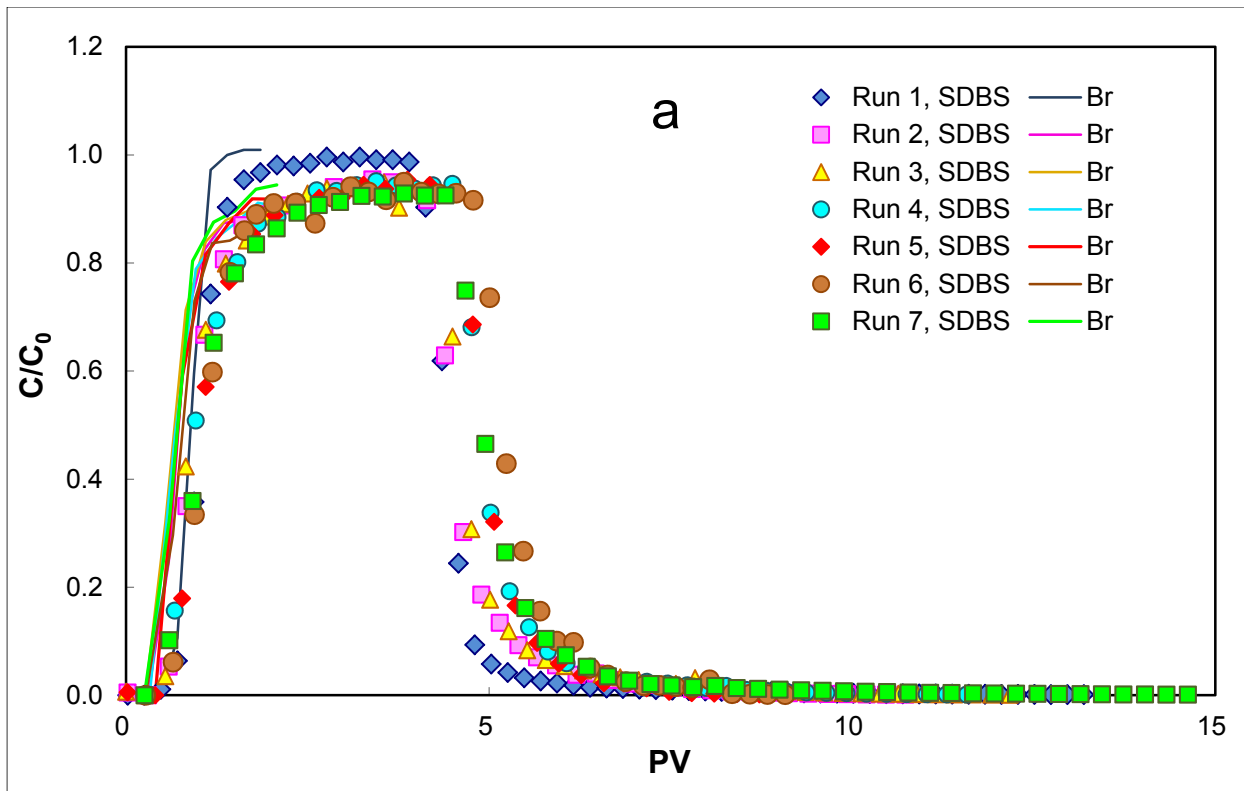
$$\gamma = (\gamma_0 - 2RT\Gamma_{max}\ln K \times 10^3) - 2RT\Gamma_{max}\ln(C_w) \times 10^3 = \alpha - \beta \ln C_w \qquad (5)$$
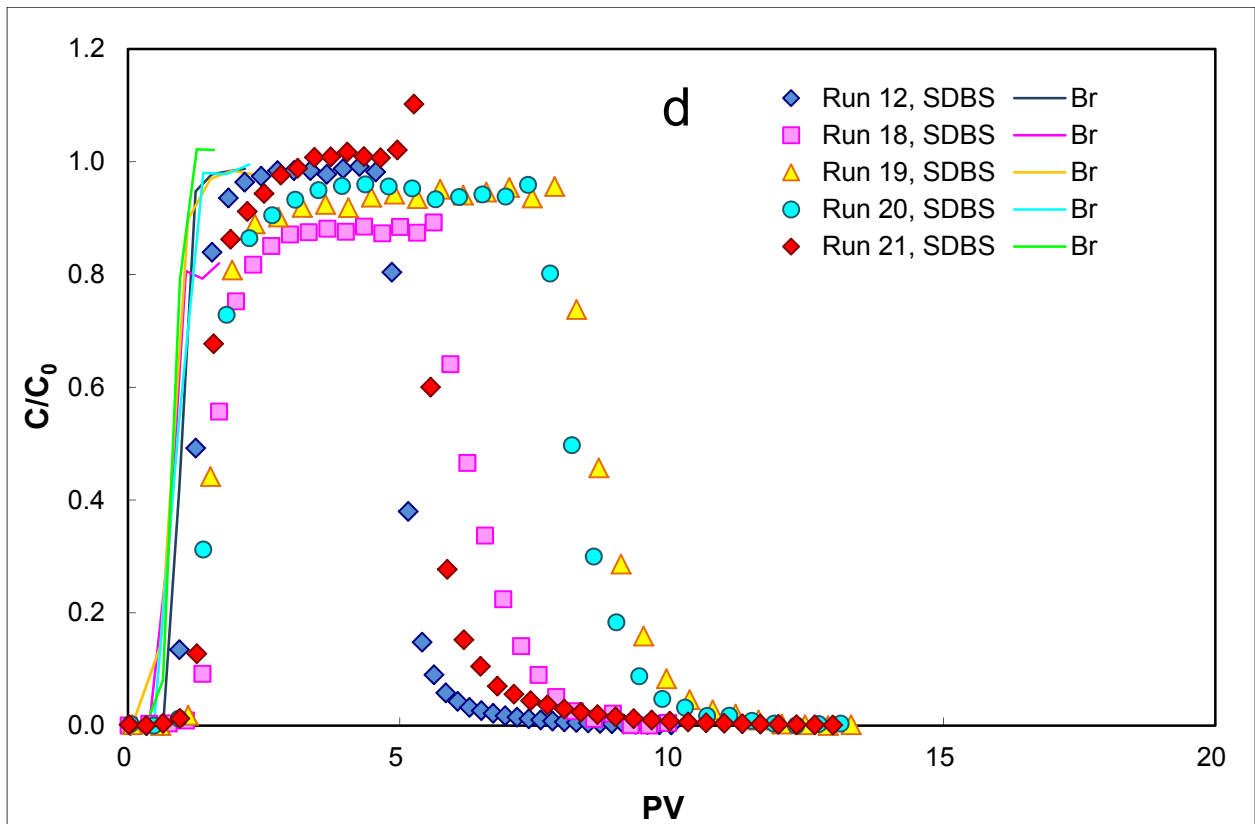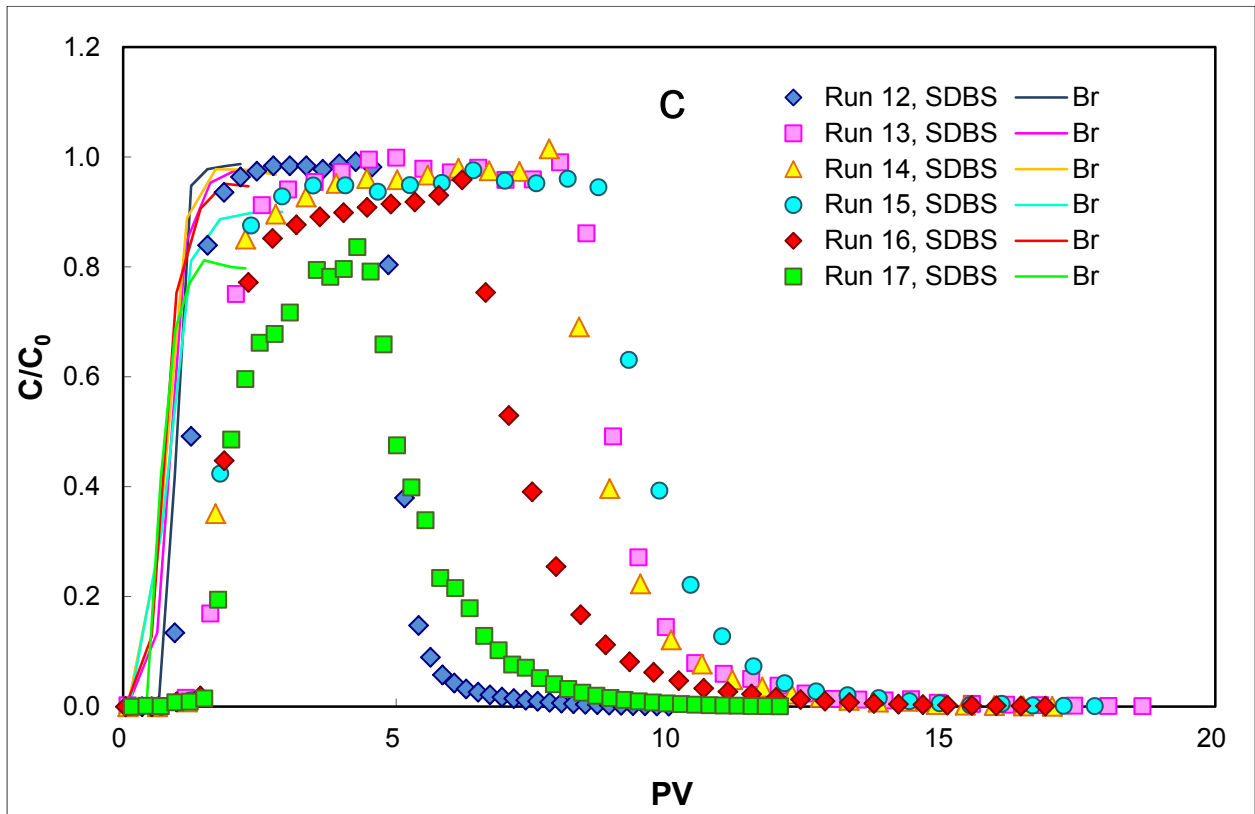
Values for α and β are obtained using the correlation presented in Figure S1. Then equation (1) becomes:

$$\Gamma = \frac{\beta}{2RT} \times 10^{-3} \qquad (6)$$

K_i is calculated using equation (7)

$$K_i = \frac{\Gamma}{C_w} = \frac{\beta}{2RTC_w} \times 10^{-3} \qquad (7)$$
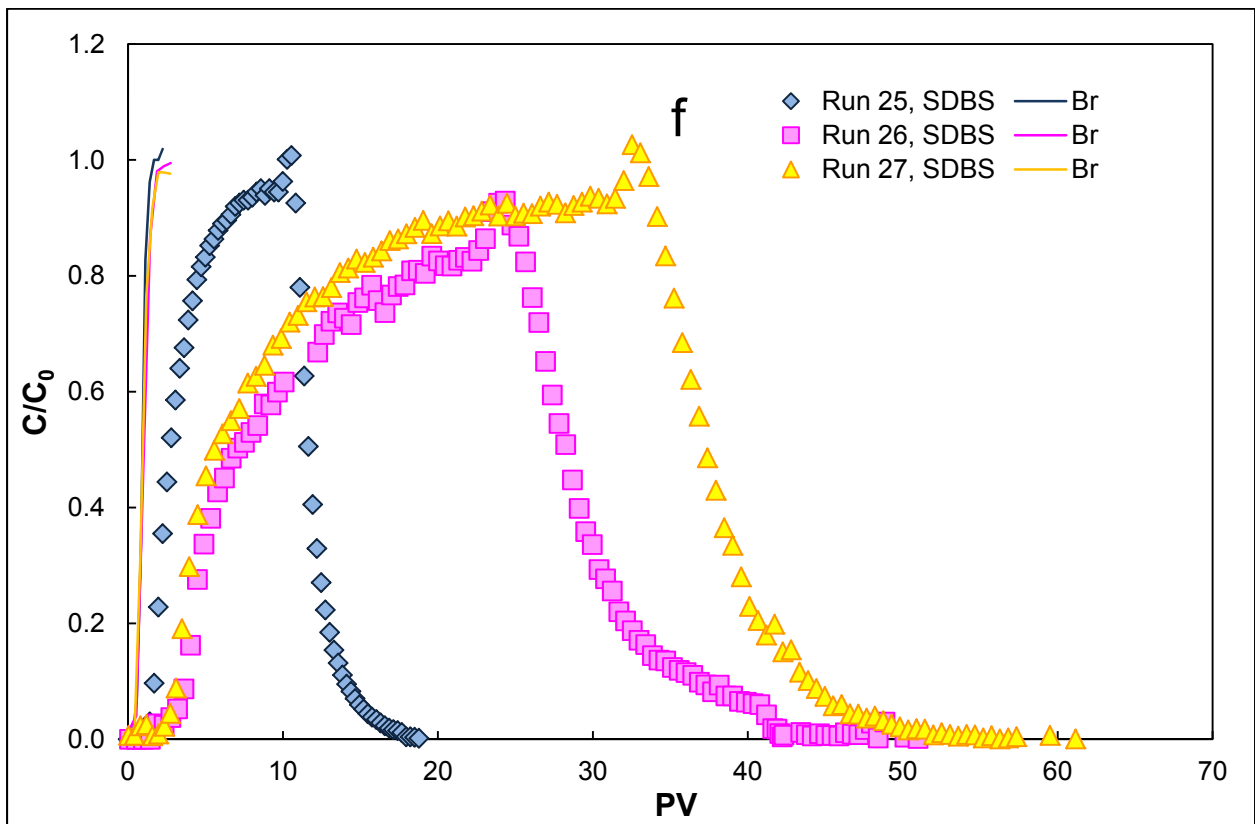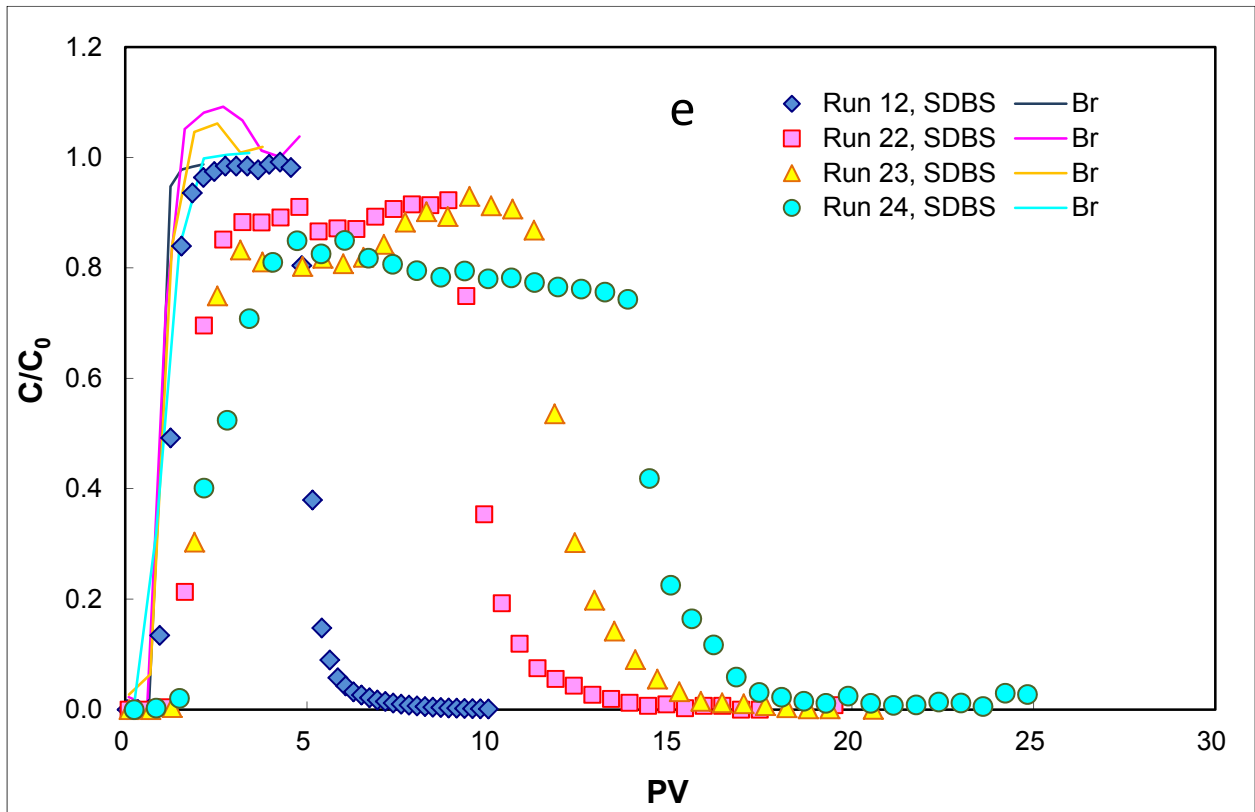
Figure S2. Breakthrough curves obtained from the interfacial partitioning tracer tests. (a) glass beads, primary drainage; (b) glass beads, secondary imbibition; (c) sand, primary drainage; (d) sand, secondary imbibition; (e) sand, secondary drainage; (f) soil, primary drainage and secondary imbibition. Each test comprises a set of paired Br^- and SDBS breakthrough curves. The flow conditions of tests are presented in Table S1. Note that the "snow plough" effect was observed for the SDBS breakthrough curves for Vinton soil. This constitutes an increase in C/C_0 when there is a decrease of ionic strength in solution for elution of a column adsorbed with ionic surfactants. This occurred with the switch from solution containing Br^- to solution with no Br^-. It was observed to a greater extent for Vinton soil because if that medium's higher capacity for SDBS adsorption.

Table S1. Flow conditions and tracer retardation factors of the IPTT experiments

EXPT #	Type of experiment [a]	Discharge-based flow rate of water (ml/min)	Discharge-based flow rate of PCE (ml/min)	Total flow rate (ml/min)	Water saturation S_w^b	SDBS retardation factor R	SDBS mass recovery
Glass beads							
1	WS	1.08	0.00	1.08	1.000±0.000	1.11	1.00
2	PD	0.95	0.11	1.06	0.769±0.004	1.17	1.02
3	PD	0.74	0.24	0.98	0.703±0.016	1.18	0.95
4	PD	0.63	0.32	0.95	0.631±0.048	1.22	0.96
5	PD	0.62	0.33	0.95	0.582±0.008	1.25	0.96
6	PD	0.36	0.37	0.73	0.533±0.028	1.27	0.93
7	PD	0.38	0.55	0.93	0.508±0.018	1.32	0.98
8	SI	0.85	0.16	1.01	0.560±0.010	1.27	0.98
9	SI	0.92	0.07	0.99	0.597±0.003	1.26	1.00
10	SI	1.00	0.01	1.01	0.661±0.027	1.22	1.01
11	SI	1.01	0.00	1.01	0.857±0.001	1.14	0.98
Sand							
12	WS	0.95	0.00	0.95	1.000±0.000	1.33	0.97
13	PD	0.97	0.13	1.10	0.659±0.002	2.01	0.96
14	PD	0.89	0.18	1.07	0.627±0.013	2.09	0.96
15	PD	0.81	0.29	1.10	0.598±0.026	2.14	0.96
16	PD	0.41	0.53	0.94	0.535±0.008	2.35	0.97
17	PD	0.21	0.69	0.90	0.470±0.011	2.59	0.81
18	SI	0.41	0.49	0.90	0.592±0.007	2.02	0.91
19	SI	0.73	0.28	1.01	0.665±0.002	1.88	0.97
20	SI	0.86	0.12	0.98	0.692±0.009	1.81	0.99
21	SI	1.01	0.00	1.01	0.790±0.004	1.62	1.00
22	SD	0.99	0.01	1.00	0.649±0.019	2.42	0.92

23	SD	0.95	0.06	1.01	0.546±0.008	2.97	0.88
24	SD	0.93	0.09	1.02	0.496±0.012	3.68	0.80
Soil							
25	WS	1.03	0.00	1.03	1.000±0.000	3.45	0.98
26	PD	0.76	0.09	0.85	0.794±0.022	9.84	0.86
27	SI	0.97	0.01	0.98	0.826±0.004	8.64	0.95

[a] WS = water saturated flow, PD = primary drainage, SI = secondary imbibition, SD = secondary drainage.

[b] Value = mean ± error of water saturations in the column before and after the tracer experiment. The error is the difference between the measured value and the mean.