Supporting Information

New Insights Provided by Solvent Relaxation NMR-Measured Surface Area in Liquids to Explain Phenolics Sorption on Silica Nanoparticles

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Data analysis. Sorption isotherms were fitted using Freundlich model:

$$Q_{\rm e} = K_{\rm F} C_{\rm e}^{\rm n} \tag{1}$$

where $K_{\rm F} [({\rm mg/kg})/({\rm mg/L})^{\rm n}]$ is the Freundlich sorption coefficient and n is the nonlinearity factor. $Q_{\rm e}$ (mg/kg) and $C_{\rm e}$ (mg/L) are equilibrium solid-phase and aqueous-phase concentrations, respectively.

Relaxation NMR. ¹H solvent relaxation NMR is based upon a theory that can be described by means of a fast exchange between solvent molecules constrained at an interface (the bound state) with a shorter T_2 and highly mobile solvent molecules in the bulk (the free state) with a longer T_2 in the relaxation experiment.¹ A spin-spin relaxation rate constant, R_2 , is determined from the reciprocal of T_2 . The average rate, R_2 , is given by:

$$R_2 = (1 - p_b)R_{2f} + p_b R_{2b}$$
(2)

where, p_b is the fraction of time each proton (hydrogen nuclei) spends in the bound state. R_{2f} and R_{2b} are the relaxation rate constants for the free and bound solvent molecules, respectively. The relaxation rate coefficient is presented in terms of a specific relaxation rate, R_{2sp} :

$$R_{2sp} = R_2 / R_2^0 - 1 \tag{3}$$

where R_2^0 is the relaxation rate constant of the free or bulk liquid, which in most cases is the pure solvent.

Several studies have suggested that the estimation of surface area measurement by NMR relaxation is related to the bound solvent molecules in contact with a particle surface has a relaxation rate significantly different from that of bulk or free solvent molecules. The calculation of SA is generally organized in processing relaxation data;^{2, 3}

$$R_2 = \psi SL\rho(R_{2b} - R_2^0) + R_2^0$$
(4)

where ψ is the particle volume to liquid volume ratio, S is the total surface area per unit weight, L is the thickness of surface layer of fluid and ρ is the bulk particle density. Then, we can define a constant, K_a:

$$K_{a} = L\rho(R_{2b} - R_{2}^{0})$$
(5)

Thus,

$$\mathbf{R}_{2\mathrm{sp}} = \psi \cdot \mathbf{S} \mathbf{K}_{\mathrm{a}} / \mathbf{R}_2^{0} \tag{6}$$

A more precise method is to use the slope of a plot of R_{2sp} as a function of volume ratio (ψ), together with presence of the intercept value (R_{2sp} at ψ =0) that is similar to the other experimental observables, giving evidence that the changes in the solutesolvent interactions in these mixtures and the microheterogeneity of the solution.⁴ Further derivation and details of this NMR technique were discussed in our previous work elsewhere.³

Table S1.	Fitted	parametei	s of sor	ption is	sotherms	of silica	NPs	using	Freund	llich
model.										

		Freundlich model fitting results							
			Water		<i>n</i> -hexane				
		$logK_{F}^{a}$	n	\mathbf{R}^2_{adj}	logK _F	n	\mathbf{R}^2_{adj}		
	S15	-1.18±0.25	2.12±0.17	0.936	1.90±0.04	1.12±0.03	0.988		
phenol	S30	-0.09 ± 0.20	1.60±0.13	0.929	1.63±0.05	1.23±0.04	0.984		
	S50	0.42 ± 0.15	1.39±0.10	0.944	1.36±0.08	1.32 ± 0.06	0.972		
	S15	0.79±0.06	0.90 ± 0.04	0.976	1.81±0.03	0.92 ± 0.02	0.994		
β-naphthol	S30	0.91±0.05	0.96 ± 0.04	0.986	1.42 ± 0.03	0.96 ± 0.02	0.993		
	S50	1.06±0.07	0.94±0.05	0.973	1.21±0.05	0.98±0.04	0.981		

 $^{a}\,(mg/kg)/(mg/L)^{n}$

S15, S30 and S50 stand for 15, 30 and 50 nm original silica NP samples, respectively.

The n values bigger than 1 probably suggest increased dispersion of nanoparticles after the sorption.

Table S2. Fitted parameters of sorption isotherms of hydroxylated silica NPs using Freundlich model.

		Freundlich model fitting results								
		Water				<i>n</i> -hexane				
		logK _F ^a	n	\mathbf{R}^{2}_{adj}		logK _F	n	R^2_{adj}		
	S15-H	0.40±0.16	1.37±0.11	0.932		2.05±0.05	1.11±0.04	0.982		
phenol	S30-Н	1.48±0.11	0.91 ± 0.07	0.931		2.19±0.06	1.13±0.05	0.973		
	S50-Н	2.03±0.05	0.67±0.03	0.975		2.30±0.05	1.09 ± 0.05	0.976		
	S15-H	0.95 ± 0.08	1.12±0.05	0.975		2.33±0.03	0.93 ± 0.03	0.987		
β-naphthol	S30-Н	1.45 ± 0.02	1.02 ± 0.02	0.997		2.38±0.05	1.10±0.05	0.977		
	S50-Н	1.83±0.04	0.90 ± 0.03	0.988		2.53±0.02	1.03±0.03	0.991		

 $^{a}\,(mg/kg)/(mg/L)^{n}$

S15-H, S30-H and S50-H stand for 15, 30 and 50 nm hydroxylated silica NP samples,

respectively.

The n values bigger than 1 probably suggest increased dispersion of nanoparticles after the sorption.

	Original particle	Hydrated particle
Surface area	t	ŧ
Surface –OH groups	None	ŧ
Sorption in polar solvents	Easily hydrated	t
Sorption in nonpolar solvents	t	ł
NMR relaxation	t	ŧ

Table S3. The comparison among adsorption of phenolics, surface –OH groups, BET and NMR data

↑Enhanced with decreased particle sizes; ↓Reduced with decreased particle sizes



Figure S1. Adsorption isotherms of phenol by original silica NPs in water (a) and *n*-hexane (b).



Figure S2. TGA comparison of different sized silica NPs in N_2 up to 1000 °C. The OH surface density is based on the weight loss between 200 and 1000 °C.



Figure S3. Adsorption isotherms of phenol by hydroxylated silica NPs in water (a) and *n*-hexane (b).



Figure S4. Adsorption isotherms of phenol by hydroxylated and dehydroxylated silica of 15 (a), 30 (b) and 50 (c) nm using different solvents.



Figure S5. Adsorption isotherms of β -naphthol on original and hydroxylated silica NPs of 15 (a), 30 (b) and 50 (c) nm in different solvents.

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