

Thermodynamics of binary gas adsorption in nanopores: Electronic Supplementary Information

1 Thermodynamics of the binary solutions

The thermodynamic data on the liquid–vapour equilibria of TBA/TOL solutions are available in the literature [V. Martínez-Soria, M.P. Peña, and J.B. Montón, J. Chem. Eng. Data 44, 148 (1999)]. In the present study, it is essential to know as an input the compositions of the gas and liquid phases at thermodynamic equilibrium at a given temperature. The procedure is as follows (in the following, x and y are respectively the TBA fraction in the liquid and gas phase):

1. The TBA and TOL activity coefficients γ_i in the binary liquids can be described by the Margules model :¹

$$\begin{aligned}\gamma_{TBA} &= \exp\left(\frac{(A + 3B)(1 - x)^2 - 4B(1 - x)^3}{RT}\right) \\ \gamma_{TOL} &= \exp\left(\frac{(A + 3B)x^2 + 4Bx^3}{RT}\right)\end{aligned}\quad (1)$$

The A and B coefficients in 1 have been empirically determined by Martinez-Soria et al.²

2. The saturation pressures P_i^{sat} of the pure components can be classically determined by the Antoine equation:

$$\log_{10}(P_i^{sat}) = a_{1i} - \frac{a_{2i}}{T + a_{3i} - 273.15} \quad (2)$$

The Antoine constants a_{ni} for TBA and TOL are available in the literature. The values used in the present study have been taken from Poling et al.¹ :

	a_{1i}	a_{2i}	a_{3i}
TBA	4.44484	1154.48	177.65
TOL	4.05043	1327.62	217.625

3. Knowing the activity coefficients from equation (1) and the saturation pressures of TBA and TOL from equation (2), the TBA volume fraction y of the gas phase is deduced from Henry law:¹

$$\frac{1}{y} = 1 + \frac{1 - x}{x} \frac{P_{TOL}^{sat}}{P_{TBA}^{sat}} \frac{\gamma_{TBA}}{\gamma_{TOL}} \quad (3)$$

where x is the TBA fraction in the liquid solution.

The figure 1 shows $y = f(x)$ for the TBA/TOL solution at equilibrium at room temperature.

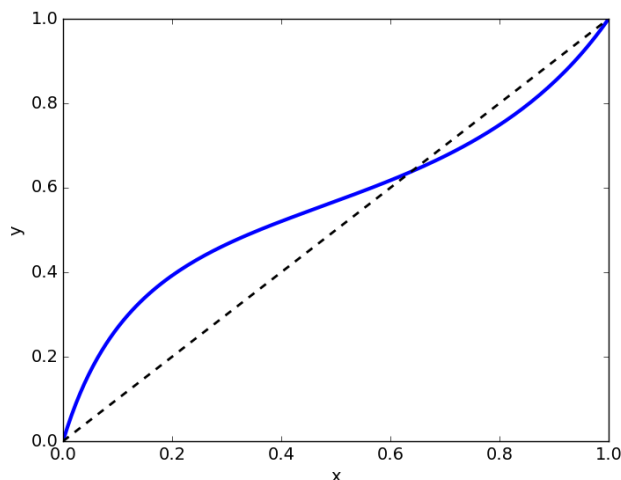


Figure 1 TBA mole fraction y in the saturation vapour versus the TBA mole fraction x in the liquid solution at thermodynamical equilibrium at $T = 35^\circ\text{C}$ (solid line). The dashed line is the $y = x$ line and serves as a guide for the eye.

2 Experimental details

2.1 PFG-NMR.

The PFG-NMR data were recorded using standard 5 mm NMR tubes in a Diff60 diffusion probe, using a standard 3-pulses stimulated echo (STE) sequence.

This NMR technique provides access to the self-diffusion properties of liquids, by monitoring the magnetization intensity $I(q, \Delta)$ versus a wave vector q for a given diffusion time Δ . The NMR vector q is proportional to the pulsed magnetic field gradient intensity used in the experiment:

$$q = 2\pi\gamma\delta g \quad (4)$$

where γ is the gyromagnetic ratio of the observed nucleus, g and δ are respectively the amplitude and duration of the pulsed field gradients. q measures the reciprocal distance over which the diffusive motion is probed, typically about $1\mu\text{m}^{-1}$ in a PFG-NMR experiment.

2.2 Additional NMR results : ^1H NMR chemical shift

The binary liquid mixtures of TBA and toluene in different compositions confined in MCM-41 were studied by ^1H Nuclear Magnetic Resonance Magic Angle Spectroscopy (NMR). Room temperature measurements were carried out on both bulk and confined liquid mixtures. The four peaks present in the NMR spectrum (see figure 2) are assigned to the methyl groups of TBA and toluene between 1 ppm and 2 ppm, to the phenyl ring of toluene around 7 ppm and the last one to the hydroxyl group of TBA. The chemical shift of this $-\text{OH}$ group appears to be very composition dependent and ranges from 5 ppm to -1 ppm.

We plot this relative change in chemical shift for both bulk and confined mixtures in figure 3. The solid line shows the change in chemical shift of the $-\text{OH}$ group in bulk mixtures. We first notice a general linear dependence of this shift versus composition in the whole concentration range except below 20% TBA (see dashed and solid line). Beyond this point, there is a much faster decrease in chemical shift values upon lowering the TBA concentration. This behaviour is reminiscent of the one observed for other bulk solutions of toluene and methylcyclohexane (MCH),³ where Raman spectroscopy studies have revealed the existence of higher order self-associated species of TBA such as tetramers, hexamers and dimers, formed thanks to hydrogen-bonding between individual molecules. Upon strong dilution of TBA with MCH, it was found that the population of these aggregated multi-molecular species start to disappear below 20% of TBA in favour of the monomers population. The NMR chemical shift of the TBA $-\text{OH}$ group is an observable directly related to the average of

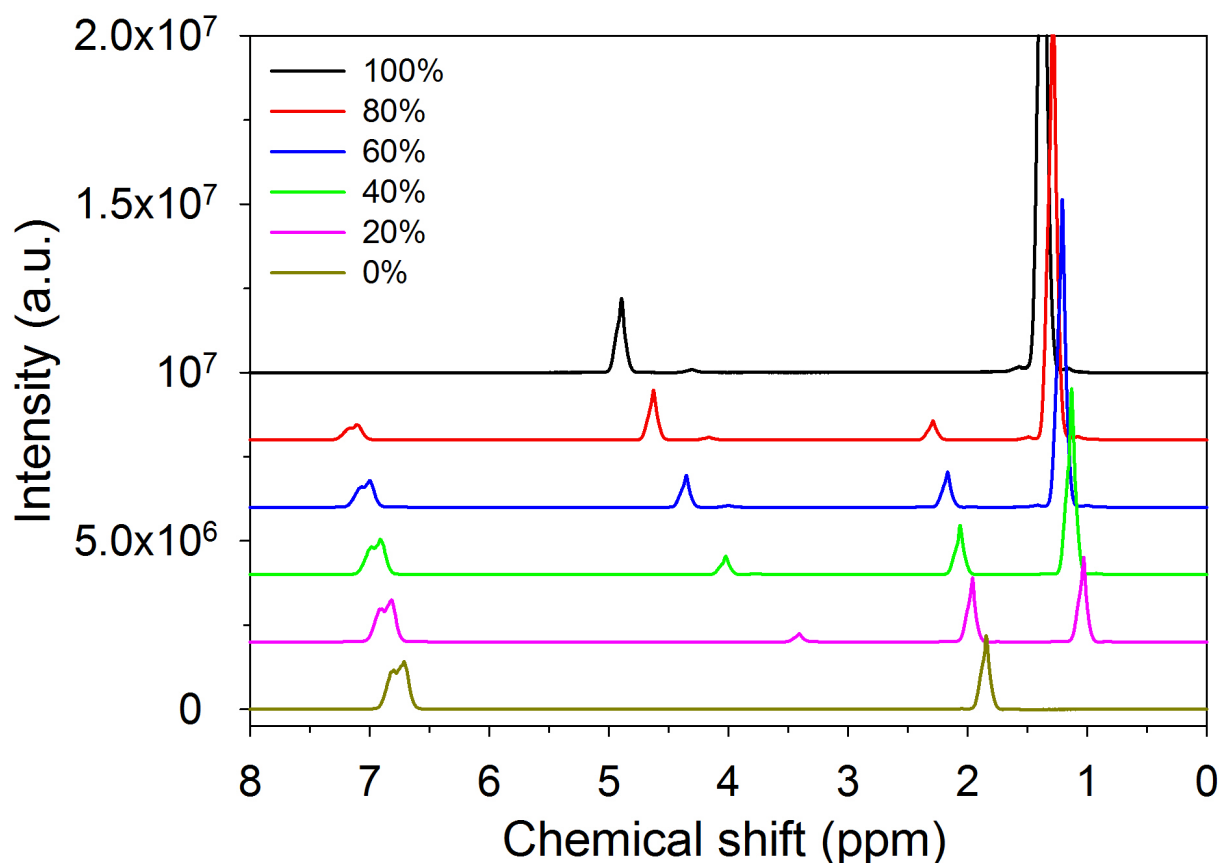


Figure 2 ^1H NMR spectra TBA:TOL bulk solutions of various TBA volume fractions.

the n -mers populations, and suggests that monomers also dominate in the bulk TBA:TOL solutions up to 20% TBA volume fraction.

The scenario under confinement is notably different. We notice (see solid circles in figure 3) that the $-\text{OH}$ chemical shift does linearly continue shifting to lower values with lowering concentration of TBA. The deviation from this linear behaviour at high TBA dilution is no longer observed in confinement. Thus, there evidently exists a persistent hydrogen-bonded network beyond what is known so far about the formation of higher order self-associated species of TBA and aggregated TBA clusters.

2.3 Vapour Sorption Isotherms.

The adsorption of binary gas mixture of TBA and toluene was carried out by the VTI-SA+ Vapour Sorption apparatus from TA instruments using nitrogen as a carrier gas. The two liquids, TBA and toluene were mixed together in a desired ratio and filled into the reservoir. The reservoir was maintained at 35°C , which was sufficient to vaporize the liquid mixture to a binary gas mixture, thanks to high volatility of the two liquids at room temperature itself. Dry nitrogen gas was connected to the setup and its pressure was maintained at 1.4 bar approximately in order to create a flow of the gas from the nitrogen cylinder to the apparatus. A flow of nitrogen gas went and mixed with binary gas mixture located in the evaporator, forming an organic vapor carried by nitrogen with a partial pressure corresponding to the binary liquid saturating pressure. This saturated gas flow is then mixed with a second flow of dry nitrogen gas in order to tune the resulting partial pressure. The concentration of the organic vapor in the gas stream reaching the sample is determined by the fraction of gas going through the organic solvent evaporator and the fraction of dry gas by using mass flow controllers, one for dry nitrogen and the other for nitrogen saturated with organic vapor. The mixture of dry nitrogen and binary gas was sent to the sample chamber consisting of a microbalance with two pans, one of which contained MCM-41 powder, while the other was left empty as a reference for measuring the change in weight of the

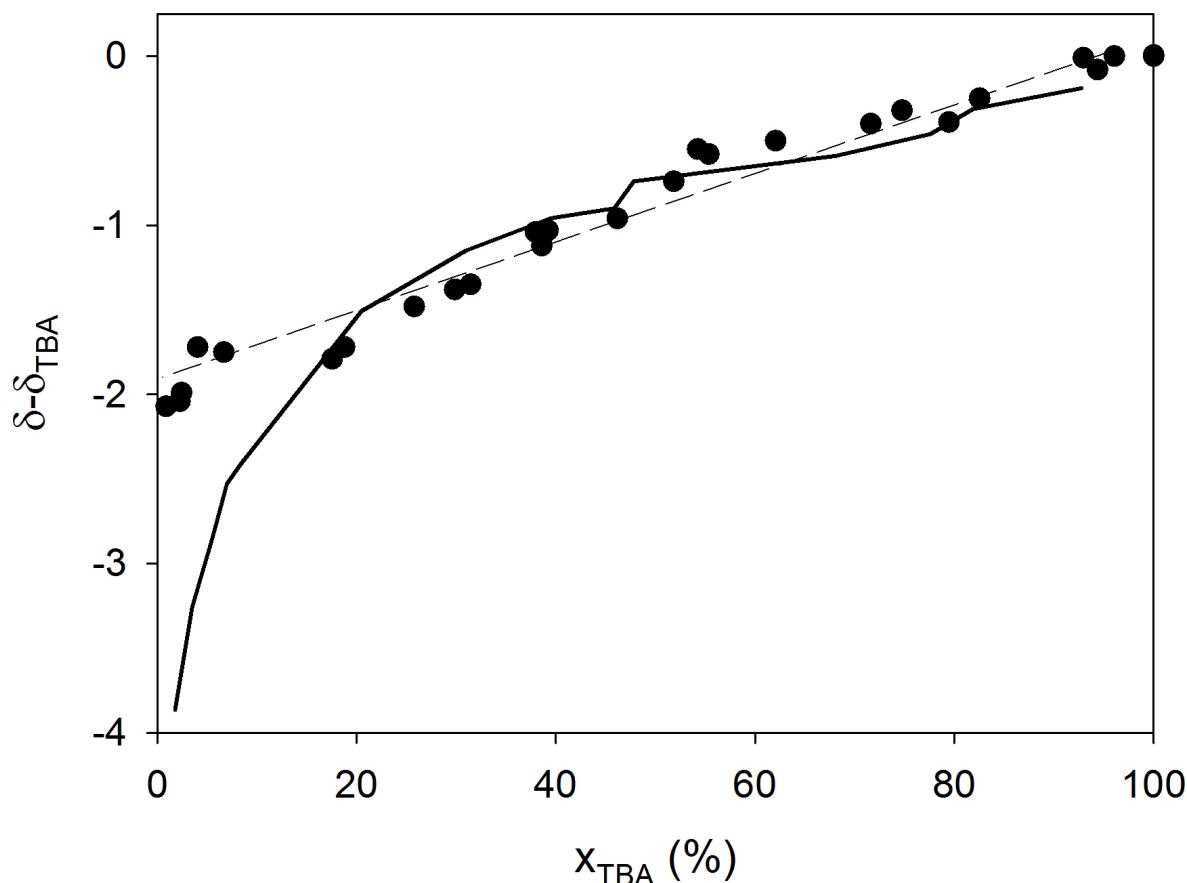


Figure 3 Composition dependence of the chemical shift of TBA:TOL solutions : bulk (solid line), or confined in MCM-41 (solid circles). The dashed line is a guide for the eye.

sample.

A drying step prior to the adsorption process was carried out, where the powder was heated to 120 °C, at a heating rate of 2 °Cmin⁻¹ under dry nitrogen flux for 120 minutes to remove any possible remaining adsorbed solvents or water inside the pores of MCM-41. After the completion of this step, a mixture of binary gas and nitrogen was being sent to the sample. The partial pressure steps which we denote by $\frac{P}{P_0}$, where P_0 is the saturating pressure for the binary gas and P is the partial pressure of the binary gas, were increased from 0 to 0.95 and decreased from 0.95 to 0 again during the adsorption and desorption steps respectively. The adsorption of gas on the MCM substrate was quantified at equilibrium. The equilibrium criterion in our experiments before moving on from a certain partial pressure step to the next one was a change in weight of the sample lower than 0.0010 % during at least 5 minutes. Both the sample cell and reservoir (saturator) of liquid are maintained at the same temperature (35 °C), with an accuracy of a few degrees. The increase/decrease in mass of the sample during adsorption/desorption respectively was recorded as percentage-change in mass of the sample and was plotted against increasing/decreasing values of $\frac{P}{P_0}$. The liquid reservoir was filled with TBA and toluene mixtures in different compositions, ranging between pure toluene and pure TBA.

Several liquid bath compositions have been studied, the corresponding list of TBA volume fractions is : 0.0, 0.2, 0.5, 1.0, 2.0, 5.0, 10.0, 30.0, 50.0, 70.0, 90.0 and 100.0 %.

2.4 Surface tension measurements.

Surface tension of the bulk liquid mixtures in air were measured in a Teclis "tracker" setup using the drop-shape method. The liquid mixture is prepared and inserted in a glass syringe. A droplet of liquid is created by a small pressure on the syringe piston and let to hang below the needle tip. The droplet is surrounded by air atmosphere which temperature is controlled by a thermoregulated liquid circulation system. An image of the droplet geometry is recorded using a focussed camera. The image analysis provides the curvature radii, the volume and the outer surface of the droplet, which can be used to derive the surface tension γ_b by numerically solving the Young–Laplace equation.

References

- [1] B. E. Poling, J. M. Prausnitz and J. P. O'Connell, *The properties of liquids and gases*, McGraw-Hill, New-York, 5th edn, 2001.
- [2] V. Martínez-Soria, M. P. Peña and J. B. Montón, *Journal of Chemical & Engineering Data*, 1999, **44**, 148–151.
- [3] A. R. Abdel Hamid, R. Lefort, Y. Lechaux, A. Moréac, A. Ghoufi, C. Alba-Simionesco and D. Morineau, *The Journal of Physical Chemistry. B*, 2013, **117**, 10221–30.