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Interfacial tension in water/n-decane/naphthenic acid systems predicted by a combined COSMO-RS theory and pendant drop experimental study

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The interfacial tension of systems containing water, n-decane, and model naphthenic acids were investigated using a predictive model based on COSMO-RS theory and experimental pendant drop measurements. Five naphthenic acid homologues that are considered to be representative of surfactants inherent to crude oil were dissolved in n-decane at equal concentrations. The interfacial tensions of the five systems at an acid concentration of 1.66 mol% relative to n-decane were experimentally determined to be 27-30 mN/m. The interfacial tensions of the five different acid-decane phases against water were also predicted using density functional theory (DFT) calculations and COSMO-RS theory. The accuracy of the predictions was very good as confirmed through pendant drop measurements of the interfacial tension. The mean-absolute-deviation between experimental and predicted values was 2.6 mN/m thus demonstrating the high predictive power of COSMO-RS theory for calculating the interfacial tension at oil-water interfaces in the presence of surface-active compounds.

Introduction

Consideration of interfacial phenomena is important to many chemical industries, and crucial to several subdivisions of the oil and gas industry.¹ Essentially, after conventional recovery methods, the residual oil in the reservoir is either inaccessible due to reservoir heterogeneities or retained in the rock due to capillary forces.² The magnitude of the capillary forces is proportional to the interfacial tension of the oil/water system³ and some more effective extraction methods rely on decreasing the interfacial tension^{4–7} making it worthwhile to investigate liquid-liquid interfacial phenomena.

Experimentally, interfacial tension can be measured using several techniques, including, pendant drop measurements.⁸ In contrast, computational modelling of interfacial tension is most often done using a single method – molecular dynamics. This method has been applied to model the surfactant structure at interfaces,^{9,10} the effect of supercritical CO₂ on the interfacial tension,^{11,12} and the effect of aqueous ions on interfacial tension.¹³

However, it was recently proposed by Andersson et al.,¹⁴ to utilise the COSMO-RS solvation theory in conjunction with

density functional theory (DFT) quantum mechanical calculations to compute the interfacial tension several orders of magnitude faster than molecular dynamics simulations. COSMO-RS theory, developed by Klamt et al.^{15–17} as an extension of their original COSMO dielectric continuum solvation model, has already shown its great applicability to solvation phenomena.¹⁸ Some examples thereof are the good predictions of COSMO-RS theory of aqueous pK_a,¹⁹ non-aqueous pK_a,²⁰ and adsorption constants and enthalpies of adsorption for organic compounds at an air-water interface.²¹ Also, the theory has been used for predicting changes in pK_a of organic acids and bases when at an organic/aqueous interface.²²

Our research utilises COSMO-RS and pendant-drop measurements to investigate the interfacial tension of water/n-decane/surfactant systems. The surfactants chosen are five members of a homologous series of model naphthenic acids: cyclohexane carboxylic acid, cyclohexyl acetic acid, 3-cyclohexyl propionic acid, 4-cyclohexyl butyric acid, and 5-cyclohexyl valeric acid. (See Figure 1).

Figure 1: Model naphthenic acids included in the study. From left to right: Cyclohexane carboxylic acid, cyclohexyl acetic acid, 3-cyclohexyl propionic acid, 4-cyclohexyl butyric acid, 5-cyclohexyl valeric acid. These acids are representative of naphthenic acids, that are naturally occurring surfactants in crude oil.²

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Therefore, this study seeks to answer three questions: What are the interfacial tensions of the five model water/n-decane systems containing solvated naphthenic acids as surfactants, and can COSMO-RS accurately predict the interfacial tension of these? Lastly, the aim is to arrive at an understanding of how the length of the surfactant's hydrophobic tail impacts interfacial tension?

Computational methods

COSMO-RS solvation theory for prediction of interfacial tension

The CONductor-like Screening Model for Real Solvents (COSMO-RS) solvation theory is an extension to the CONductor-like Screening Model (COSMO) dielectric continuum model. The COSMO solvation model assumes that the solute is embedded in a conductor representing the solvent. This greatly simplifies the calculation of the screening charge densities acting onto the segmented molecular surface using computational methods.¹⁵ COSMO-RS uses this idealised solvation state as a reference state. Fluids are then treated as ensembles of pairwise interacting surface segments that have a surface charge density. The composition of an ensemble is determined by the molecular composition of the fluid and the screening charge densities of the surface segments of the molecules in the fluid.¹⁶ Applying statistical thermodynamics to this ensemble allows for the calculation of chemical potentials of solutes in solvents relative to the ideally screened reference state.¹⁷ From the chemical potential, the two-phase partitioning of solutes, and solvation energies amongst others can be calculated. COSMO-RS calculates energies relative to the reference state using only inputs from the original quantum mechanical calculation. Thus, COSMO-RS calculations can be performed using maximum two DFT calculations for each species in the system (gas + conductor reference state). Because COSMO-RS treats a molecule as an ensemble of charged surface segments it enables the calculation of the chemical potential of a solute at a flat interface when it is interacting with two phases. This is achieved by letting one portion of the molecule's surface segments interact with one

Figure 2: Visualisation of the segmented surface of 3-cyclohexyl propionic acid. The color indicates the surface charge density of the surface segment, where red and blue represent negative and positive charges respectively.

Figure 3: Illustration of the COSMO surface of cyclohexane carboxylic, where one part is interacting with the organic phase, while the other is interacting with the aqueous phase.

phase, while the other interacts with the other phase (Figure 2).²³ Andersson et al.¹⁴ utilised this interfacial solvation energy calculation along with the calculation of the two-phase equilibrium composition of the system to calculate the interfacial tension of systems in an iterative manner. The same method is applied in this study.

Conformer search

Molecules were drawn using Avogadro^{24,25} software with a subsequent MMFF94^{26–30} geometry optimization. Then, for each molecule, conformers were generated using the Open Babel Confab code.³¹ The geometries of the generated structures were then optimized using the semi-empirical PM7 method³² in Gaussian16.³³ Optimized structures that did not terminate normally, were discarded. After this they were sorted by *Root-Mean-Square-Deviation* using the Kabsch algorithm.^{34,35} Structures with RMSD below 0.1 were removed to identify unique structures and to avoid artificial degeneracies in the following Boltzmann distribution calculation. In this calculation, conformers amounting to less than 0.5% of the population were removed. An overview of the sorting process is outlined in the supporting information. A total of 3, 6, 24, 44, 71 conformations for the five carboxylic acids, as sorted by increasing chain length, was found.

DFT calculations

The resulting conformations were geometry optimized, as embedded within a conductor, i.e. using the COSMO assumption with infinite dielectric constant. It was confirmed from analysis of vibrational frequencies that all optimised geometries represented energetic minima. The DFT calculations were performed using the TURBOMOLE software package,^{36,37} in which, COSMO has been implemented.³⁸ The DFT calculations utilised the BP86 exchange-correlation functional^{39,40} and def-TZVP basis set.^{41,42}

COSMO-RS calculations

COSMO-RS calculations were performed using the COSMOtherm program,^{43,44} For the calculations, water and n-

decane COSMO-files were found in the COSMOtherm database at the BP-TZVP level, while the carboxylic acids were generated from the DFT calculations. The chosen parameterisation was BP-TZVP_C30_1601.⁴⁵ Using COSMOtherm, the phase partitioning of the individual carboxylic acids was calculated as expressed by the logP of the distribution of the acids between the n-decane phase and the water phase. Calculation of interfacial tension was done using the method and implementation as developed by Andersson et al.¹⁴ These calculations, were executed using a computer program written in the python language by Nikolajsen et al.⁴⁶ in accordance with the method of Andersson et al. The program utilises the *liquid-liquid extraction (LLE)* and *flatsurf* modules of the COSMOtherm program to calculate the interfacial tension of the system. The calculations were done at a concentration of acid in n-decane of 1.66 mol%.

In order to keep the mass balance in the system, the liquid liquid extraction calculation was based on mole numbers. Generally, the COSMO-RS calculations of the interfacial tension converged in a matter of minutes for the systems considered.

Experimental methods

Interfacial tension instrumentation

The interfacial tensions were measured with the pendant drop technique using the Attension Theta Optical Tensiometer instrument from Biolin Scientific. The instrument records images of a drop suspended from a needle into another fluid with which the drop does not mix. From the shape of the drop, the interfacial tension can be calculated when the density difference between the two phases are known.⁴⁷ The mathematical relation is given in Eq. 1.

$$\gamma = \frac{\Delta\rho g r_o^2}{\beta}, \quad (1)$$

Where the interfacial tension is γ and $\Delta\rho$ is the density difference between the liquid phases, g is the gravitational constant, r_o is the radius of curvature at the drop's apex, while β is a shape parameter that is unique for each drop shape and is determined by the computer software.^{48,49}

Density measurements of the surfactant solutions and water were taken on an Anton Paar DMA 4500 M density meter, and it was measured at 22°C – the temperature of the laboratory. Measured densities are shown in supporting information.

Chemicals

The five carboxylic acids were acquired from Sigma-Aldrich and used as delivered. Purities of the acids were 98%, 98%, 99%,

99%, and 98%, respectively, for homologues 1 through 5. n-decane was from local stock and was purified by passing it through a clean silica column four times. After this procedure, the interfacial tension was measured and found to be stable over 600 seconds, signifying no noteworthy diffusion of surface-active impurities to the surface. For the measurements, Milli-Q® water (Resistivity of 18.2MΩcm) was used.

Surfactant solutions were prepared by weighing out the appropriate amount of the liquid carboxylic acid into a clean container and adding the purified decane using a clean glass pipette until a concentration of 1.66 mol% was reached.

Procedure

Measurements were conducted by immersing a 500 µL gas-tight syringe with a J-shaped needle into a cubic quartz cell containing Milli-Q® water. Drops of surfactant solution or pure n-decane were created manually with the syringe and measurements were recorded using the OneAttension software. Measuring on drops that are close to the maximum volume that can be sustained improves the precision of the method,⁵⁰ and drops were measured at volumes around 95% of the maximum volume. For each system, three drops were measured, and, after forming the drop, it was repeatedly imaged every fourth second yielding a total of 46 images over a period of 180 s. The experimental data for each system is thus three replicate measurements, each consisting of 46 measured IFT values. In between measurements on different salt solutions, the quartz cell and needle were cleaned, before the quartz cell was filled with a new aqueous phase. IFT values for pure water against surfactant solutions were conducted for all five acids. For cyclohexane propanoic acid the IFT value decreased by a unit before stabilizing after ten minutes, after which the drop was imaged repeatedly over 180 s.

Statistical data treatment

Obtained data sets were checked for outliers using the two-tailed Grubb's test for outliers⁵¹ at a confidence level of 95%. Using the Shapiro-Wilk test for normality⁵² with an alpha level of 0.05 it was found that around 95% of data sets were normal distributed. Hence, all data sets were assumed to be normal distributed. Uncertainties were expressed as 99.5% confidence intervals computed from the standard deviation of the measurements. The uncertainty on the system's average IFT was calculated as the square root of the sum of the squared uncertainties of each replicate as per standard error propagation procedures.

Accuracy and precision

The accuracy of the method was tested by measuring the IFT between pure n-decane and water. Obtained average IFT results for four measurements measured over 600s were 51.5 mN/m, 52.0 mN/m, 51.4 mN/m, and 51.2 mN/m. Compared to literature values in the range of 51.1 mN/m to 53.2 mN/m, the accuracy is very good.^{53–57} Uncertainties were found to be between ± 0.1 mN/m and ± 0.3 mN/m when calculated as described in Statistical Data Treatment. Additionally, by using repeated measurements on the same system, it was found that measured values could vary up to ± 0.23 mN/m simply from small changes in the position of the needle when repositioning it after the cleaning procedure. Consequently, the total uncertainty of the systems in this study are given simply as the sum of this uncertainty and the random uncertainties mentioned in Statistical Data Treatment. The simple summation of uncertainties allows for a wider margin of error on the average value.

Results

Phase partitioning

The calculated partition coefficients (Table 1) reveal that in two phase systems, where the carboxylic acid is initially solubilised in the n-decane phase, most of the acids are best solubilised in the organic phase. The only exception is cyclohexane carboxylic acid, where more of the acid is predicted to diffuse into the aqueous phase than is retained in the organic phase. Also, expectedly, the water solubility decreases as the chain length of the hydrophobic tail of the acid surfactants increase.

Calculated IFT

Table 1 shows the calculated interfacial tension values for the five different systems each containing one carboxylic acid in 1.66 mol% relative to the n-decane phase. The results are from calculations using the absolute number of moles to represent the composition of the system. Looking at the trend in IFT when increasing the chain length of the surfactant, the smallest acid cyclohexane carboxylic acid is predicted to produce the highest interfacial tension, while there seems to be a minimum at 3-cyclohexyl propionic acid, before the interfacial tension increases again for the two largest acids. The minimum at 3-cyclohexyl propionic acid is the result of the following. As the oil solubility of the naphthenic acid increases, there is less energetic gain in migrating to the interface, but since it is an equilibrium, the higher concentration in the oil phase fosters migration to the interface. For the aqueous phase, the energetic gain increases with chain length while the concentration decreases. Evidently, there is an optimum between these two developments in both phases resulting in the highest interfacial coverage and, consequently, lowest IFT for 3-cyclohexyl propionic acid.

Comparison with experiment

Table 1: Calculated values for logP for the phase partitioning, interfacial tension, and the surface mole fraction from the interfacial tension calculation. Lastly, the experimental IFT is listed as well.

	logP (22°C)	IFT (Calc.)	Surface Mole Fraction	IFT (Exp.)
Cyclohexane carboxylic acid	0.17	28.8	0.44	30.4 $\pm$ 0.4
Cyclohexyl acetic acid	-0.27	25.7	0.48	28.8 $\pm$ 0.4
3-cyclohexyl propionic acid	-0.77	25.1	0.49	27.6 $\pm$ 0.3
4-cyclohexyl butyric acid	-1.3	26.0	0.48	29.6 $\pm$ 0.4
5-cyclohexyl valeric acid	-1.9	26.9	0.46	28.9 $\pm$ 0.4

Comparison with the measurements of the interfacial tension can be seen in figure 4. The quality of the predictions is good, with a mean-absolute-deviation (MAD) of only 2.6 mN/m. Considering that the original error estimate on the predictive method is ± 3 mN/m¹⁴ and that experimental uncertainties were around ± 0.4 mN/m, the experimental interfacial tension is predicted with reasonable accuracy in all cases. The systems with cyclohexane carboxylic acid and 5-cyclohexyl valeric acid are accurately predicted when considering errors on both the calculation and experiment. The predictions are also able to reproduce the trend in the interfacial tension versus the length of the hydrophobic backbone of the carboxylic acid.

Sensitivity Analysis of the IFT calculations

To probe the sensitivity of interfacial tension towards the concentration of the acid, a series of calculations were done for acid concentrations in the range 0.001-10 mol%. The results are shown in Figure 5, where it is seen that the concentration dependence is overall quite similar for all the acids in our study. However, subtle differences occur. The slope of the curves in the active region (~ 1 mol% acid), i.e. the change in interfacial tension as a function of acid concentration varies systematically with acid size. The concentration dependence is largest for the smallest acid (cyclohexane carboxylic acid) and smallest for the largest acid (5-cyclohexyl valeric acid). Contrary to this observed trend, the concentration at which the interfacial tension begins to be affected by the presence of the acid (~ 0.1 mol%) has the opposite trend, where the largest acid(s) become active at a lower concentration than the smallest acid.

We do not currently know the physical reason for the variations in concentration dependence, but the range of acids we have

Figure 4: Comparison of calculated and experimental interfacial tension values. Error bars are added to express the uncertainty on the experimental value (vertical error bars) and computational values (horizontal error bars).

Figure 5: Development of interfacial tension versus concentration for the five acids.

chosen have a partition coefficient P between oil and water that is close to 1 ($\log(P) = 0$), which could be a contributing factor. It is beyond the scope of this study, but investigating even longer homologues could help understand the observed trends.

Discussion

The prediction of the interfacial tensions is satisfactory considering the error estimates on both the computational and experimental results. Sayed et al.⁵⁷ investigated the same homologues as this study with the exception of cyclohexyl acetic acid, at similar concentrations and reported interfacial tension values of 29.1 mN/m for cyclohexane carboxylic acid, while for the propionic-, butyric-, and valeric acid derivatives they report values of 25.4 mN/m, 27.8 mN/m, and 28.2 mN/m respectively. These values are in good agreement with our findings, especially with the predicted IFTs. One thing that should be noted is the timescale of the experimental measurements. COSMOtherm computes thermodynamic properties at equilibrium conditions, while the experimental measurements were conducted over a period of 180s for each drop. It has previously been found that diffusion of surfactants to surfaces and interfaces and the establishment of equilibrium conditions is seldom complete after 180s^{50,58,59}. We monitored the development of interfacial tension versus time while conducting the measurements, which indicates stable interfacial tension in the measuring interval. However, it is quite possible that over longer time scales, the system might reach an equilibrium state with slightly lower interfacial tension values compared to the ones stated in this work, which would agree better with the theoretical predictions.

Another point in the comparison is that our calculations underestimate all the measured interfacial tensions by at least 2 mN/m, which is still smaller than the typical accuracy from IFT predictions using COSMO-RS, 3 mN/m.¹⁴ However, as this study considers only five surfactants, it is difficult to assess whether this is a systematic deviation of the COSMO-RS treatment.

One possible source of error is the somewhat naive neglect of dissociation of the acids in the COSMO-RS calculations, as the input for these were the protonated species. Using COSMO-RS, the pK_a 's of the acids were calculated to be in the range of 4.7–4.8, and indeed dissociation is possible. Several

researchers have noted that the pK_a of a species at an interface is drastically different from that of the bulk phase, off-set by at least one unit, meaning that species at the interface is deprotonated less severely than would be expected.^{22,60–62} Nevertheless, accounting for dissociation of the acids in the calculation would likely produce even lower IFT values considering the increased affinity of the deprotonated species for the interface. The effect on interfacial tension from deprotonation would be expected to be larger for the smallest (more water soluble) acids, as deprotonation in the oil phase is likely negligible.

As for the speed of the calculations, it is quite clear when considering the preparation of surfactant solutions, calibration of instrument, repeated measurements and the strict requirements to the cleanliness of the apparatus, that determining the interfacial tension of systems experimentally is a quite lengthy procedure relative to the COSMO-RS computations. The real strength of COSMO-RS is in its definition of a reference state and the fact that it requires only a database of DFT calculations for compounds. These two properties in combination allow for very cheap calculations of multiple different thermodynamic properties of fluid mixtures.

Conclusion

The interfacial tension of five n-decane/water systems containing n-decane solubilised naphthenic acids has been determined by the pendant drop method. They were found to be in the range of 27.6 mN/m to 30.4 mN/m showing a non-monotonous development as the length of the surfactant is increased. It was found that for the series of homologues, the lowest interfacial tension was for 3-cyclohexyl propionic acid. The measured values were accurately predicted by the computational method developed by Andersson et al., using density functional theory calculations and the COSMO-RS implicit solvation model. Thus, it has also been shown, that the computationally cheap COSMO-RS calculations predict the interfacial tension values of oil-water-carboxylic acid systems very satisfactorily. The COSMO-RS theory based model is therefore promising and applicable for the efficient and fast screening of multiple interfacial systems.

Conflicts of interest

There are no conflicts to declare.

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