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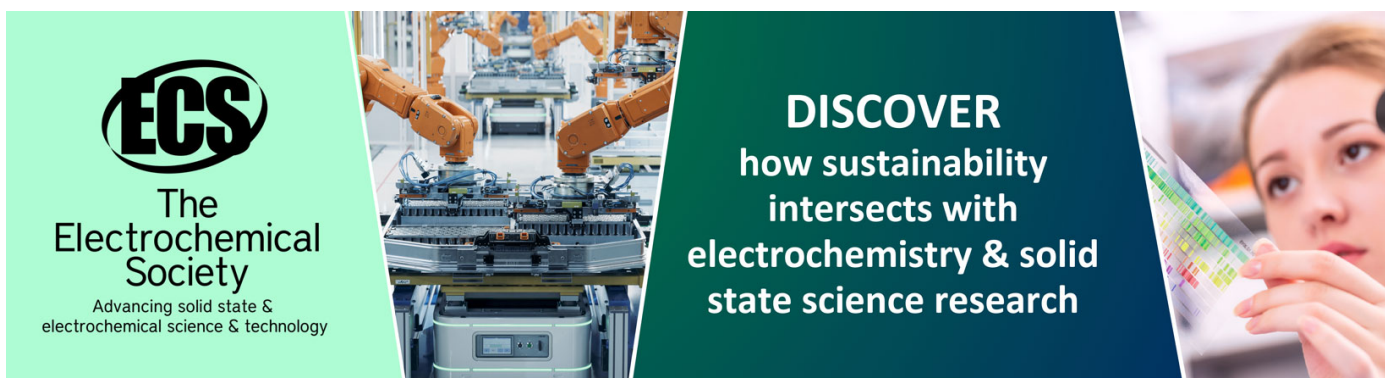
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To cite this article: A Galia *et al* 2008 *J. Phys.: Conf. Ser.* **121** 022022

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Inclusion complexes of triphenylphosphine derivatives and peracetylated- β -cyclodextrin in supercritical carbon dioxide

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Abstract. The supramolecular chemistry of peracetylated- β -CD (perAc- β -CD) as a host for triphenylphosphine derivatives has been studied in supercritical (scCO₂) using UV absorption spectroscopy. It was found that the association constant in scCO₂ at 40 °C and 300 bar is 10 to 1000 times smaller compared to analogous systems in aqueous solvent. Studies of the thermodynamics of the inclusion process found an enthalpy of association of -30 kJ/mole and an entropy of -55 J/moleK. This difference with respect to water is attributed to the absence of the hydrophobic effect in scCO₂ due to the much smaller polarity of scCO₂ versus water. To further explore the effect of the solvent on the association constant, values of solvent polarity intermediate between the limits of scCO₂ and water could be useful. To this end, methanol is added to the scCO₂ as a cosolvent to modify the overall polarity. By taking advantage of the tunability of the supercritical phase, a wide range of solvent polarity can be accessed by varying the temperature (35 to 50 °C), pressure (200 to 400 bar), and mole fraction of methanol. This study is pursued to obtain a better comprehension of the inclusion process in CO₂-based supercritical fluids to make the association constant of the phosphine-perAc- β -CD system comparable to those observed in aqueous systems.

1. Introduction

Viewed as an alternative solvent system for industrial chemical syntheses, supercritical carbon dioxide (scCO₂) presents many opportunities and challenges in its application. The insufficient solubility of common organometallic catalysts in scCO₂ impedes its use for many reactions employing homogeneous catalysis. [1] In practice, limited solubility is a common problem for a wide range of solutes in scCO₂ and is sometimes resolved by modifying the compound to make it more CO₂-philic. Predominantly, this entails the addition of fluorinated groups which renders many compounds quite expensive and difficult to apply on an industrial scale.

The use of native β -cyclodextrin as a molecular host in aqueous solutions is well established as a means for enhancing the solubility of otherwise poorly soluble organic compounds. By forming inclusion complexes, the cyclodextrin increases the concentration of the organic compound in the aqueous phase and consequently, can increase reaction rates. This effect has been studied for the

inclusion interaction of water-soluble sulfonated triarylphosphines with β -cyclodextrin. It was found that values of the association constant (K_f) were often 10^3 to 10^4 with native β -cyclodextrin and up to 10^5 with modified analogues[2,3].

We have demonstrated an enhanced solubility of triarylphosphines in $scCO_2$ using a host-guest interaction between the phosphine and peracetylated- β -cyclodextrin (perAc- β -CD). [4]. Considering the high solubility of perAc- β -CD in $scCO_2$ [5], it could offer a means to increase the solubility of organometallic catalysts without changing their structure and potentially altering their activity. For this approach to be practical, the association constant should be large to encourage the solubility of the guest compound. Recently, studies of three candidate arylphosphines were conducted to determine which host-guest interactions would be most favorable in $scCO_2$. [6] The compounds diphenyl(4-phenylphenyl)phosphine, diphenyl[4-(4-tert-butylphenyl)-phenyl]phosphine, and diphenyl(4-adamantylphenyl)phosphine (AdTPP) were found to have association constants of near 10^2 . The strongest host-guest interaction among these phosphines was the AdTPP for which the K_f was twice that of the other candidates.

The smaller K_f of these phosphines in $scCO_2$ relative to similar phosphines in water, was attributed to the absence of a solvent hydrophobic effect in $scCO_2$. Thus, a more polar supercritical phase may lead to a more favorable host-guest interaction. The tunable properties of the supercritical phase offer an opportunity to explore the influence of the solvent on the complexation process. A wide range of solvent polarity can be accessed by varying the temperature (35 to 50 °C), pressure (200 to 400 bar), and mole fraction of methanol when used as a modifier of the supercritical phase. As demonstrated by studies of the dielectric constant of methanolic $scCO_2$, large increases in the dielectric constant of the supercritical solution occur with the addition of a relatively small mole fraction of methanol. [7] If we take the dielectric constant of the solvent as an indicator of solvent polarity, significant enhancements of the polarity may be obtained with small amounts of methanol. For example, a 20% increase in dielectric constant, relative to pure $scCO_2$, is expected from the addition of 8 mole % of methanol. The present work investigates the complexation between AdTPP and perAc- β -CD in pure $scCO_2$ and in methanolic solutions of $scCO_2$ using the adjustable solvent polarity to probe the thermodynamics of the host-guest interaction.

2. Experimental

2.1. Materials

Peracetyl- β -cyclodextrin [$(C_{12}H_{16}O_8)_7$; $M_w = 2017.8$ g/mol] and HPLC-grade methanol purchased from Aldrich Chemicals, and carbon dioxide (99.998% purity) purchased from Air Liquide were used without further purification. Diphenyl(4-adamantylphenyl)phosphine (AdTPP) ($M_w = 396.5$ g/mol) was prepared as reported in the literature. [6]

2.2. Apparatus

The experiments were performed in a windowed stainless steel reaction vessel. The reactor was fitted with a pressure transducer monitored by a digital voltmeter. Temperature was measured with a K-type thermocouple with a resolution of 0.1 °C. A small magnetic stirring bar was placed into the reactor to promote mixing. The free volume of the vessel was determined to be 24.17 mL. The reaction vessel was placed in an insulated enclosure and heated by a forced-air heating element regulated by a temperature controller.

Samples of the phosphine and perAc- β -CD were weighed and deposited into the reaction vessel as solids. Methanol was added to the vessel using a syringe after introduction of the dry samples. The quantity of methanol was determined gravimetrically. The vessel was then charged to the required pressure with liquid CO_2 using a high-pressure hand pump after which the vessel was weighed again to determine the mass of CO_2 . Typical operating conditions for the experiments were 30 ± 0.8 MPa at a temperature of 40 ± 0.2 °C. This gives a density of 0.9 g/mL.

Absorbance measurements were made using an Avantes SD2000 spectrometer equipped with a DH2000 deuterium light source. All connections between components and optical fibers were made with SMA 905 connectors. Light from the deuterium lamp was connected to the reaction vessel by an interface optic which collimates the input beam to an approximately 10 mm diameter spot inside the reactor and condenses the output beam to couple with the detector-side fiber optic. The sapphire optical windows on the reaction vessel are 20 mm diameter and approximately 20 mm thick such that the path length for absorbance measurements is 5 mm. The output beam was then sent the spectrometer. The spectrometer signal was recorded as transmitted intensity then converted to absorbance using a previously recorded blank spectra of carbon dioxide or methanol-CO₂ solution at equivalent operating conditions as the other experiments. It was determined experimentally that the blank spectra were invariant with respect to temperature.

2.3. Mathematical models

The mathematical models used for the determination of the association constants are derivations of the Beer-Lambert Law for systems of two absorbers. Both have been described thoroughly in the literature. [6,8] Method 1 calculates K_f at each wavelength in the spectrum via a least-squares minimization. Method 2 is an algorithmic approach which uses the integrated area beneath the first derivative spectral curve. This approach thus calculates a single value of K_f over the selected spectral interval rather than individual values at each wavelength.

3. Results

Shown in figure 1 are absorbance spectra recorded at 45 °C for three molar ratios of AdTPP to perAc- β -CD in pure scCO₂. With increasing amounts of perAc- β -CD, a shoulder between 235 and 240 nm becomes more intense. This feature is attributed to absorbance arising from the complex. Relatively high ratios of perAc- β -CD were necessary to observe this change in the spectrum. The collection of data was limited on the one hand by too little difference between the phosphine and complex spectra

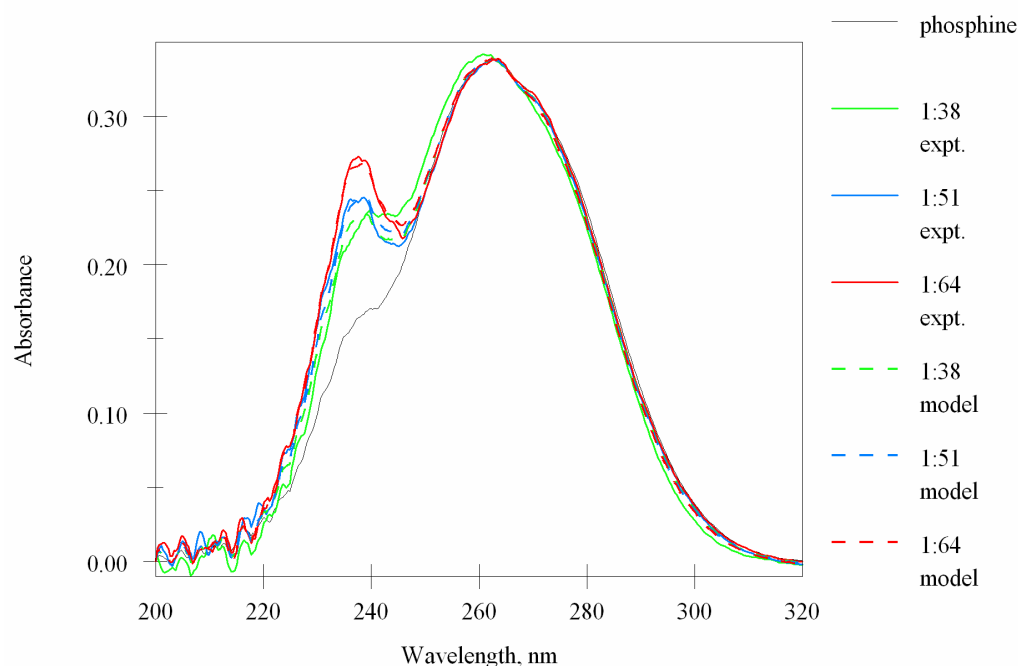


Figure 1. Experimentally measured absorbance spectra (solid lines) of 0.11 mM AdTPP with varying molar ratios of perAc- β -CD at 45 °C and 34 MPa, nominal density of 0.91 g/mL. Modelled spectra (dashed lines) are results from the calculation of K_f with Method 1.

below a ratio of 1:10 and the solubility limit of the perAc- β -CD above 1:70. Also shown in figure 1 are the calculated spectra resulting from Method 1 in which the three experimental spectra are fit to a single value of K_f . The match between the measured absorbance and the fitted result is quite good.

A series of spectra similar to those shown in figure 1 were recorded at 35, 40, 45, and 50 °C to determine the thermodynamic parameters of the inclusion process. The values of K_f determined at each temperature are presented in figure 2 as a Van't Hoff plot. From this relationship, the enthalpy and entropy of the process were determined to be -30 ± 2 kJ/mole and -55 ± 6 J/moleK, respectively. The thermodynamic values determined by the two methods of calculating K_f were equivalent within the experimental error. Compared to the thermodynamic properties found for *o*-, *m*-, and *p*-substituted monosulfonated triphenylphosphines in aqueous solutions (average $\Delta H^\circ = -41$ kJ/mole and $\Delta S^\circ = -57$ J/moleK), AdTPP has a similar behavior. [3] The entropy in both cases is effectively equivalent and more notably negative, signaling an entropy disfavored process. As in the case of the water soluble phosphines, AdTPP is only partially inserted into the perAc- β -CD cavity which leads to a reduction of its degrees of freedom that outweighs any positive entropic contribution from the displacement of solvent from host or guest. The AdTPP complex is enthalpy favored, however, its ΔH° is about 11 kJ/mole less negative than the water soluble analogs. This weaker interaction is reflected in the significantly small K_f values originally found for AdTPP in scCO₂.

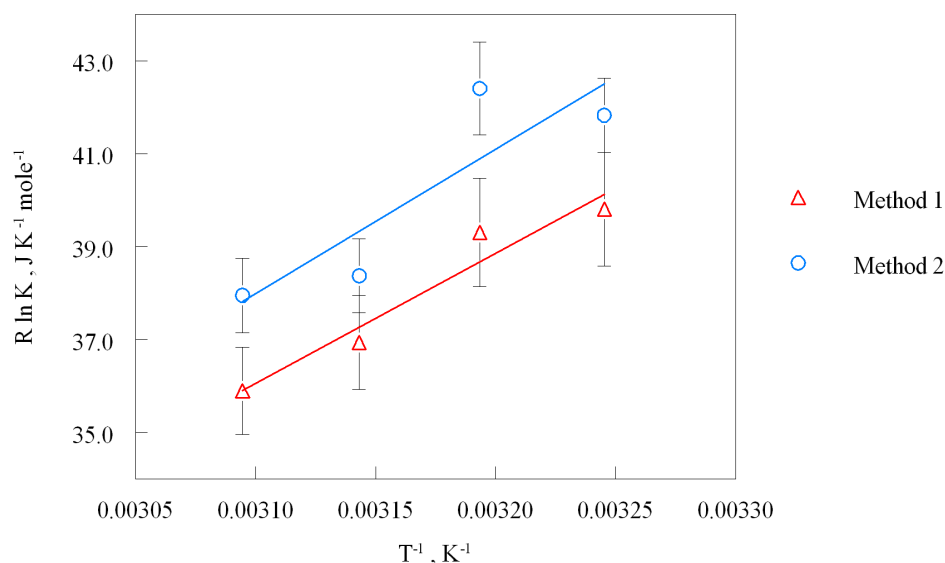


Figure 2. Van't Hoff plots for AdTPP.

Preliminary results of AdTPP inclusion reactions in methanolic scCO₂ show some important differences with respect to pure scCO₂. Three spectra from studies of AdTPP in 8 mole % methanolic scCO₂ are shown in figure 3. As before, a shoulder on the short-wavelength side of the spectrum appears in the presence of perAc- β -CD. In methanolic scCO₂ the absorbance maximum is about 30 % more intense with an equivalent amount of phosphine compared to figure 1. Additionally, the absorbance feature centered at 265 nm appears to decrease in intensity with high loadings of perAc- β -CD whereas in pure scCO₂ this feature was invariant. This part of the absorbance spectrum has been attributed to the two phenyl groups of the phosphine which are not inserted into the perAc- β -CD cavity. Thus, it is not yet clear what is the origin of this effect. From these sparse data, it is evident that the addition of methanol as a cosolvent has some effect on the host-guest interaction. It appears that there is a modest increase in the K_f and somewhat more negative values of both ΔH° and ΔS° .

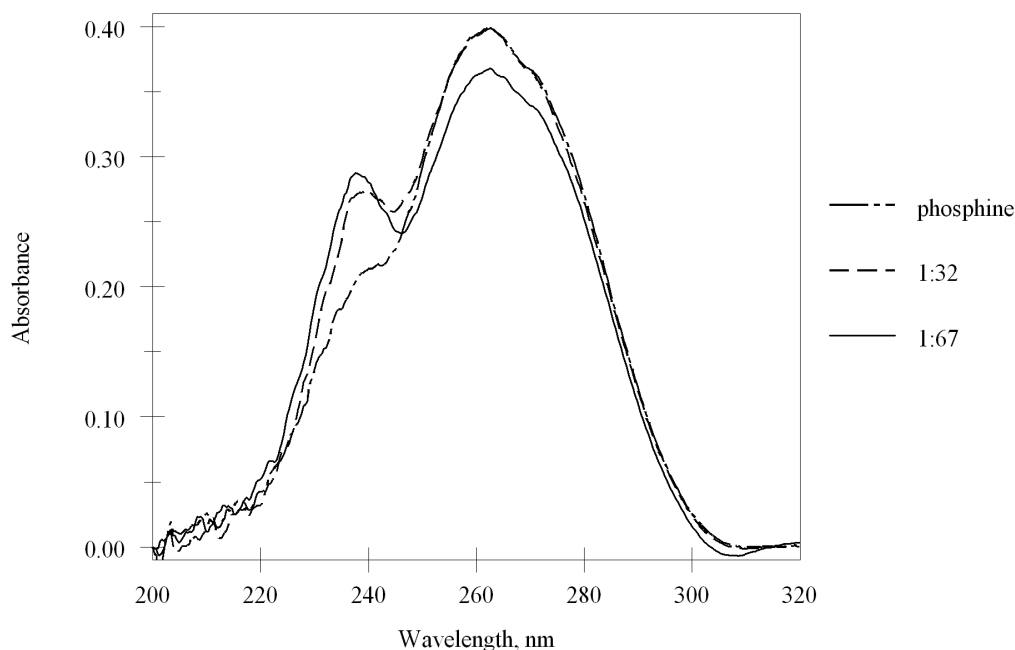


Figure 3. Absorbance spectra of 0.11 mM AdTPP with varying molar ratios of perAc- β -CD in 8 mole % methanolic scCO₂ recorded at 50 °C and 37 MPa, nominal density of 0.97 g/mL.

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