

QUARTERLY PROGRESS REPORT

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SUPERCritical THERMODYNAMICS OF SULFUR AND NITROGEN SPECIES

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ABSTRACT

Significant opportunity exists for the application of supercritical fluid (SCF) technology to coal processing, both for pretreatment of high sulfur coals, as well as liquefaction and treatment of coal liquids. Supercritical fluids are attractive solvents for a variety of coal processing applications because of their unusual solvating and mass transfer properties. Solubility studies have been carried out for a number of model coal and coal-liquid compounds, primarily in pure supercritical fluids. We are extending this database of model coal compound equilibria using modern techniques that have the advantage of being much more rapid than traditional techniques. Cosolvent effects on solubility are being investigated over a variety of solvent properties. In addition, specific molecular interactions are being investigated through spectroscopic techniques. The resulting data are being used to develop a chemical-physical equation of state (EOS) model of SCF solution with meaningful parameters. The equation of state will be used to predict solubility behavior, which will permit the design and tailoring of SCF cosolvent systems for specific coal processing applications.

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OBJECTIVES

The focus of this work is the application of supercritical fluid (SCF) solvents to the precombustion desulfurization and denitrogenization of coal, as well as to the liquefaction and subsequent processing of coal liquids. In particular, we focus on the design of solvent-cosolvent systems for treating nitrogen and sulfur heterocycles. A novel technique using supercritical fluid chromatography measures rapidly the cosolvent effect on solubility and is used to extend the existing database of solubility data. Further details of molecular interactions in supercritical fluids, including specific solvation and the "clustering phenomena" in the near critical region, are investigated using high-pressure spectroscopic experiments. Data obtained from these experiments will be used in the development of a chemical-physical equation of state that accounts for the unique solvation properties of supercritical fluid solutions using accurate and chemically-meaningful parameters.

Supercritical fluids (SCF) show potential for coal processing because they possess some unique properties. A SCF is quite dense, which gives a large capacity for solutes; it has high diffusivity and low viscosity, which makes it an ideal medium for efficient mass transfer; and the fluid is highly compressible, which yields large solubility changes with small changes in temperature and pressure. The addition of a small amount of cosolvent (usually less than 5%) can dramatically enhance solubility. These phenomena suggest extraordinary selectivity possibilities. Therefore, we are proceeding with the measurement of solubilities in these novel fluids and fluid mixtures.

Solubility data exist for a wide variety of chemical compounds for pure solid solutes in several pure SCF's. The majority of these data are taken in SCF systems with a low critical point. Solubility data has recently been extended to include some heavier compounds typical of coal structures and solubilities in supercritical fluids with higher critical temperatures. These data have been correlated with a variety of cubic equations of state (EOS's) and semitheoretical expressions. However, in order to account for the effect of cosolvent on solubility and exploit potential selectivities in model coal compound systems, an EOS developed through a molecular approach is necessary.

Our ongoing studies of cosolvent effects both support the development of a chemical-physical EOS as well as extend the existing database of solubilities of model coal compounds in SCF solutions. The supercritical fluid chromatography technique permits rapid measurement of these effects. The solvent, cosolvent and solute are carefully chosen to gain maximum information on the relative importance of solute and cosolvent properties such as polarity, acidity, and basicity on phase equilibria.

Direct spectroscopic measurements of the specific interactions which yield extreme solubility and cosolvent effects will also be used to understand the relative

importance of specific interactions in SCF's. The spectroscopic phenomena investigated include charge-transfer complexing, hydrogen bonding, and dipole coupling. A high-pressure UV-vis spectrometer and a high-pressure fluorescence spectrometer are being used to probe these interactions. From the spectra information can be derived about the strength of both solute/solvent and solute/solute and solute/cosolvent forces and how they change with proximity to the critical point. Both the solubility and spectroscopy data are vital to the development of an equation of state model that will take into account both the physical and chemical forces that are important in SCF solutions.

PROGRESS THIS QUARTER

PHASE EQUILIBRIA AND COSOLVENT EFFECTS

Under past DOE support, we compiled an extensive database of coal model compound solubilities. Although cosolvent-modified SCF's show much promise in facilitating difficult separations, relatively little data exist on the effects of these modifiers. Both the magnitude and the importance of specific molecular interactions on cosolvent effects are yet unknown. Therefore, we are now extending this solubility database by using two novel techniques for measuring solubilities in supercritical fluid solutions containing cosolvents. Through carefully designed experiments, we are also working to delineate the effects of various specific interactions on model coal compounds solubilities in SCF solutions.

One reason that solubility and cosolvent data are scarce is that conventional techniques to measure solubilities are time consuming and require large amounts of solute. A chromatographic technique that we developed to measure these thermodynamic phenomenon in SCF solutions is attractive because chromatographic measurements are rapid, require little solute, and inherently separate impurities from the solute. With this technique, we are measuring solubilities and cosolvent effects from the retention time of the solute in the column using the SCF solution of interest as the mobile phase. We define the cosolvent effect, Ψ , for a solute as the ratio of its solubility in the fluid mixture to the solubility in the pure fluid at the same temperature and pressure. We have demonstrated the viability of this technique (Ekart et al., 1992); the absolute solubilities measured using this technique compare favorably with literature data.

In a recently completed study of the role of specific interactions on cosolvent effects, Kamlet-Taft solvatochromic parameters (Kamlet and Taft, 1976; Kamlet et al., 1977, 1983), dipole moments, and polarizabilities guided our cosolvent selection. Cosolvents possessing either relatively extreme hydrogen bond donating abilities or hydrogen bond accepting abilities were of particular interest to our investigation. Solubilities and cosolvent effects were measured for several solutes, again chosen for their ability to participate in various specific interactions. Although hydrogen bonding apparently contributes to cosolvent effects, our results also show that other specific interactions such as charge transfer complexing, dipole/dipole alignment and polarity/polarizabilities can be exploited to improve selectivities and loadings. In order to understand the contributions of these effects better, a wider range of cosolvents must be studied.

For this reason, we have chosen to study of series of cosolvents, as listed in Table 1, with only minor perturbations in structure. These cosolvents vary widely, not only in their ability to hydrogen bond, but in polarity, polarizability, and Lewis acidity/basicity. The solutes to be investigated are a homologous series of fluorene

and anthracene compounds, shown in Figure 1. Nitrogen-containing compounds and sulfur compounds such as these are also of interest to coal processing. Minor perturbations in chemical structure of both the cosolvent and solute will allow us to study a variety of specific interactions. All studies will be conducted in SCF mixtures of ethane, which does not participate in specific interactions with the cosolvents or solutes, modified with 3.5 mole% cosolvent.

High pressure VLE data with ethane is currently not available for these cosolvents. However, the phase boundaries are critical to ensure operation within the one phase region in the mixing bomb, pump, and column, all of which can be at different temperatures. Therefore, we are currently measuring these phase boundaries at the temperatures of interest for SCF ethane/cosolvent mixtures using a visual, static technique. After this preliminary screening, we will proceed with the measurement of the cosolvent effects for the previously described systems using our chromatographic technique.

We have also measured the absolute solubility of 7-azaindole in SCF ethane, SCF CO₂, and 3.25 mol% methanol/CO₂ systems (Table 2). The cosolvent effect was measured for direct comparison with spectroscopic phenomena measured for these systems. (See below.) The increase in solubility due to the addition of the cosolvent varies from a factor of about 6 at 90 bars to about 3 at 150 bars, even after the correction for the density effect. Our previous work suggests that this correction is significant in some systems. The magnitude of the increase suggests specific interactions between 7-azaindole and methanol. The relative decrease of the "cosolvent effect" with increasing pressure is consistent with the local composition enhancement picture (see, for example, Johnston et al., 1987). No reliable results were obtained for the solubility of 7-azaindole in supercritical mixtures of ethane with 1-4% ethanol, perhaps due to the adsorption/desorption of the ethanol on the solute bed.

SPECIFIC INTERACTIONS THROUGH SPECTROSCOPY

An important modelling aspect of SCF solution behavior is the solvent structure about a solute molecule. Previously, we had studied local composition effects around the probe molecule 7-azaindole in SCF cosolvent mixtures using fluorescence spectroscopy. The emission features of 7-azaindole of interest, namely fluorescence from a cyclic alcohol/azaindole tautomer species and an alcohol/excited-state azaindole exciplex, are well characterized in liquids. Results indicate that the interactions between azaindole and the alcohol cosolvent, although significant, are not sufficiently structured to support the cyclic hydrogen bonding necessary for tautomer formation. Further information on the extent of hydrogen bonding in this system can be obtained from absorption measurements; hydrogen bonding between azaindole dimers or between azaindole and alcohol occurs in the ground state.

This hydrogen-bonded dimer or complex can be observed as a red-edge shoulder to the azaindole spectrum. Hydrogen bonding conditions were made more favorable by studying the absorption behavior in liquid and supercritical ethylene ($T_c = 9.2\text{ }^\circ\text{C}$) modified with acetic acid. The acetic acid cosolvent may form a cyclic hydrogen bonded complex with azaindole more easily than alcohols due to its strong hydrogen bonding abilities. Experimental difficulties (adsorption on cell windows) prevented the use of concentrated azaindole solutions.

Figure 2 shows normalized absorption spectra of 10-2 mol/l azaindole in ethylene with 0, 0.5, and 3.0 mol% acetic acid. The reference cell contained no acetic acid when zeroing the instrument, therefore the intensities of similar azaindole concentrations may not be the same. The normalized spectra show the change in shape with the addition of acetic acid. The shoulder on the red-edge of the absorption, which is not due to the dielectric shift but grows with increasing acid concentration, is indicative of hydrogen bonding in solution and warrants further study.

Our recent investigation of cosolvent effects using a chromatographic technique (above) has shown that specific interactions other than hydrogen bonding also contribute to the enhanced solubilities of solutes in SCF cosolvent systems. Of these contributing interactions, spectroscopic techniques are particularly suited to quantifying the extent of charge transfer complexing. From a series of experiments in our double-beam UV-vis spectrometer adapted for high-pressure applications, the equilibrium constant of the charge transfer complex can be calculated. These equilibrium constants are integral to the development of predictive chemical-physical equations of state. In addition, knowledge of equilibrium constants in the near-critical region as a function of density provides insight into the local environment of these solute molecules and the effect of SCF solutions on chemical reactions.

Specifically, we are determining the equilibrium constants of the charge transfer complex of hexamethylbenzene (HMB) and tetracyanoethylene (TCNE) in SCF ethane. Ethane was chosen as our SCF fluid for the same reasons that it is used in our cosolvent studies: it has a moderate critical temperature and pressure and does not participate in specific interactions with our electron donor or acceptor species. TCNE is a powerful electron-withdrawing species which accepts a pi electron from HMB. The complex formed by this interaction, which has been well studied in liquid solutions, absorbs light in a region about 250 nm from the reactants. In addition, the molar extinction coefficient is sufficiently large that the complex can be observed in even dilute solutions. An absorption spectrum for this complex and components in liquid CH_2Cl_2 is given in Figure 3.

A Benesi-Hildebrand approach is used to determine equilibrium constants from the measured UV intensities of the complex at known concentrations of TCNE and HMB in supercritical ethane (Eqn. 1). This approach is only applicable when the

mole fraction of HMB is much greater than that of TCNE. This analysis also assumes that the absorption of the complex follows Beer's law. Unlike the standard Benesi-Hildebrand equation, the equilibrium constant is found in pressure - independent mole-fraction units for a nonideal system. Therefore, a thermodynamic model is necessary to calculate absolute equilibrium constants. The equilibrium constant (K_x) and extinction coefficient (ϵ) at a specific solvent density are determined from the slope and intercept of a linear plot.

$$\frac{y_{a,o} * L * \rho}{d} = \frac{\gamma^*}{K_x * \epsilon * y_{d,o}} + \frac{1}{\epsilon} \quad (\text{Eqn. 1})$$

- $y_{a,o}$ = initial mole fraction TCNE
- $y_{d,o}$ = initial mole fraction HMB
- L = UV cell path length (cm)
- ρ = solution density (mol liter⁻¹)
- d = maximum absorption of UV complex
- γ^* = nonideality ratio ($\gamma_{ad}/(\gamma_a * \gamma_d)$)
- ϵ = extinction coefficient (liters cm⁻¹ moles⁻¹)
- K_x = equilibrium constant (mole fraction units)

The evaluation of these constants requires a data set of the absorption maximum of the complex for varying concentrations of TCNE/HMB at constant temperature and pressure. These data are collected from a series of runs in the high-pressure double-beam UV. The UV sample cell is loaded with a known quantity of TCNE and HMB; the reference cell will contain pure ethane. At a given temperature, the cells are then pressurized with ethane to reach a desired solvent density. A UV spectrum is taken and the absorption of the charge transfer complex is measured. The component mole fractions are calculated from the solvent density and the known sample size. Pressure in the cells is increased to the next desired setpoint by adding ethane. The system is allowed to equilibrate before another spectrum is taken. This process is repeated until absorption of the complex has been measured at each desired density point. For each loading of the cell, approximately ten measurements are made at varying densities. The cell is then depressurized, cleaned, and reloaded with a different mole fractions of TCNE and HMB. Measurements are taken at the same density points for the new concentration. An equilibrium constant is determined from a data set of approximately five experiments done in this way at identical temperatures and pressures.

To date, we have shown the feasibility of measuring complex absorption in a system of TCNE/HMB/ and SCF ethane. Preliminary results show that equilibrium constants can be measured in SCF solutions. Complete analysis of these results requires a comprehensive comparison of our measured equilibrium constants with those measured in liquids at high pressures, as well as fine-tuning of our thermodynamic model. In addition to continuing the analysis of these results, we will proceed with our measurements of equilibrium constants of charge transfer systems in SCF solutions.

PLANS FOR NEXT QUARTER

We have measured cosolvent effects on solubility for the SCF/cosolvent/solute systems using a chromatographic technique. The solvents, cosolvents, and solutes were carefully chosen to gain maximum understanding of the importance of specific chemical interactions, in particular hydrogen bonding, on cosolvent effects. The results of this study suggest that other specific interactions also contribute to hydrogen bonding. Therefore, we are completing initial screening of a wider range of cosolvents with only mild perturbations in structure. These cosolvents vary widely, not only in their ability to hydrogen bond, but in polarity, polarizability, and Lewis acidity/basicity. Following this preliminary work, we will measure cosolvent effects in SCF ethane/cosolvent/solute systems.

We have shown the feasibility of measuring charge transfer complex formation in SCF solutions over a range of densities using a Benesi-Hildebrand approach. Next quarter we plan to continue these measurements and fine-tune the thermodynamic model associated with this analysis. These results will be compared with equilibrium constants in liquid systems as a function of pressure.

We will continue testing and improving our new chemical-physical equation of state based upon our solubility, cosolvent, and spectroscopic data. Equilibrium constants, such as those measured spectroscopically for charge transfer complexes, are potential chemically-meaningful parameters in this equation of state.

SUMMARY

Supercritical fluids show potential for a variety of coal processing applications. Application of SCF technology to these processes is limited by a dearth of information on the phase equilibria of coal compounds in SCF solutions and cosolvent effects on these solubilities. We are taking a molecular-based approach to developing and improving a chemical-physical equation of state with chemically-meaningful parameters. The goal of this work is the ability to tailor SCF cosolvent

systems to specific coal processing applications through knowledge of the chemical interactions which are significant to the SCF system.

Future work will include further investigations of cosolvent effects using supercritical fluid chromatography, fluorescence spectroscopy, and UV absorption. This information and the database of solubility measurements will be used in the further development of an equation of state model to predict solubilities for the design of coal treatment processes.

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- Johnston, K.P.; Kim, S., "Clustering in Supercritical Fluid Mixtures," *AIChE J.*, 1987, 33, 1603.
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Table 1. Cosolvents and their properties.

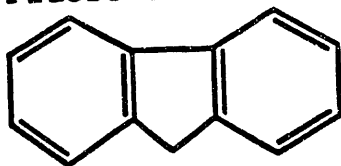
COSOLVENT	Π^*	α	β	μ (D)	T_c (°C)	P_c (atm)
Acetonitrile $\begin{array}{c} \text{H} \\ \\ \text{H}-\text{C}-\text{C}\equiv\text{N} \\ \\ \text{H} \end{array}$	0.75	0.19	0.31	3.5	274.7	47.7
Nitromethane $\begin{array}{c} \text{H} \\ \\ \text{H}-\text{C}-\text{NO}_2 \\ \\ \text{H} \end{array}$	0.85	0.22	0.25	3.1	314.8	62.3
1,1,1-Trichloroethane $\begin{array}{c} \text{H} \quad \text{Cl} \\ \quad \\ \text{H}-\text{C}-\text{C}-\text{Cl} \\ \quad \\ \text{H} \quad \text{Cl} \end{array}$	0.49	0.81	0.1	1.7	271.9	42.4
Ethanol $\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ \text{H}-\text{C}-\text{C}-\text{OH} \\ \quad \\ \text{H} \quad \text{H} \end{array}$	0.54	0.83	0.77	1.7	240.8	60.6
Acetic Acid $\begin{array}{c} \text{H} \quad \text{O} \\ \quad \\ \text{H}-\text{C}-\text{C}-\text{OH} \\ \\ \text{H} \end{array}$	0.6	0.56	0.45	1.3	321.6	57.2
Methyl Acetate $\begin{array}{c} \text{H} \quad \text{O} \\ \quad \\ \text{H}-\text{C}-\text{C}-\text{OCH}_3 \\ \\ \text{H} \end{array}$	0.6	0	0.42		233.7	46.3
Methylcyclohexane $\begin{array}{c} \text{H} \\ \\ \text{H}-\text{C}-\text{C}_6\text{H}_{11} \\ \\ \text{H} \end{array}$	0.01	0	0		299.1	34.3
Bromoform $\begin{array}{c} \text{Br} \\ \\ \text{H}-\text{C}-\text{Br} \\ \\ \text{Br} \end{array}$						

Table 2. Solubility of 7-azaindole.

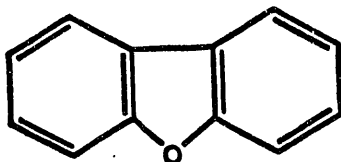
Solvent	Temperature (°C) ± 0.05	Pressure (bars) ± 0.3	Solubility (mole fraction) ± 5%
CO ₂	35.0	90	0.00086
	35.0	100	0.00134
	35.0	120	0.00165
	35.0	150	0.00192
CO ₂ /methanol (3.25%)	35.0	90	0.00532
	35.0	100	0.00544
	35.0	120	0.00657
	35.0	150	0.00728
Ethane	36.3	57.7	0.00037
	36.3	65.2	0.00046
	36.3	78.2	0.00056
	36.3	100	0.00077

Fluorene Series

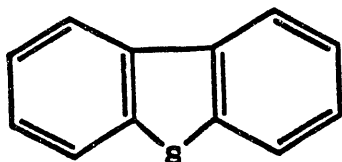
Fluorene



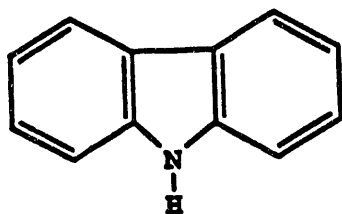
Dibenzofuran



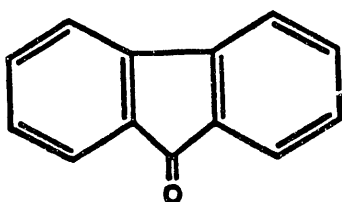
Dibenzothiophene



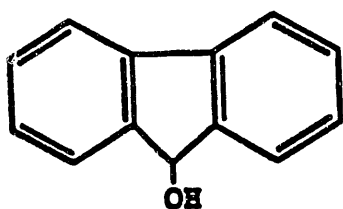
Carbazole



Fluorenone

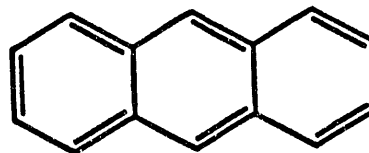


9-Hydroxyfluorene

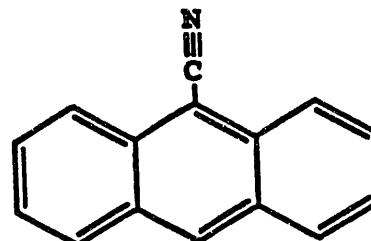


Anthracene Series

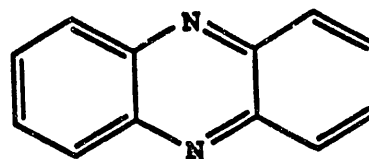
Anthracene



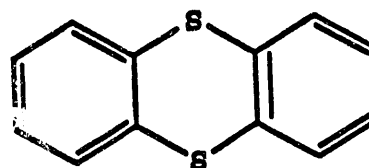
9-Cyanoanthracene



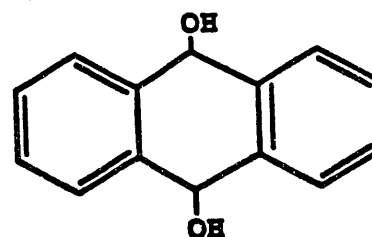
Phenazine



Thianthrene



9,10-Dihydroxyanthracene



Anthraquinone

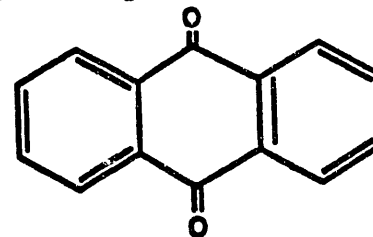


Figure 1. Series of solutes.

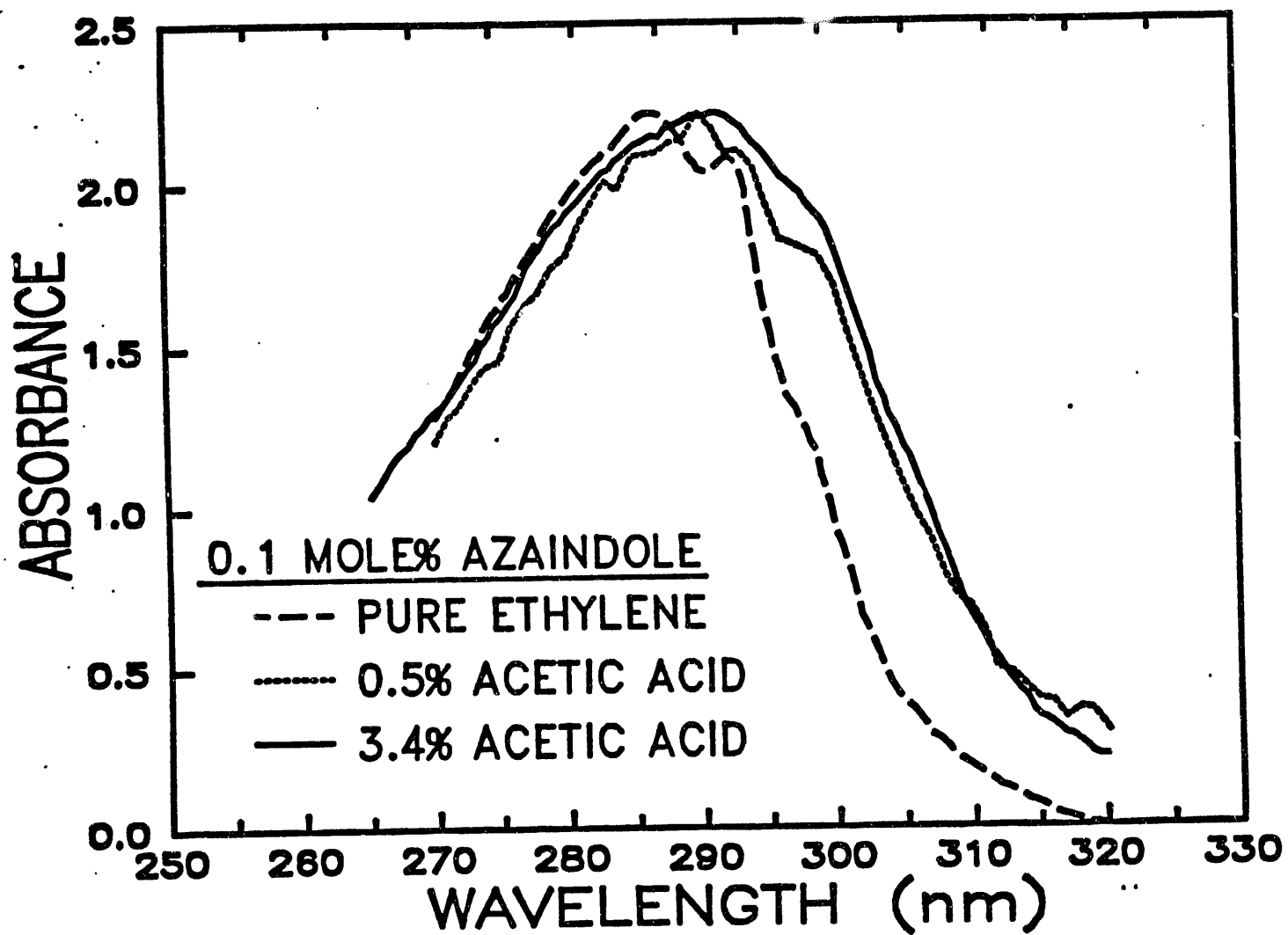


Figure 2. UV absorption spectra of 7-azaindole in supercritical C_2H_4 with 0, 0.5, and 3.4% acetic acid cosolvent. Spectra have been normalized to the maximum intensity.

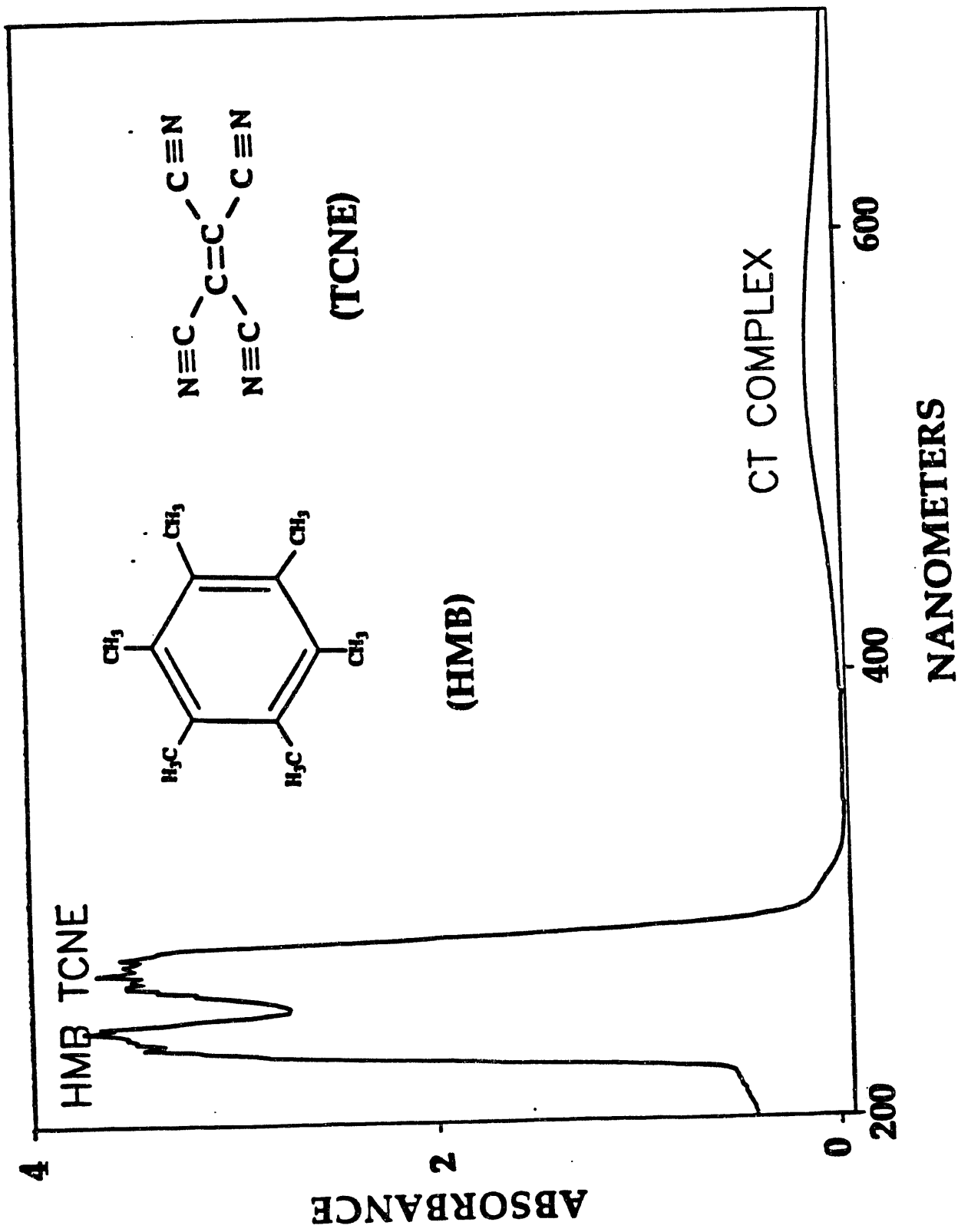


Figure 3. Absorption spectrum of tetracyanoethylene, hexamethylbenzene, and charge transfer complex in liquid CH_2Cl_2 .

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