

TERNARY SOLUBILITIES OF ANTHRACENE IN PRESSURIZED BINARY WATER/ETHANOL MIXTURES AT TEMPERATURES RANGING FROM 393 K TO 473 K

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ABSTRACT

Solubility measurements were conducted for (1- x) water – x ethanol mixtures at mole fractions, $x = 0, 0.02, 0.03$ and 0.04 of ethanol in pressurized water/ethanol system at 50 bar between 393 K and 473 K. A static equilibrium method was utilized to measure the solubilities of anthracene. Experimental data shows that the addition of a small amount of a volatile co-solvent to an aqueous mixture enhances the solubility of a hydrophobic compound. It was found that the addition of ethanol is much more effective in enhancing the solubility of anthracene at the higher temperatures. At every concentration of ethanol studied, a plot of the log of solubility of anthracene versus temperature yields a near linear plot. Thermodynamic functions of transfer from water to water/ethanol mixtures were also derived from solubility data. The free energy of transfer for anthracene was found to decrease with the increase of x ; validating that anthracene is less hydrophobic as the concentration of ethanol increases. The present study extends the database for polyaromatic hydrocarbon solubilities in subcritical water system in the presence of a volatile co-solvent. It is concluded that the use of a small amount of co-solvent in a subcritical water system can expand the use of subcritical technology while maintaining relatively mild operating conditions.

INTRODUCTION

The increased emphasis on sustainability and green processes has resulted in the increased use of water as a processing medium. Subcritical water technologies have been applied to the removal or decomposition of pollutants and the extraction of compounds from soil and plants, and recently, to the micronization of hydrophobic drugs (Karasek et al., 2006, Yang et al., 1995, Miller et al., 1998, Carr et al., 2010). While the use of subcritical water to process materials is gaining ground, a limitation to the development of the technology is a lack of fundamental data. The complexity, the non-ideality and the non-linearity of subcritical water characteristics make it difficult to predict its behavior and that of the compounds involved under subcritical water conditions. The lack of predictability, hence,

requires extensive, expensive and time-consuming trial and error experimental studies. Thus, accurate thermodynamic models for highly non-ideal mixtures are essential.

Water is most pervasive on Earth. It is present in all biological systems and many chemical reaction and separation processes. One of the well known characteristics of liquid water is the presence of the hydrogen bond network which gives rise to strong attraction between water molecules in liquid water. The strong hydrogen-bond attraction between water molecules in liquid water causes a water molecule to prefer its own species rather than other hydrophobic compounds that exist in liquid water. The strong hydrogen-bonding energy of cohesion between water molecules causes it to surround hydrophobic molecules to form water cages or clathrates, inside which solvation may occur; thus creating a strong attraction between hydrophobic molecules, which is known as the “hydrophobic effect” (Jeffrey, 1997). However, solvation may only occur at high dilution and only for small molecules, since the hydrophobic effect contributes to the low solubility of hydrocarbons in water and aqueous solutions (Marechal, 2007).

Solubilities of a number of hydrophobic solid substances in water have been investigated in recent years and found to be as low as 10^{-6} and even 10^{-7} mol fractions (Bennett and Canady, 1984, Zhou et al., 2003, Li and Yalkowsky, 1994). However, numerous studies have also shown that the solubilities of hydrophobic compounds in liquid water increase exponentially above 100 °C (Karasek et al., 2006, Miller and Hawthorne, 1998, Miller et al., 1998, Carr et al., 2010, Karasek et al., 2010). Solubilities of hydrophobic solid substances including hydrophobic organic pollutants (HOPs) are also known to be affected by the addition of co-solvents and co-solutes into water and are important in the treatment of industrial wastewater (Ruckenstein and Shulgin, 2005). While many data are available for the solubilities of HOPs in water, the availability of such data in water-cosolvent mixtures is lacking (Ruckenstein and Shulgin, 2005). Hence, experimental data and the thermodynamic properties which predict the behavior of HOPs in aqueous solutions are necessary.

Solubility is the analytical composition of a solution at equilibrium with one of the components of the solution at a particular temperature and pressure (Gamsjager et al., 2008, Özel et al., 2000). Solubility studies are essential as they quantify the ability of subcritical water or subcritical water and co-solvent to act as a solvent and consequently show the feasibility of a particular process for a particular application (Macnaughton et al., 1993, Lucien, 1996). It also plays an important role in determining the economic effectiveness of a particular process (Domanska, 2007) since solubility provides the thermodynamic limit to it. As such, there is a need to investigate the factors that affect solubility in subcritical water and subcritical water and co-solvent to allow for a continual development in the many potential applications, as well as the design and scale of sbcw processes.

In this paper, the solubilities of anthracene were measured for (1- x) water – x ethanol mixtures at mole fractions, $x = 0, 0.02, 0.03$ and 0.04 of ethanol in pressurized water/ethanol systems between 393 K and 473 K, and 50 bar. This study is necessary due to a lack of available data on the effects of adding organic co-solvents to the aqueous solubility of anthracene at subcritical conditions. Also, the effects of added organic solvents

on the thermodynamics of solubilization for anthracene and the temperature dependence of the solution process is necessary, and might enlighten the process of solubilization of a fairly bulky hydrocarbon compound. The aqueous solubility of solid organic non-electrolytes such as anthracene is also valued for the fundamental information it provides particularly in acquiring structural information in aquo-organic mixtures (Bose and Kundu, 1977, Karasek et al., 2006). The solubility of anthracene at relatively lower temperatures (25 – 40 °C) had been measured by Zhou et al. (2003).

EXPERIMENTAL SECTION

In this study, a static equilibrium method was utilized to measure the solubilities of anthracene and is shown in Figure 1. Anthracene of 99% purity was purchased from Sigma Aldrich. A detailed discussion on the performance and validation of the static equilibrium method is reported elsewhere (Teoh et al., 2011). Solid solutes were preloaded into a 6 ml equilibrium vessel. The vessel was then placed in a GC oven and connected to the system. A syringe pump was used to deliver water into the system. The system was then heated to a required temperature. When the desired temperature was achieved, the system was equilibrated for a designated amount of time while being stirred by a magnetic bar. Equilibration time for each condition (Figure 2) was predetermined as low solubilities at lower temperatures required longer mixing time than at higher temperatures. The pressure of the system was maintained at 50 bar. Near the end of the equilibration time, a weighed collection vessel (CV) dipped into a cold water bath was connected to valve V2. At the end of the equilibration time, the magnetic stirrer was stopped while nitrogen at 52 bar was allowed to contact the solution. The solution was then decanted into the collection vessel with N₂ acting as the force to push the solution into the vial while maintaining the liquid state of the solution. When the collection vessel had cooled, it was removed, externally dried and weighed. The solvent and the precipitated solutes in the collection vessel were collected in a glass vial. Further washings with acetone were conducted to ensure all solutes were collected in the glass vial. Valve V2 was also washed with acetone. The liquid was collected in a glass vial and dried. The solutes were then dissolved in analytical grade methanol and analyzed by UV. Three experimental runs were conducted on each solubility data point with a maximum of 5% relative standard deviation (RSD) obtained. The reported solubility data is expressed as the mean values of the three experimental runs and given as mole fractions of the solute in water.

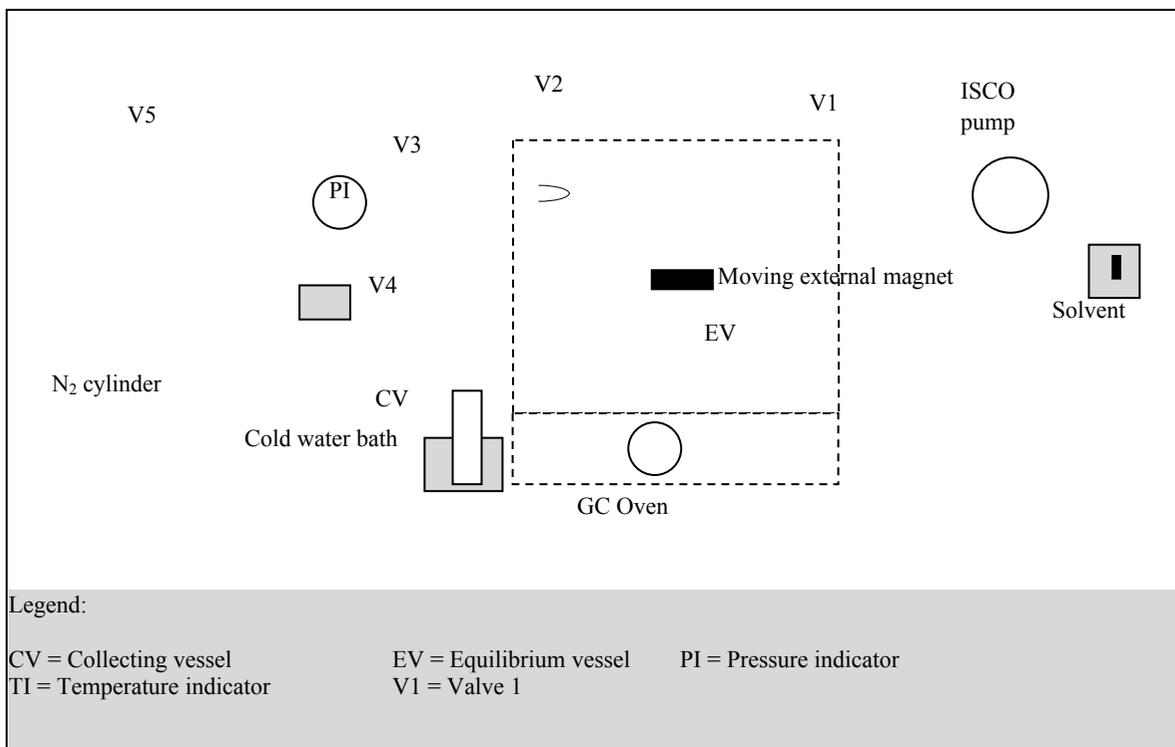


Fig. 1: Schematic diagram of the solubility apparatus

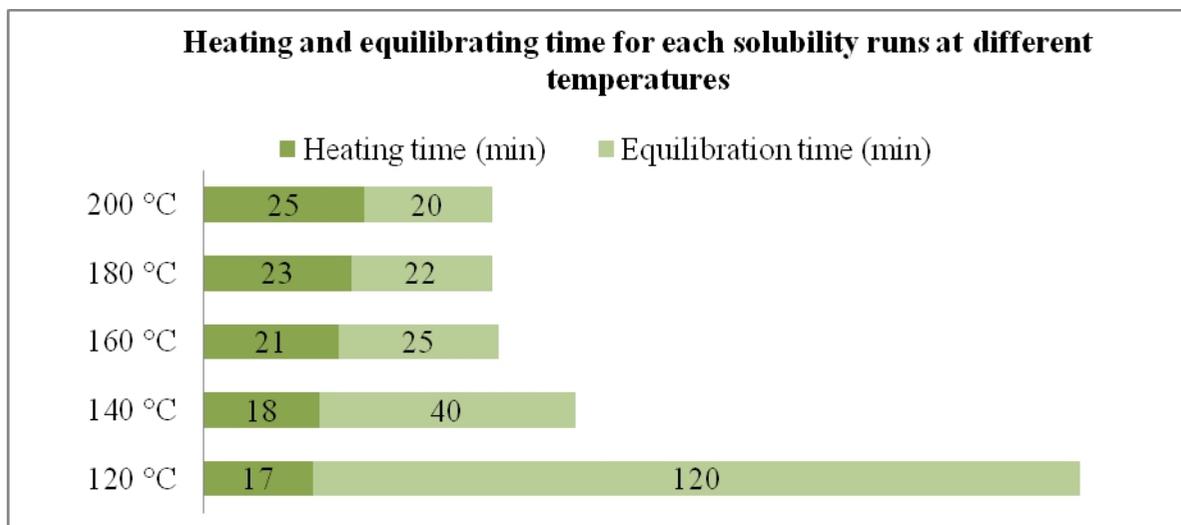


Fig. 2: Heating and equilibration times required for solubility runs at different temperatures

RESULTS AND DISCUSSION

Solubility

The solubility of anthracene was found to increase with temperature and co-solvent concentration as shown in Figure 3. The standard deviations for every data point were found to be less than 5% and are included as error bars in Figure 3. A plot of natural logarithm of solubilities of anthracene as a function of temperature yields a near linear plot, as shown in Figure 4. A simple empirical equation can be used to describe the solubility behavior of anthracene at various concentrations of ethanol given by equation (1):

$$\ln S = mT + c$$

(1)

where S is the solubility of anthracene, T is the absolute temperature, m and c are constants. The values of m and c are given together with the correlation coefficients, in Table 1.

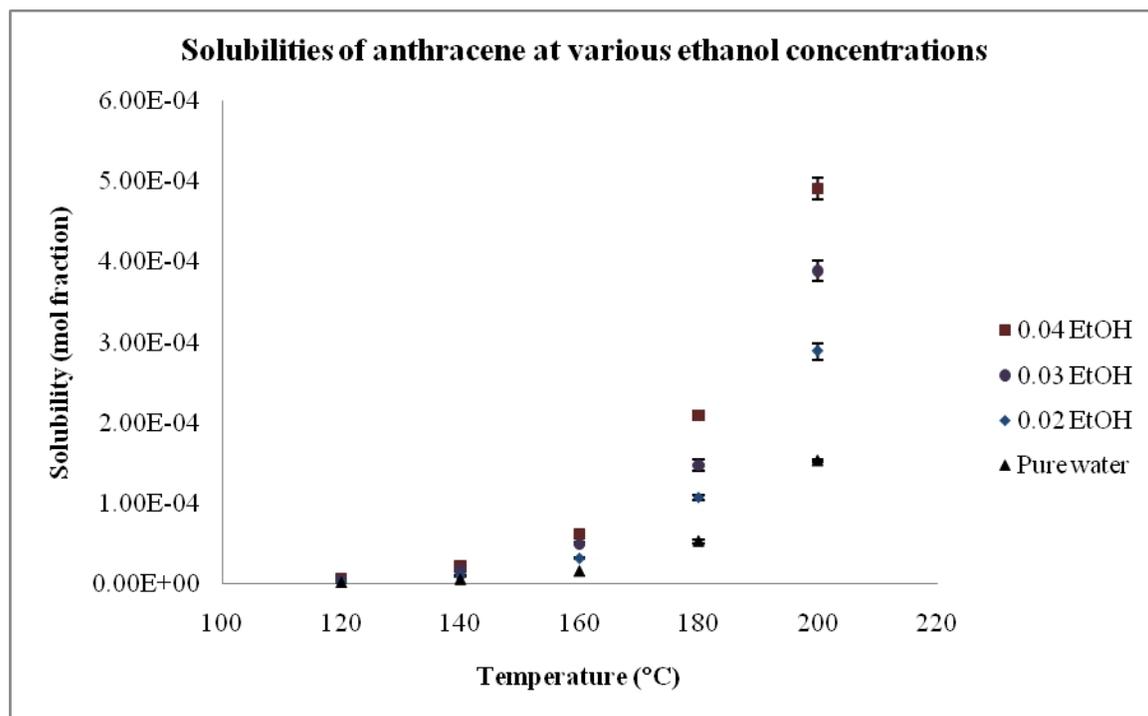


Fig. 3: Solubilities of anthracene at various ethanol concentrations

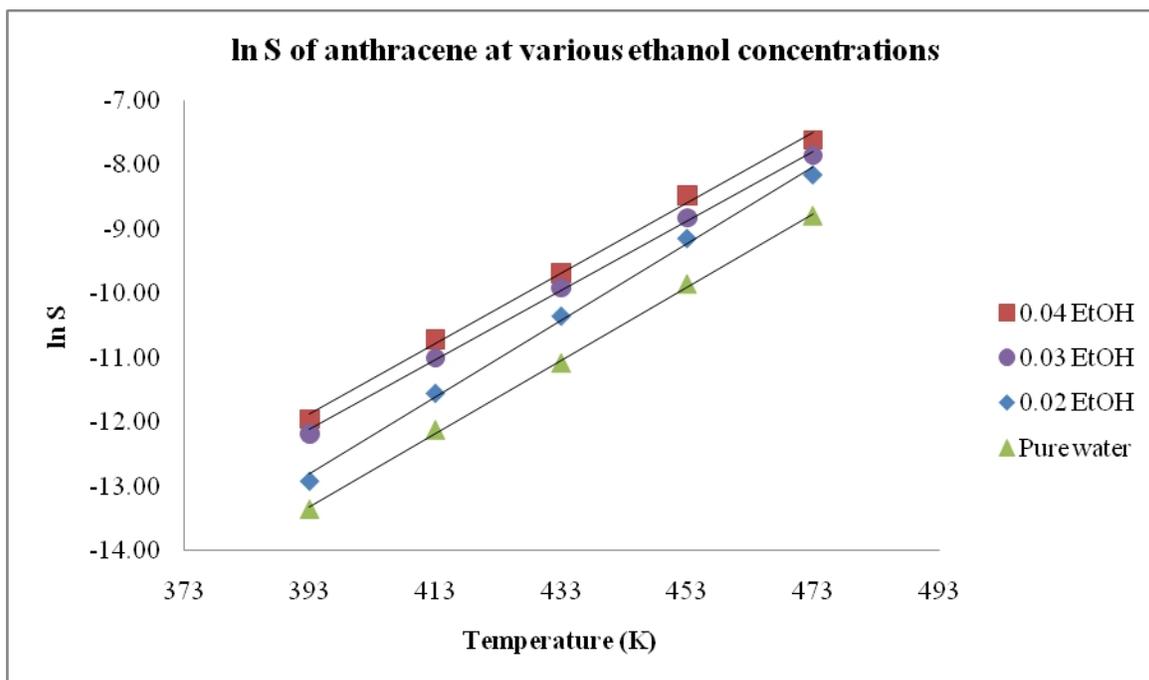


Fig. 4: Plot of the natural logarithm of the solubility of anthracene versus temperature

Tab.1: Parameters m and c derived from equation (1) for different concentrations of ethanol in water and the correlation coefficients

Parameters	ln (S)			
	Pure water	0.02 EtOH	0.03 EtOH	0.04 EtOH
m	0.057	0.060	0.054	0.055
c	-35.72	-36.29	-33.38	-33.30
correlation coefficient, r	0.9992	0.9997	0.9989	0.9966

Thermodynamic functions of transfer

The standard Gibbs free energy of transfer, $\Delta_{tr}G^\circ$, of a solute from water to an aqueous solution is the free energy change necessary to move 1 mol of solute from the water phase to the aqueous phase under standard state conditions. A negative value of $\Delta_{tr}G^\circ$ demonstrates that the transfer process is thermodynamically favorable. The $\Delta_{tr}G^\circ$ of

anthracene from water to a water/ethanol mixture can be described by equations (2) and (3) where

$$\Delta_{tr}G^\circ = \mu_m^\circ - \mu_w^\circ \quad \Delta_{tr}G^\circ = \mu_m^\circ - \mu_w^\circ \quad (2)$$

$$\Delta_{tr}G^\circ = RT \ln \frac{a_w}{a_m} \quad \Delta_{tr}G^\circ = RT \ln \frac{a_w}{a_m} \quad (3)$$

μ_m° is the chemical potential of anthracene in the aqueous phase while μ_w° is the chemical potential in the water phase. a_m and a_w stand for the activity of anthracene in the aqueous and water phase respectively. As the solubilities of anthracene in water as well as in the water/ethanol mixtures are low, the activity of anthracene can be taken to be the solubility of anthracene in the respective phases (Serafin, 2003). Thus, equation (3) can be rewritten as:

$$\Delta_{tr}G^\circ = RT \ln \frac{S_w}{S_m} \quad \Delta_{tr}G^\circ = RT \ln \frac{S_w}{S_m} \quad (4)$$

The free energy of transfer, $\Delta_{tr}G$ of anthracene from water to water/ethanol mixture at any given temperature can also be equated to the free energies of solution of anthracene in water/ethanol mixture ($\Delta_{s,m}G$) and in water ($\Delta_{s,w}G$), given by:

$$\Delta_{tr}G = \Delta_{s,m}G - \Delta_{s,w}G \quad \Delta_{tr}G = \Delta_{s,m}G - \Delta_{s,w}G \quad (5)$$

where $\Delta_{s,m}G$ is the free energy of solution for anthracene in water/ethanol mixture while $\Delta_{s,w}G$ is the free energy of solution for anthracene in water.

The free energy of solution (Δ_sG) of a solute in a solution relates to temperature and the solubility of the solute through equation (6) whereby:

$$\Delta_sG = -RT \ln S \quad \Delta_sG = -RT \ln S \quad (6)$$

The entropy of transfer, $\Delta_{tr}S$ and enthalpy of transfer, $\Delta_{tr}H$, at any given temperature are related to $\Delta_{tr}G$ in the forms of:

$$\Delta_{tr}S = - \left(\frac{\partial \Delta_{tr}G}{\partial T} \right)_P \quad \Delta_{tr}S = - \left(\frac{\partial \Delta_{tr}G}{\partial T} \right)_P \quad (7)$$

$$\Delta_{tr}H = \Delta_{tr}G + T \Delta_{tr}S \quad \Delta_{tr}H = \Delta_{tr}G + T \Delta_{tr}S \quad (8)$$

In order to calculate $\Delta_{tr}S$ and $\Delta_{tr}H$, a functional relationship between Δ_sG and temperature was used whereby:

$$\Delta_sG = a + bT + cT \ln T \quad (9)$$

where a , b and c are constants independent of temperature but vary with composition and species. Equations (6) and (9) are then combined to yield:

$$-RT \ln S = a + bT + cT \ln T \quad (10)$$

and rearrangement of equation (10) yields:

$$\ln S = -\frac{a}{RT} - \frac{b}{R} - \frac{c}{R} \ln T \quad (11)$$

Thus, parameters a , b and c can be obtained through multiple regressions on equation (11). In this paper, the least squares method was utilized to obtain the three parameters. Simultaneous equations were solved using Excel. Through the combination of equations (5) and (9), the free energy of transfer of anthracene from water to water/ethanol mixture at any given temperature is given by equation (12) as:

$$\Delta_{tr}G = \Delta_{s,m}G - \Delta_{s,w}G = (a_m - a_w) + (b_m - b_w)T + (c_m - c_w)T \ln T \quad (12)$$

where subscript m represent the water/ethanol mixtures while w refers to water. Hence, the entropy and enthalpy of transfer at any given temperature can be derived (Zhou et al., 2003) where:

$$\Delta_{tr}S = -\left(\frac{\partial \Delta_{tr}G}{\partial T}\right)_P = (b_w - b_m) + (c_w - c_m)(1 + \ln T) \quad (13)$$

$$\Delta_{tr}H = \Delta_{tr}G + T\Delta_{tr}S \quad (8)$$

The thermodynamic functions of transfer for anthracene at 473K are shown in Table 2. This study finds that the free energies of transfer from water to aqueous mixtures decrease with increased percentage of ethanol as shown in Table 2. The negative $\Delta_{tr}G$ values obtained for anthracene, from water to water/ethanol solutions, and the overall decrease of $\Delta_{tr}G$ with increased x demonstrates preferential solvation of anthracene by ethanol. The key effect is believed to result from a decrease in the surface tension of the aqueous mixtures, which allows the aqueous mixtures to accommodate non-polar solute molecules

with more ease (Serafin, 2003, Breslow and Guo, 1990).

Table 2: Thermodynamic functions of transfer for anthracene in (1-x) water + x ethanol mixtures at 473K

x	$\Delta_{tr}G$ (J/mol)	$\Delta_{tr}S$ (J/mol·K)	$\Delta_{tr}H$ (J/mol)
0.02	-2.50×10^3	-12.60	-8.46×10^3
0.03	-3.67×10^3	-16.03	-1.13×10^4
0.04	-4.59×10^3	-21.09	-1.46×10^4

Conclusion

The $\ln S = mT + c$ model is the simplest representation of the solubilities of anthracene in aqueous mixtures at various temperatures and ethanol concentrations. The linear plots obtained allowed for an easy prediction of anthracene solubility at higher temperatures. However, the simplicity of the empirical model limits its ability to forecast solubility behavior across a very wide range of temperatures and ethanol concentrations. The free energy of transfer, $\Delta_{tr}G$, for anthracene, was found to decrease with the increase of x . It is evident that the extent of solubilization of anthracene depends not only on temperature but also on the concentration of ethanol in the aqueous mixture. A higher ethanol concentration would yield a higher mol fraction of anthracene at equilibrium.

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BRIEF BIOGRAPHY OF PRESENTER

Wen Hui Teoh is a fellow of the University of Malaya and is currently a PhD student under the supervision of Prof. Neil R. Foster and Dr. Raffaella Mammucari.