

# Solubility and Solubility Modeling of Polycyclic Aromatic Hydrocarbons in Subcritical Ethanol and Water Mixtures

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## S Supporting Information

**ABSTRACT:** The solubilities of anthracene and *p*-terphenyl in subcritical ethanol and water mixtures were measured using a static analytical equilibrium method between 393 and 473 K and at 50 and 150 bar. Temperature and ethanol composition in the subcritical solvent mixtures were found to have significant effects on the solubility of polycyclic aromatic hydrocarbons (PAHs). The effect of pressure on solubility is negligible when the range of pressure considered is relatively small. An empirical model was proposed in the present study to correlate the solubility of PAHs to temperature and ethanol mole fraction. UNIQUAC, O-UNIFAC, and M-UNIFAC models were compared, with the UNIQUAC model found to be in good agreement with experimental data.

## 1. INTRODUCTION

Solubility studies of solid hydrophobic compounds in subcritical water have been investigated in recent years<sup>1–3</sup> due to the dramatic increase in the solvating power of water at higher temperatures. Although an increase in temperature may increase the solubility of hydrophobic compounds in water, the same can happen with the addition of a cosolvent (or modifier). The introduction of an organic cosolvent into a solution is one of the many methods that have been used to enhance the solubility of nonpolar solutes.<sup>4–6</sup> Systematic investigations into the solubility of hydrophobic organic compounds in subcritical water with organic modifiers are currently limited to a small number of studies.<sup>6,7</sup>

In the present study, a static equilibrium method was employed to measure the solubility of anthracene and *p*-terphenyl at 50 bar between 120 and 200 °C in ethanol-modified subcritical water mixtures. Solubility measurements were conducted at ethanol mole fractions, *f*, of 0.01, 0.02, 0.03, 0.04, 0.06, and 0.10. The solubilities of solid PAHs in subcritical ethanol were also studied and included in the present paper. The motivation behind the solubility measurements of solid PAHs in subcritical ethanol was, however, purely for thermodynamic modeling, where the binary interaction parameters between PAHs and ethanol were obtained for the UNIQUAC model. A detailed discussion is given in the following sections.

## 2. PHASE BEHAVIOR OF PAHS IN SUBCRITICAL ETHANOL AND WATER MIXTURES

The present solubility study requires that sufficient pressure is applied to maintain the liquid state of the solvents. A review conducted on saturated vapor pressures for various ethanol–water compositions found that a minimum of 30 bar is required to ensure solvents are maintained in the liquid state at all experimental conditions. The vapor pressures for various

ethanol–water compositions at various temperatures can be obtained from ref 8. Moreover, the sublimation pressures of anthracene and *p*-terphenyl up to 200 °C are found to be below 0.03 bar.<sup>1</sup> Hence, solubility measurement at a pressure of 50 bar was sufficient to maintain the liquid state of the solvents in the present study.

A phase behavior study conducted on anthracene and *p*-terphenyl in subcritical ethanol and water mixtures resulted in the observation of melting point depression for both anthracene and *p*-terphenyl. A detailed discussion of the phase behavior experimental setup and methodology is presented elsewhere.<sup>1</sup> At 200 °C, melting point depression was observed for anthracene at ethanol fractions, *f*, between 0.06 and 1.0. Similarly for *p*-terphenyl, at 200 °C, melting point depression was observed between ethanol fractions of 0.02 and 1.0. The presence of a third gaseous phase was not observed.

## 3. SOLUBILITY MEASUREMENT

A static equilibrium method was utilized to measure the solubility of PAHs in modified subcritical water, shown in Figure 1. Anthracene and *p*-terphenyl of 99% purity were purchased from Sigma-Aldrich. Both compounds were used as received. Ethanol absolute (99.9%) was purchased from Scharlau Chemie. Degassed and deionized water was used in all experiments. A detailed experimental setup and method, validation, and performance for solubility measurement have been discussed elsewhere.<sup>1</sup>

Briefly, solid solutes, together with a magnetic bar, were preloaded into a 6 mL equilibrium vessel and placed in a GC oven. A syringe pump was used to deliver solvents into the

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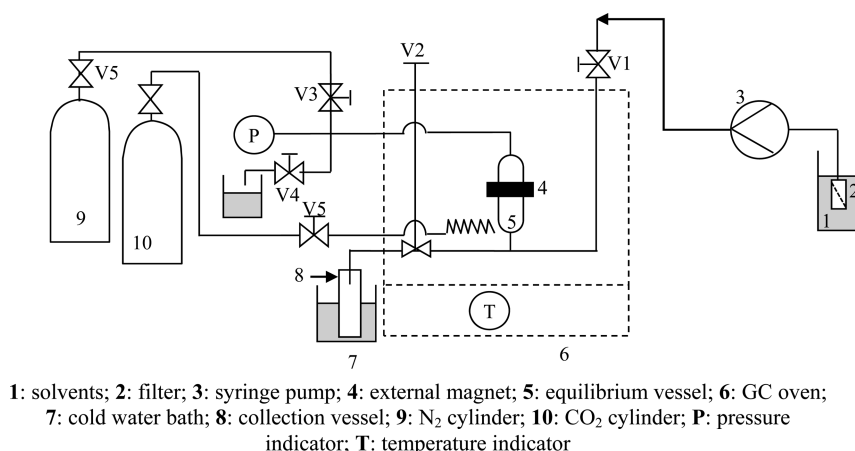


Figure 1. Schematic diagram of the solubility apparatus.

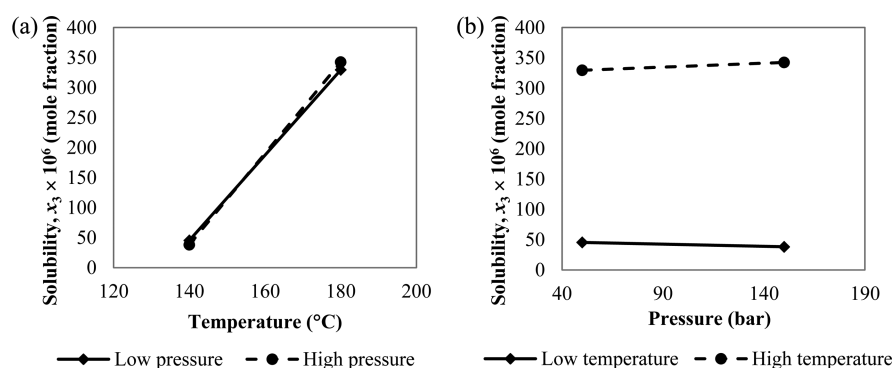


Figure 2. Interaction plots: effects of temperature and pressure on the solubility of anthracene in a subcritical water–ethanol system at  $f = 0.06$ .

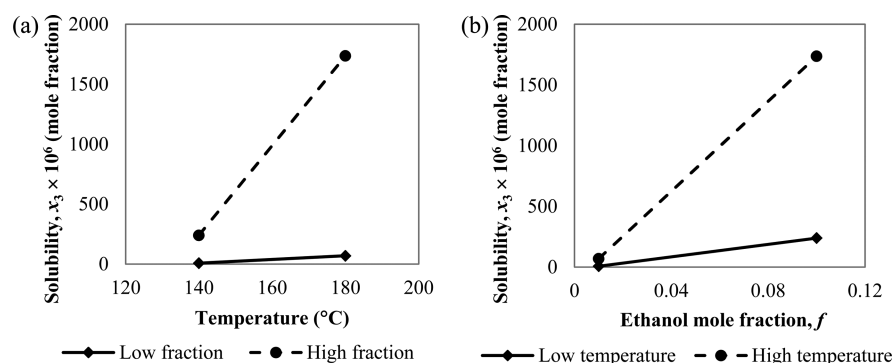
system. The system was heated to a required temperature, with stirring commencing at the onset of heating. When the system attained the desired temperature, it was allowed to equilibrate for a designated amount of time. The system was continuously stirred during equilibration. Pressure was maintained at 50 bar with the syringe pump. At the end of equilibration, stirring was stopped, and gas N<sub>2</sub> preset to 54 bar was allowed to contact the solution in the equilibrium vessel to allow for the withdrawal of samples without disturbing the equilibrium condition. Valve V2 was then opened, and the dissolved solutes together with the solvents were collected in a collection vessel. The collection vessel was removed, dried, and weighed, and the contents were collected in a glass vial. Further washing with acetone on the collection vessel and valve V2 was conducted to ensure all solutes were collected in the glass vial. The contents in the glass vial were then dried and dissolved with analytical grade methanol for UV analyses. For each solubility data point, three experimental runs were conducted. Solubility data are expressed as mole fractions of the solute in the mixture.

For the measurement of PAH solubility in subcritical ethanol, an additional CO<sub>2</sub> supply line was introduced into the GC oven as a fire hazard preventive measure. If leakages were to occur in the rig while the experiment was running, CO<sub>2</sub> as a sweeping gas would dilute the concentration of oxygen and ethanol vapor in the oven and prevent combustion from occurring. The flow of CO<sub>2</sub> into the oven was controlled by a micrometering valve. The CO<sub>2</sub> line-end in the oven was coiled, allowing CO<sub>2</sub> to attain oven temperature prior to its release and to prevent temperature fluctuations in the oven. The lines external to the oven were also changed to bigger tubes to cater to the higher

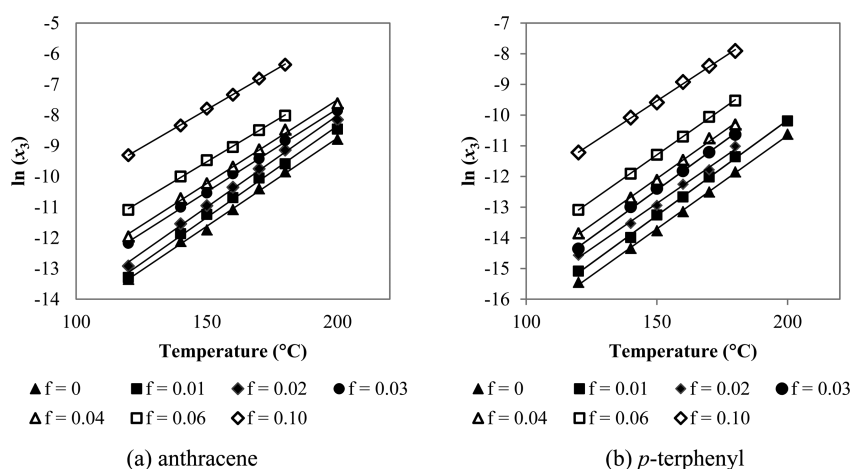
solubility of the PAHs in subcritical ethanol. The amounts of solutes and ethanol collected were measured gravimetrically.

**3.1. Preliminary Study on the Effect of Temperature, Pressure, and the Addition of Ethanol on the Solubility of PAHs in Modified Subcritical Water System.** The effects from small pressure changes on the solubility of a PAH in subcritical water have been found to be almost negligible.<sup>1</sup> However, the addition of small amounts of ethanol could potentially change the “cause and effect” behavior of a PAH in subcritical conditions. Hence, in a preliminary two-level, two-factorial study, the effects of pressure and temperature and their joint effect on the solvating power of ethanol-modified subcritical water were studied. Solubility measurements were conducted in 6 mol % of ethanol, at 140 and 180 °C and at pressures of 50 and 150 bar. Interaction plots between pressure and temperature, shown in Figure 2, indicate the significant role played by temperature in solubility. It can also be concluded that the effect of pressure on solubility in ethanol-modified subcritical water mixtures remains insignificant when the range of pressure considered is relatively small. The combined effect of temperature and pressure (i.e., liquid mixture density) on the solvating power of ethanol-modified subcritical water systems is also insignificant, as apparent from the calculated sums of squares shown in Table S1 (Supporting Information).

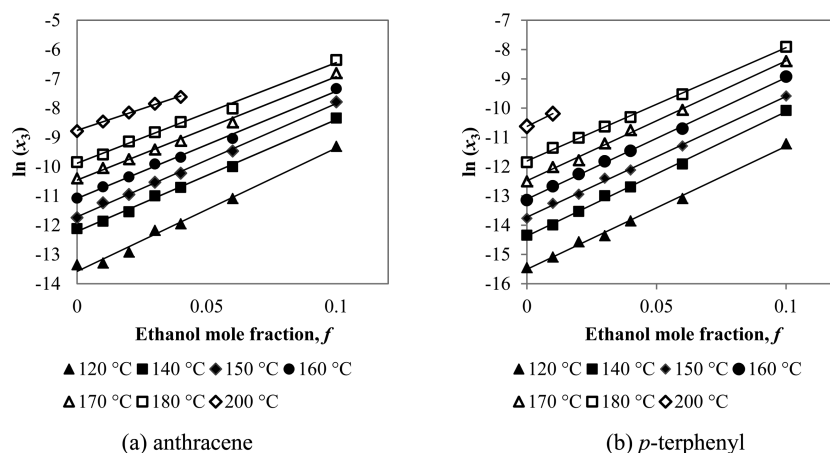
A further extension to the preliminary study was to investigate the effects of temperature, ethanol mole fraction, and the two factors combined on the solvating power of ethanol-modified subcritical water systems. A two-level factorial design, consisting of high and low temperatures of 140 and 180 °C and high and low ethanol fractions at  $f = 0.01$  and 0.10, was



**Figure 3.** Interaction plots: effects of temperature and ethanol mole fractions on the solubility of anthracene in a subcritical water–ethanol system at 50 bar.



**Figure 4.** Plot of  $\ln(x_3)$  versus temperature for subcritical water (1)–ethanol (2)–PAH (3) systems. Data for  $f = 0$  (subcritical water) were obtained from ref 1.



**Figure 5.** Plot of  $\ln(x_3)$  versus ethanol mole fraction for subcritical water (1)–ethanol (2)–PAH (3) systems. Data for  $f = 0$  (subcritical water) were obtained from ref 1.

used in this study. The interactions between the two factors (temperature and ethanol mole fraction) are shown in Figure 3. Although the significant contribution of temperature to increasing the solvating power of subcritical water–ethanol mixtures have been proven, the sums of squares (Supporting Information Table S2) indicate also the prominent role played by ethanol. In fact, the sums of squares suggest that ethanol plays a slightly more prominent role than temperature in elevating the solvating power of the modified subcritical water

systems. The results from the present preliminary investigation match the findings of Curren and King<sup>7</sup> in that the rate of increase in solubility is higher with the addition of ethanol rather than with an increase in temperature.

**3.2. Effect of Temperature and Ethanol Mole Fraction on the Solubility of PAHs in Ethanol-Modified Subcritical Water Systems.** Whereas solubility measurements were conducted at high and low temperatures of 180 and 140 °C in the preliminary study, the temperature range was

extended to include 120 and 200 °C in a detailed investigation on the effect of temperature and ethanol mole fractions on solubility. Hence, solubility measurements of anthracene and *p*-terphenyl in ethanol-modified subcritical water systems were conducted at 120, 140, 150, 160, 170, 180, and 200 °C. The fractions of ethanol used in the present study are  $f = 0.01, 0.02, 0.03, 0.04, 0.06, \text{ and } 0.10$ . When a liquid solute phase was observed at 200 °C, solubility measurements were not conducted.

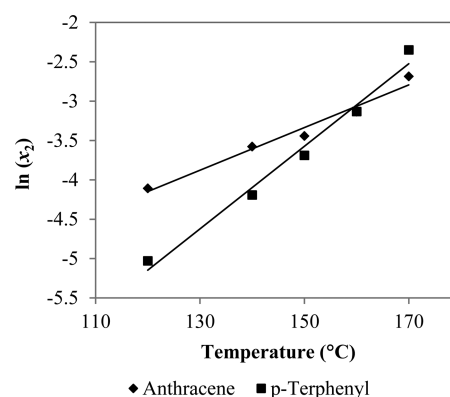
The solubility data of anthracene and *p*-terphenyl in ethanol-modified subcritical water systems are shown in Tables S3 and S4 of the Supporting Information. The solubilities of both PAHs were found to increase exponentially with temperature as well as ethanol fraction as shown in Figures S1 and S2 (Supporting Information) as a function of temperature and in Figures S3 and S4 (Supporting Information) as a function of ethanol mole fraction. Plots of the natural logarithm of PAH solubility  $[\ln(x_i)]$  in subcritical water and ethanol–water mixtures as a function of temperature yield nearly linear relationships (Figure 4). The slopes ( $m$ ) and  $y$ -intercepts ( $c$ ) calculated for each graphs are shown in Table S5 of the Supporting Information. Plots of  $\ln(x_i)$  as a functions of ethanol fraction are shown in Figure 5.

Anthracene solubility was found to increase by 19–43-fold in modified subcritical water systems as the temperature was raised from 120 to 180 °C. The solubility of anthracene was found to increase between 25 and 54-fold when ethanol composition was raised from 0.01 to 0.10 mole fraction. The effect of adding a cosolvent has greatly enhanced the solubility of anthracene and *p*-terphenyl in subcritical water. In fact, the results obtained show that a small addition of 0.01–0.02 mole fractions of ethanol could yield the same increase in the solubility of the PAHs as when the temperature was increased by 10 °C. For example, the solubility of *p*-terphenyl in subcritical water at 160 °C is  $1.96 \times 10^{-6}$  (mole fraction). The solubility of *p*-terphenyl increased to  $3.71 \times 10^{-6}$  (mole fraction) when the temperature was increased to 170 °C. The same increase in the solubility of *p*-terphenyl can also be obtained by adding approximately 0.015 mole fraction of ethanol into the solutions while maintaining the same temperature at 160 °C. Hence, the use of a modifier can easily reduce the need for higher processing temperatures and, subsequently, lower the temperature at which subcritical water processes such as extraction and micronization can be conducted.

It is apparent that both temperature and modifier contribute to the overall increase in the solubility of the two PAHs studied. The results obtained therefore show the flexibility in terms of using temperature, cosolvent, or both to enhance the performance of subcritical water processes. However, a cost benefit analysis is required to indicate the better choice, as increasing temperature increases energy cost, whereas a cosolvent has the added cost of extraction/elimination of the cosolvent at process end.

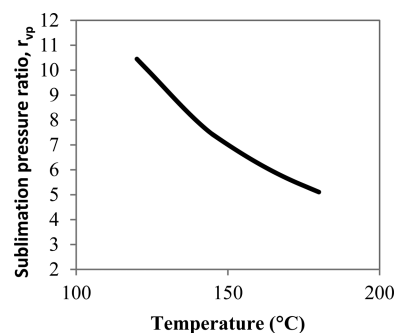
**3.3. Effect of Temperature on the Solubility of PAHs in Subcritical Ethanol.** Solubility measurements in subcritical ethanol were conducted between 120 and 170 °C. Solubility measurements did not proceed above 170 °C due to rig limitation as solutes began to clog the lines external to the oven. The pressure of the system was kept constant at 50 bar. The solubility data of pure anthracene and *p*-terphenyl in subcritical ethanol were found to increase exponentially with temperature and are shown in Table S6 and Figure S5 of the Supporting

Information. A plot of the natural logarithm of the solute  $[\ln(x_2)]$  as a function of temperature is shown in Figure 6. The



**Figure 6.** Plot of  $\ln(x_2)$  as a function of temperature in subcritical ethanol (1)–anthracene (2) and subcritical ethanol (1)–*p*-terphenyl (2) systems.

rate at which the solubility of *p*-terphenyl increases with temperature was also found to be higher than that for anthracene. It is noteworthy that a similar observation can be made for ethanol-modified subcritical water systems, with slightly higher  $m$  values observed for *p*-terphenyl than for anthracene. In a previous paper,<sup>1</sup> the authors have suggested that solubility in subcritical water is predominantly governed by the sublimation pressures of the solutes. Hence, a possible explanation for the lower observed rate for anthracene solubility is the lower rate of increase of its sublimation pressure over *p*-terphenyl. The sublimation pressure ratio of anthracene relative to *p*-terphenyl is shown in Figure 7, of which, the sublimation pressure ratio decreases with rising temperature.



**Figure 7.** Sublimation pressure ratio of anthracene relative to *p*-terphenyl as a function of temperature, with sublimation pressure values obtained from correlations provided in ref9.

## 4. THERMODYNAMIC FRAMEWORK

**4.1. Empirical Model: Solubility Variation with Temperature and Ethanol Fraction.** In consideration of the observed linear plots of the natural logarithm of PAH solubility with temperature, as well as with ethanol fraction, an empirical equation that relates solubility to both temperature and ethanol fraction may be considered, given by eq 1.

$$\ln x_{\text{solute}} = pT + qf + r \quad (1)$$

$x_{\text{solute}}$  is the solubility of the solute,  $T$  is the absolute temperature,  $f$  is the fraction of ethanol in water, and  $p$ ,  $q$ ,



and  $r$  are constants. The values of  $p$ ,  $q$ , and  $r$  are given in Table 1. The average absolute standard deviations (AASDs) obtained

**Table 1.** Values of Constants  $p$ ,  $q$ , and  $r$  Used in Equation 1

compound	$p$	$q$	$r$
anthracene	0.055648	38.0579	−35.2512
<i>p</i> -terphenyl	0.060806	39.3768	−39.3707

for anthracene and *p*-terphenyl are 0.88 and 0.51%, respectively. The absolute standard deviation (ASD) equation is given by eq 2. Deviations between experimental and calculated values using eq 1 are shown in Figure 8. Whereas the results obtained from eq 1 allow for an easy prediction of PAH solubility, the simplicity of the empirical model limits its ability to forecast solubility to the range of temperatures and ethanol fractions investigated in the present study.

$$\text{ASD} = \left| \frac{\ln x_i^{\text{exptl}} - \ln x_i^{\text{calcd}}}{\ln x_i^{\text{exptl}}} \right| \times 100\% \quad (2)$$

**4.2. UNIQUAC, O-UNIFAC, and M-UNIFAC Models.** In the present study, the universal quasi-chemical equations (UNIQUAC)<sup>10</sup> and the universal functional activity coefficient method models<sup>11–15</sup> (O-UNIFAC and M-UNIFAC) were applied to all solute–solvent systems investigated. One major consideration in the use of the UNIQUAC and UNIFAC models was that these models were conceived on the basis of low-pressure data. Hence, there is an approximation when these models are applied at high pressures. However, as established in the literature<sup>1</sup> and present paper, the effects of pressure on solubility in subcritical water and ethanol mixtures are negligible, particularly when the range of pressure considered is relatively small. Hence, the use of the UNIQUAC and UNIFAC models in the present work is still valid. The UNIQUAC, O-UNIFAC, and M-UNIFAC calculated solubility data of PAHs are shown together with experimental data in Figures 9 and 10. Comparisons of their activity coefficients as functions of temperature are shown in Figures S6 and S7 of the Supporting Information.

**4.2.1. Correlation via the UNIQUAC Method.** The parameters employed in the UNIQUAC method are obtained from Poling et al.<sup>16</sup> Group volume parameter ( $R_k$ ) and surface area parameter ( $Q_k$ ) values are taken from updated O-UNIFAC group specifications data because the combinatorial part of the activity coefficient ( $\ln \gamma_i^C$ ) in the O-UNIFAC model was taken

directly from the UNIQUAC model. In the UNIQUAC model, the two adjustable binary parameters,  $\tau_{ij}$ , were calculated on the basis of an objective function (OF) given by eq 3. An initial calculation of the two adjustable binary parameters,  $\tau_{ij}$ , with a single  $a_{ij}$  variable (eq 4) could not provide a fitting trend that reflects the rate of increase of PAHs solubility in water and water–ethanol systems. Hence, a quadratic temperature function was used in the present study, given by eq 5.

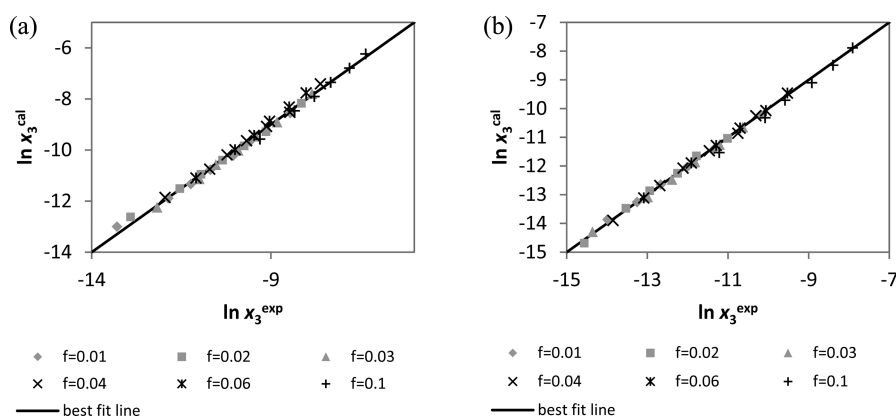
$$\text{OF} = \sum_{i=1}^N (\ln \gamma_i^{\text{exptl}} - \ln \gamma_i^{\text{calcd}})^2 / N \quad (3)$$

$$\tau_{ji} = \exp\left(-\frac{u_{ji} - u_{ii}}{RT}\right) = \exp\left(-\frac{a_{ij}}{T}\right) \quad (4)$$

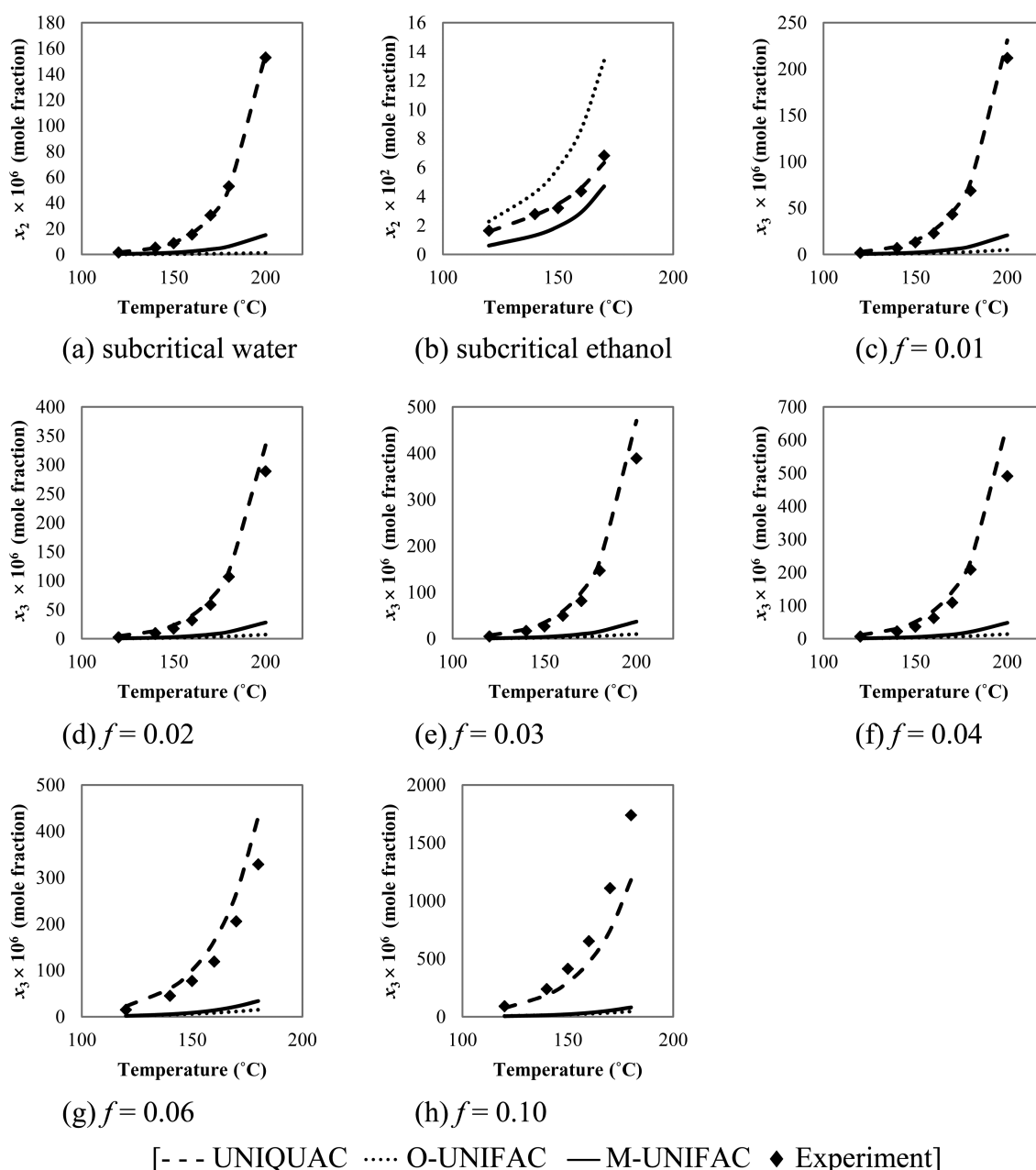
$$\tau_{ji} = \exp\left(-\frac{u_{ji} - u_{ii}}{RT}\right) = \exp\left(-\frac{a_{ij} + b_{ij}T + c_{ij}T^2}{T}\right) \quad (5)$$

The fitted energy parameters,  $a_{ij}$ ,  $b_{ij}$ , and  $c_{ij}$  shown in Table 2, were obtained from binary systems, and these values were extended to ternary systems. For PAH–ethanol systems, the energy parameters were calculated directly from experimental data collected in the present work. The  $a_{ij}$ ,  $b_{ij}$ , and  $c_{ij}$  values for PAH–water systems were obtained from a previous work,<sup>1</sup> whereas the values for the water–ethanol system were obtained from the DECHEMA series.<sup>17</sup> The binary interaction parameters for water–ethanol systems were chosen from a VLE system that best describes the temperature range of this investigation. The use of VLE parameters in this analysis is perhaps a cause for concern because it is not the same as experimental conditions. However, it has been ascertained that activity coefficients for SLE can often be estimated from VLE data at higher temperatures.<sup>18</sup> Moreover, the VLE effect in the modeling of the ternary systems was found to be negligible as the variations in the solubility data calculated with different VLE-related  $u_{ij}$  and  $u_{ji}$  values were <2%. The main contributions to the calculated solubility data in the ternary systems were due to the interaction parameters that came from the PAH–ethanol and PAH–water interactions.

The ability of the UNIQUAC model to calculate PAH solubility in the ethanol-modified systems was found to deviate further from experimental values as the ethanol fraction increased. However, the average standard deviations of the UNIQUAC calculated values were well within 7% of experimental values. Hence, it can be concluded that the



**Figure 8.** Deviation between experimental and calculated values using eq 1 for (a) anthracene and (b) *p*-terphenyl.



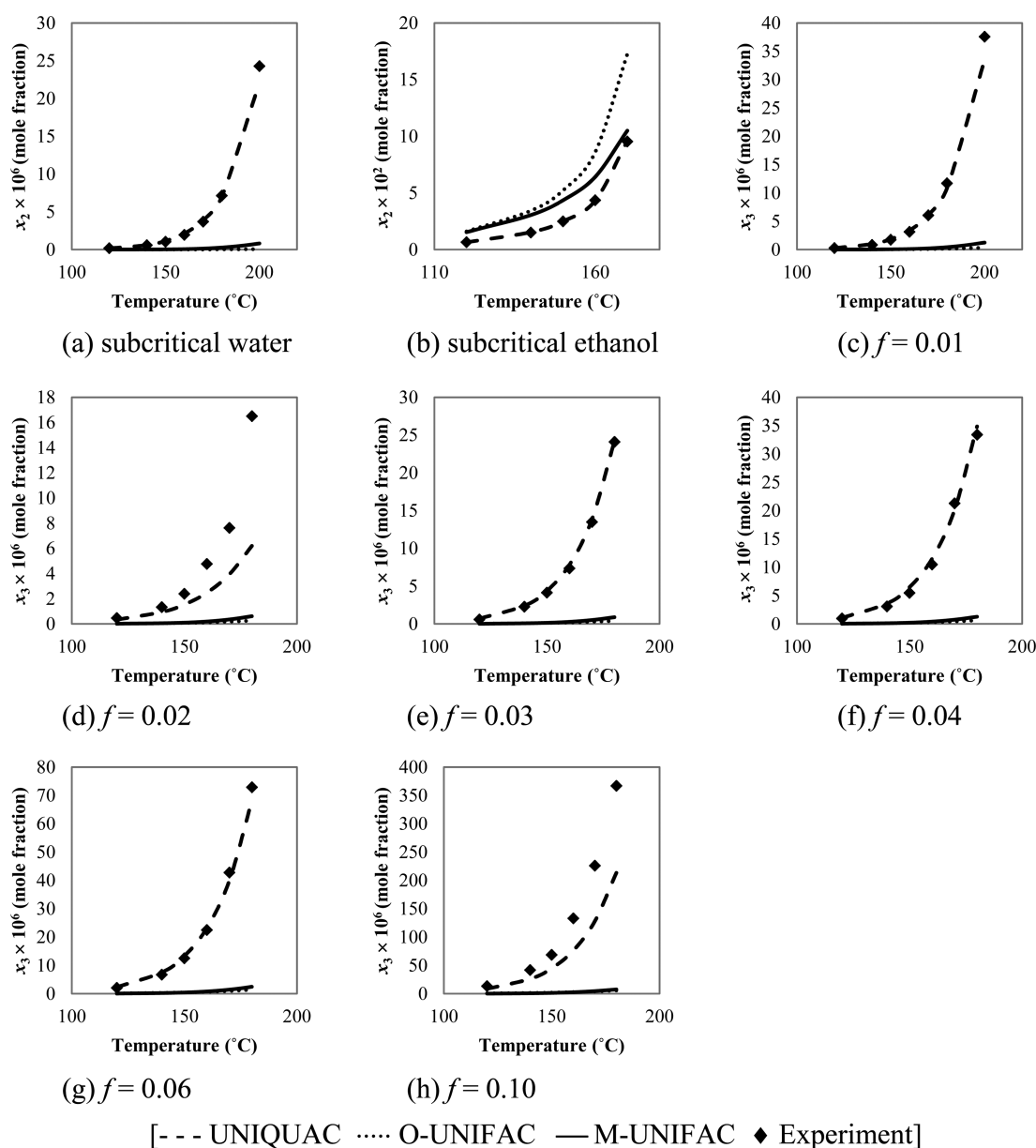
**Figure 9.** Anthracene solubility ( $x_i$ ) in various solvent systems calculated from various models and in comparison with experimental data.

UNIQUAC model can predict very well the solubility of the ternary systems containing ethanol within the range considered in this study.

**4.2.2. Correlation via the O-UNIFAC Model.** The parameters used in the O-UNIFAC model are taken from Poling et al.<sup>16</sup> O-UNIFAC is found to predict fairly inaccurately the solubility of both PAHs in all systems containing water, particularly at temperatures above 150 °C. Whereas the O-UNIFAC model could provide a fitting trend that reflects the solubility of PAHs in subcritical ethanol, the deviations are very high in that the majority of the calculated values did not fall within the same order of magnitude as experimental values.

**4.2.3. Correlation via the M-UNIFAC Model.** The surface, volume, and interaction parameters used in this section of the study were obtained from Gmehling et al.<sup>13</sup> The M-UNIFAC model was also found to perform poorly, particularly in water-containing systems, at temperatures above 150 °C. Similar to its

predecessor, the solubility data calculated from the M-UNIFAC model were not in the same order of magnitude as experimental data. In fact, the margin of error between the two UNIFAC models was almost similar. The M-UNIFAC model generally performed better than the O-UNIFAC model in binary subcritical ethanol and subcritical water systems. However, in ternary systems containing ethanol, both models performed poorly, particularly as the concentration of ethanol increased. Fornari et al.<sup>19</sup> found that the quality and predictive power of the UNIFAC models degrade for compounds with low solubility as solutes with low solubility tend to have higher molecular weight, size, and melting temperature. In contrast, the M-UNIFAC model is based on regressing VLE and excess enthalpy data of mixtures containing only low molecular weight aromatic compounds, the consequence of which can be seen in the present study.



**Figure 10.** *p*-Terphenyl solubility ( $x_i$ ) in various solvent systems calculated from various models and in comparison with experimental data.

**4.2.4. Comparing the UNIQUAC, O-UNIFAC, and M-UNIFAC Models.** Of the three models considered, the UNIQUAC method was found to provide the best representation of solubility because the binary interaction parameters per binary compounds were matched with experimental data. The extension of the UNIQUAC model to ternary systems also yielded good results. Both O-UNIFAC and M-UNIFAC models performed poorly in the binary and ternary systems investigated, yielding AASDs between 13 and 42%. In water-based solvent systems, both UNIFAC models rarely fall within the same order of magnitude as experimental data and fail to account for the dramatic rise in solubility with temperature. All three models showed higher deviations from experimental data as ethanol mole fraction increased.

The systems investigated in the present paper are nonideal, in that these systems involve nonpolar solutes interacting with polar solvents that associate through hydrogen bonding. The failure of the O-UNIFAC to account for the substantial increase in solubility due to temperature change is understandable, given

that the activity coefficient used in the original form of the UNIFAC model is not temperature-dependent. The M-UNIFAC model overcame this weakness with a temperature-dependent activity coefficient which, for all accounts, could reflect well the trend observed in experimental data. However, the M-UNIFAC model fell short in terms of its accuracy, with error margins as high as 42% in comparison to experimental data. The UNIQUAC model, in its original form, shared the same energy interaction parameters with the O-UNIFAC, in which the lack of temperature dependency of its energy parameters is already known. Thus, when the original form of the energy interaction parameters (eq 4) was first used in the present study together with the UNIQUAC model, the solubility trend observed was not representative of experimental data. The inclusion of a quadratic temperature function in the energy interaction parameters changed the quality of the UNIQUAC values and reduced the deviations to <7%. The small deviation was not surprising because the energy

**Table 2.**  $a_{ij}$ ,  $b_{ij}$ , and  $c_{ij}$  Values in Water (1)–Ethanol (2)–PAH (3) Systems Obtained with  $z = 10$  and  $[(u_{ij} - u_{ii})/R = a_{ij} + b_{ij}T + c_{ij}T^2]$

	anthracene	<i>p</i> -terphenyl
$a_{12}$	368.6547	368.6547
$a_{21}$	−102.5521	−102.5521
$a_{13}$	389.2981	394.1085
$a_{31}$	−2.5598	−0.5681
$a_{23}$	−97.7478	225.6717
$a_{32}$	420.0203	−35.6459
$b_{12}$	0	0
$b_{21}$	0	0
$b_{13}$	1.4879	1.2796
$b_{31}$	0.8981	0.5100
$b_{23}$	0.3158	0.5530
$b_{32}$	−0.3389	−0.2773
$c_{12}$	0	0
$c_{21}$	0	0
$c_{13}$	−0.0025	−0.0026
$c_{31}$	−0.0028	−0.0015
$c_{23}$	−0.0012	−0.0018
$c_{32}$	0.0023	0.0012

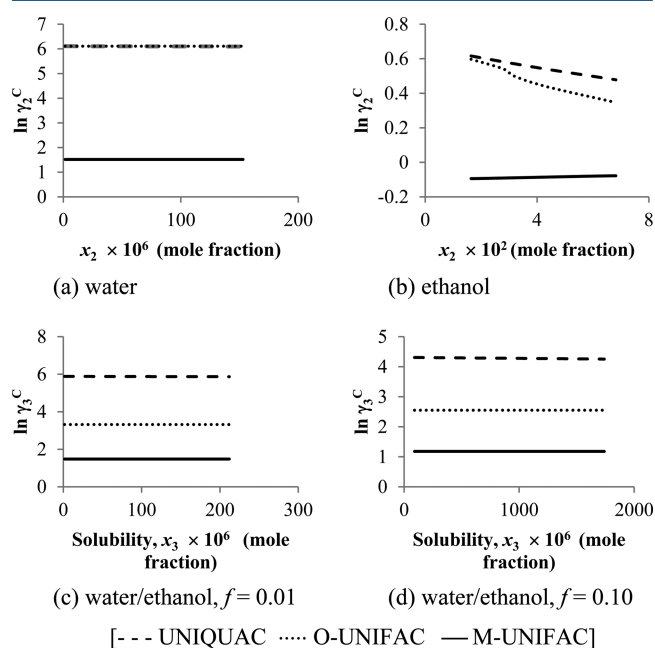
interaction parameters were based on experimental data for binary systems.

In ternary systems, all three models tended to deviate further from experimental data as the concentration of ethanol increased. UNIQUAC and UNIFAC models had been shown to *not* represent the relationship between activity coefficient and concentration well.<sup>20</sup> The lack of concentration dependence of the group activity coefficient is reflected in this study wherein the calculated values deviate further with increasing ethanol and PAH concentrations. The reason could be that the interaction energies derived in the UNIQUAC/UNIFAC models were based on lattice theory and assumed to be concentration independent, which might not describe the actual pair distribution of solute–solvent involved over a wide concentration range.<sup>20</sup>

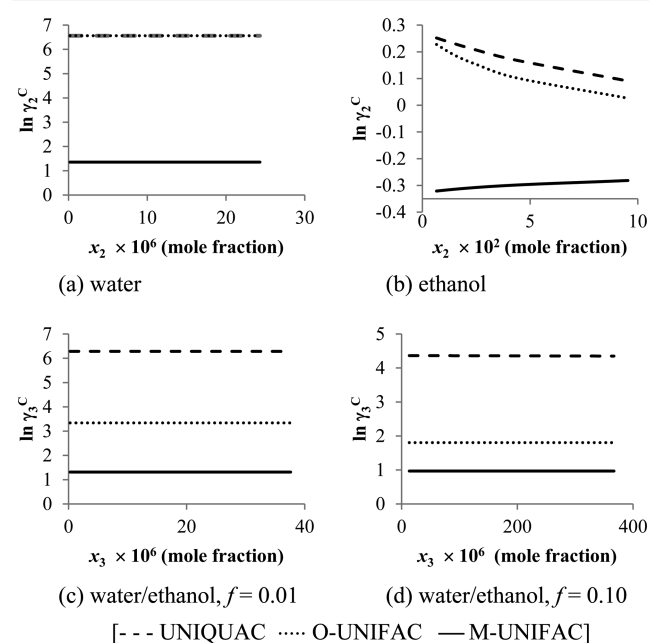
All three models considered in this study are based upon the sums of two parts of activity coefficient: the combinatorial part, which takes into account the difference in size and shape of the components, and the residual, which takes into account the energetic effects. Of the three, the UNIQUAC model is based on interactions between *components*, whereas the UNIFAC models are based upon interactions between functional *groups*. As both the UNIFAC models failed considerably in representing the SLE data in the highly nonideal subcritical solvent systems, identification on the shortcomings of the models is necessary. Given that the UNIFAC models are, to a certain extent, similar to the UNIQUAC model, in terms of being a sum of their combinatorial and residual activity coefficients, qualitative identification of the weakness in the UNIFAC models is made easier by breaking them into their combinatorial and residual terms and by comparing them to the UNIQUAC model. Such comparison may, to a certain extent, shed light on the causality of the shortcomings, wherein molecular interactions (residual), size, and shape (combinatorial) and/or additional associative factors come into question.

The UNIQUAC and O-UNIFAC models share the same combinatorial term and identical surface and volume parameters. The combinatorial term, based upon the assumption that no association or solvation exists, takes into

consideration *only* differences in size and shape. Hence, an examination on the combinatorial term of the two models found that the  $\ln \gamma^C$  values calculated by the two models in subcritical *water* were almost similar (Figures 11a and 12a). In



**Figure 11.**  $\ln \gamma^C$  plotted against experimental solubility ( $x_i$ ) of anthracene in various subcritical solvent systems.



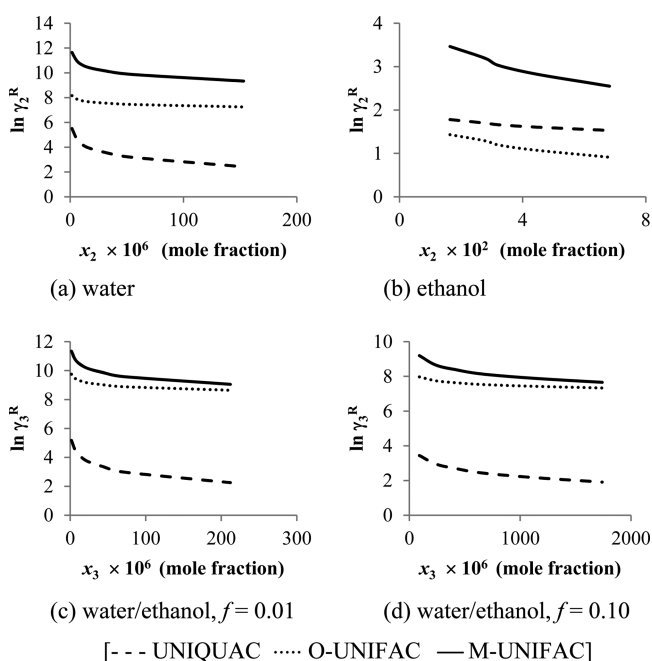
**Figure 12.**  $\ln \gamma^C$  plotted against experimental solubility ( $x_i$ ) of *p*-terphenyl in various subcritical solvent systems.

subcritical ethanol, the  $\ln \gamma^C$  values of both models were quite similar at lower PAH solubility, but diverged as the solubility of PAHs increase (Figure 11b and 12b). Meanwhile, the  $\ln \gamma^C$  values for both models in ethanol-modified subcritical systems were found to be very far apart (Figures 11c,d and 12c,d). Whereas it seems that the combinatorial activity coefficient in the UNIQUAC model is based only upon surface and volume parameters, it is, in fact, affected by the residual part of the

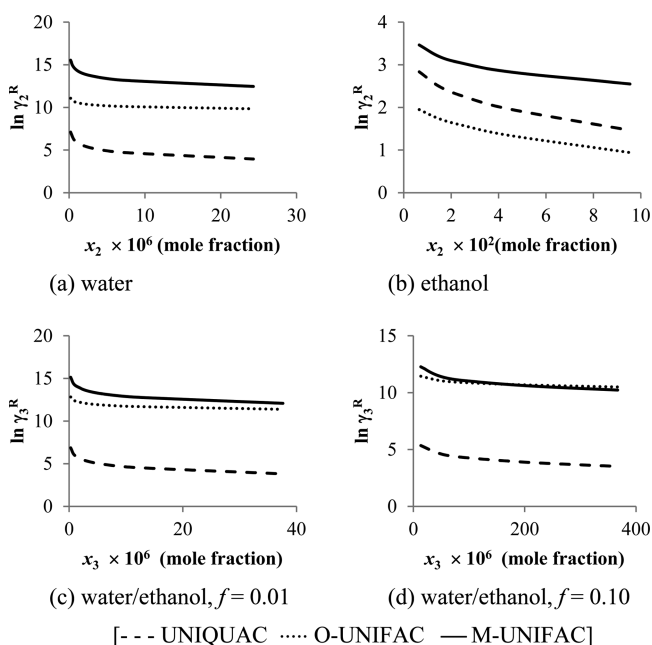


activity coefficient. It can be seen from the UNIQUAC model that the concentration of the solutes,  $x_i$ , enters into both the combinatorial and residual parts. Because numerical iterations are involved in the calculation of solute solubility and because solute solubility is partly affected by the residual term, the effect from the residual activity coefficient penetrates also into the combinatorial term.

For systems containing subcritical water, the residual term for the O-UNIFAC model was found to be considerably higher than that for the UNIQUAC model (Figures 13a and 14a).



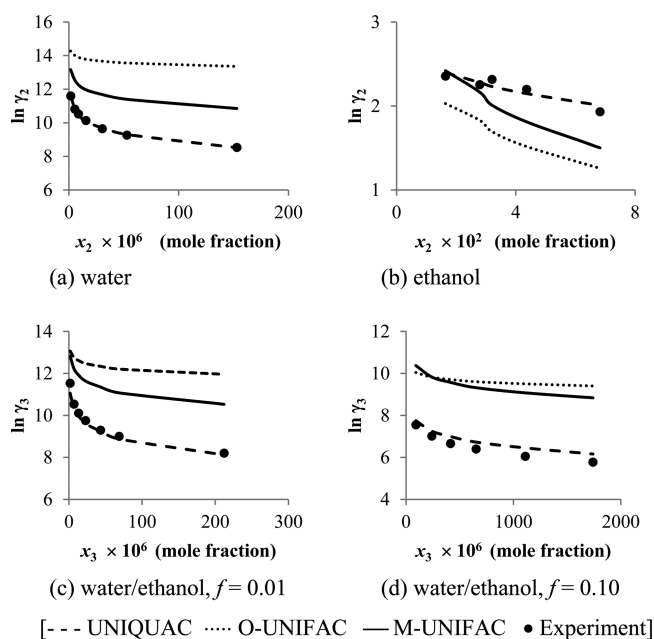
**Figure 13.**  $\ln \gamma^R$  plotted against experimental solubility ( $x_i$ ) of anthracene in various subcritical solvent systems.



**Figure 14.**  $\ln \gamma_2^R$  plotted against experimental solubility ( $x_i$ ) of *p*-terphenyl in various subcritical solvent systems.

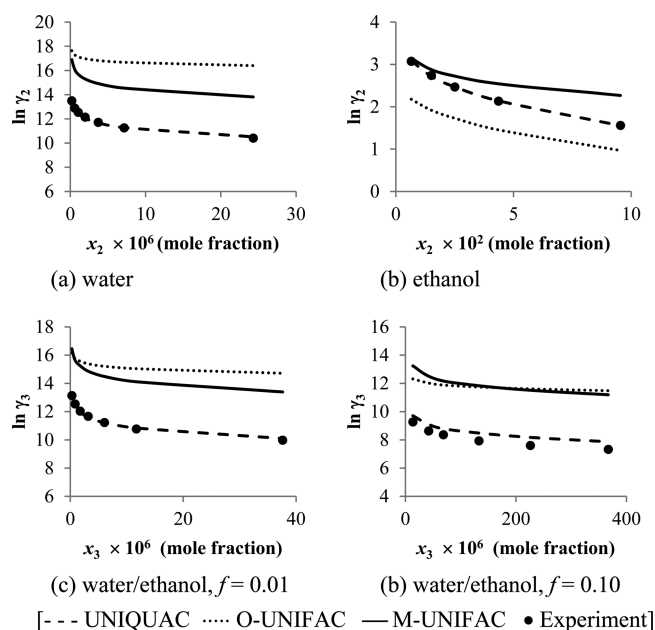
Because it has already been established that the combinatorial terms for both O-UNIFAC and UNIQUAC are of similar values in the PAH–water system, it can only be deduced that the major cause of the shortcomings in the O-UNIFAC model comes from its residual term. In fact, the residual activity coefficient seemed to have been excessively estimated for systems containing subcritical water and PAHs. Hence, the O-UNIFAC model seemed to fail to account for molecular interactions in the mixtures, of which the H-bond and system polarity play significant roles. For PAH–subcritical water systems, the residual term appeared to be overestimated, giving rise to lower solubility forecast. In PAH–subcritical ethanol systems, the residual term appeared to be underestimated (Figures 13b and 14b), yielding higher forecasted solubility values. Consequently, improvements to the O-UNIFAC model would require changes be made to its residual term.

In the M-UNIFAC model, the combinatorial term was found to be much lower than in the UNIQUAC model (Figures 11 and 12). The huge difference observed in the combinatorial term for the M-UNIFAC, in contrast to the UNIQUAC model, is due to the surface and volume parameters that were dealt with empirically in the M-UNIFAC model. In contrast, the residual term for the M-UNIFAC model was found to be substantially higher than the UNIQUAC model (Figures 13 and 14). For water-containing systems, the sums of the combinatorial and the residual terms in the M-UNIFAC were found to exceed that of the UNIQUAC model (Figures 15 and



**Figure 15.** Natural logarithm of the activity coefficient as a function of experimental anthracene solubility ( $x_i$ ) in various subcritical solvent systems.

16), pointing to excessive estimation of the residual term in the M-UNIFAC. Meanwhile, the sums of the two activity coefficient terms in subcritical ethanol systems were found to be also overestimated for *p*-terphenyl (Figure 16b) but underestimated for anthracene (Figure 15b), with both  $\ln \gamma$  plots diverging from the UNIQUAC model as PAH solubility increased. A possible explanation for the differences observed in the  $\ln \gamma$  plots of M-UNIFAC model between anthracene and *p*-terphenyl may be due to their structural and electron donor–



**Figure 16.** Natural logarithm of activity coefficient as a function of experimental *p*-terphenyl ( $x_i$ ) solubility in various subcritical solvent systems.

acceptor characteristics that are not properly distinguished and accounted for, in both the combinatorial and residual portions of the M-UNIFAC, particularly at higher temperature.

It can therefore be deduced that the insufficiency of the O- and M-UNIFAC models for subcritical solvent systems arose mainly due to the inadequacy of their residual terms, which fail to account for changes in system polarity and component interactions at higher temperature. Hence, the residual term in the M-UNIFAC model, as in the case of the O-UNIFAC, may require a revision before these models can be applied to systems containing PAHs in subcritical ethanol and water mixtures. Modifications to the UNIFAC models would require changes be made to the residual term or to include an additional term to account for system polarity and the associative effect among the solute and solvent molecules. Various modifications to the UNIFAC models have been undertaken along with many variations that adopted an association-based activity coefficient term. Further investigation into the associative activity coefficient term would be required in the near future. However, as suggested by Fornari et al.,<sup>19</sup> the association term would require a temperature-dependent term to provide substantial improvement to the UNIFAC models.

## 5. CONCLUSION

The solubility of anthracene and *p*-terphenyl in ethanol-modified subcritical water systems has been found to increase exponentially with temperature, as well as with ethanol concentration. In a modified subcritical water system, the temperature and the composition of a cosolvent are significant contributors to solubility. The effect on solubility from pressure in the 50–150 bar range and the combined effect of pressure and temperature in a modified subcritical water system are negligible for the fraction of ethanol considered in the present study. The solubilities of anthracene and *p*-terphenyl in subcritical ethanol are shown in this study to increase exponentially with temperature. An empirical model proposed in the present study may be used to predict the solubility of

anthracene and *p*-terphenyl in ethanol-modified subcritical water, limited to the range of temperature and ethanol fraction investigated in this paper. The UNIQUAC model provides a good representation of the solubility of anthracene and *p*-terphenyl in ternary systems. Both the O-UNIFAC and M-UNIFAC models performed poorly, mainly due to the inadequacy of the residual component of the activity coefficient. In ternary systems, all three models show increasing deviations from experimental data as ethanol concentration increases. Further work is required to find a suitable, nonempirical thermodynamic model for solubility calculation of PAHs in subcritical conditions.

## ■ ASSOCIATED CONTENT

### Supporting Information

Additional figures and tables as described in the text. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Author Contributions

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### Notes

The authors declare no competing financial interest.

## ■ NOMENCLATURE

$a_{ij}$ ,  $b_{ij}$ ,  $c_{ij}$  = fitted energy parameters

$c$  =  $y$ -intercept

$f$  = ethanol mole fraction [ $f$  = moles of ethanol/(moles of ethanol + water)]

OF = objective function

$m$  = slope

$P$  = pressure

$p$ ,  $q$ ,  $r$  = constants

$r$  = correlation coefficient

$r_{vp}$  = ratio of the sublimation pressure of anthracene relative to *p*-terphenyl

$T$  = temperature

$u_{ij}$  = energy interaction parameters

$x_i$  = solubility (or mole fraction) of solute  $i$

### Greek symbols

$\gamma$  = activity coefficient

$\tau_{ij}$  = binary adjustable parameters

### Abbreviations

AASD = average absolute standard deviation

PAHs = polycyclic aromatic hydrocarbons

### Subscripts

$ij$  component  $i$  or  $j$

### Superscripts

<sup>exptl</sup> experiment

<sup>calcd</sup> calculation

<sup>C</sup> combinatorial

<sup>R</sup> residual

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