

Liquid-Liquid Equilibrium in the Systems Furfural+Light Lubricating Oils using UNIFAC

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Abstract

In the lubricating oil manufacturing process, the aromatic content of vacuum distillates is reduced by solvent extraction, frequently with furfural. The complex composition of such mixtures makes the description of the liquid-liquid equilibrium involved difficult. In previous studies, the possibility to describe such equilibrium by using a reduced number of pseudo-components and the NRTL model has been stated. In this work, a different approach model was checked by using four model-molecules and a group contribution method. The molecular structure of model-molecules was determined regarding their different chemical nature and their physical properties. Dortmund modified UNIFAC model was used and the interaction parameters were calculated by correlating equilibrium data using AspenPlus[®]. The developed model was applied to describe the extraction operation of a light lubricating oil with furfural. Two sets of extraction experiments were considered. One of them was used to fit the needed parameters and the second one to check the predictive capability of the model. In both cases good agreement was obtained between experimental and calculated values for yields, furfural content composition and sulfur content of the involved mixtures. Most calculated values are as accurate as those obtained with the previously model, but a better description of the sulfur content was obtained.

Keywords: Aromatic extraction, furfural, lubricating oils, liquid-liquid equilibrium, UNIFAC, model-molecules.

1. Introduction

The removal of aromatic hydrocarbons from vacuum distillates is required in the process of manufacturing lubricating oil base stocks to improve several lubricating properties [1, 2]. The residue from the crude oil atmospheric distillation (long residue) is transferred to a vacuum distillation column and separated into different lube oil cuts and characterized by their boiling range and viscosity. Five raw cuts are commonly obtained. They are called SPD (spindle distillate), LND (light neutral distillate), MND (medium neutral distillate) HND (heavy neutral distillate) and BSD (bright stock distillate).

The aromatic extraction process requires a good solvent which maximizes differences in properties between the liquid phases. For many years, several works have been focused on looking for a suitable solvent. Furfural is one of the most widely used solvents because its selectivity towards aromatic compounds is high enough and decreases slowly when increasing temperature. Likewise, it is acceptable for both light and heavy vacuum distillates as reported by different authors [3-5].

The design and simulation of solvent extraction processes have been done mostly by fully empirical methods [6]. This approach is limited because the experimental information is not usually available and a more rigorous model is needed to simulate changes in operating conditions or feed quality. To properly describe the extraction process a consistent thermodynamic model should be based on the liquid-liquid equilibrium (LLE) established. However, solvent+lubricating oil systems are very complex because the high number of components in these mixtures, and therefore, simplified methods of characterization and calculation are needed.

The composition of such complex mixtures can be determined by standard test methods, such as ASTM D2007 [7]. However, the use of such methods is time and

money consuming and composition data are not usually determined. Usually, petroleum mixtures are characterized by their physical properties while their composition is estimated by known correlations [8]. However, the use of most of the developed correlations is limited and, therefore, new methods are needed especially for heavy petroleum fractions. In previous papers [9, 10] a method to determine physical properties of lubricating oil mixtures using pseudo-components properties has been presented.

The pseudo-component approach based on distillation curves is widely used to represent the complex composition of petroleum fractions in vapor-liquid equilibrium calculations. The model-molecules approach, however, also takes the chemical nature of compounds into account. The chemical structure of the compound has a much larger effect on the LLE than the boiling temperature and consequently the second approach should be more reliable. Recently, a method based on three pseudo-components with different chemical nature (saturates, aromatics and polars) has been reported to describe LLE in the systems furfural+heavy (HND) [9] and furfural+light (SPD) lubricating oils [10].

Different thermodynamic models can be used to describe the LLE in the system solvent+lubricating oils. NRTL [11] and UNIQUAC [12] models have been used to correlate LLE data for the system furfural+hydrocarbon systems [9, 10, 13, 14]. Group contribution methods such as UNIFAC [15] have been widely used to describe the LLE for several solvent+hydrocarbon systems including sulfolane+ hydrocarbon [16]; aniline+paraffin and furfural+paraffin systems [17]. Vakili-Nezhaad et al. [18] applied a UNIFAC based method to describe the extraction of aromatics from lubricating oils using N-methylpyrrolidone as solvent. These authors have described the composition of

lubricating oil mixtures by using three model-molecules. However, predictions of yields and physical properties of raffinates and extracts were not reported.

In this work, the model-molecules approach [18] was used. The composition of the lubricating oil mixtures was represented by four model molecules grouped in two families according to the chemical nature: saturates and aromatics. The aromatic fraction was considered to be formed by mono-aromatics, di-aromatics and sulfur-containing di-aromatics according to the study of Al-Zaid et al. [19]. These authors have determined the average molecular structure of the aromatic compounds in vacuum distillates within the range SPD-HND by using different experimental characterization techniques (NMR, GPC and elemental analysis). The Dortmund modified UNIFAC model (DMU) [20] was used to describe the LLE established in the extraction operation. The developed model was used to predict the LLE by means of AspenPlus[®]. Calculated values were compared with experimental values and with those calculated with the model developed by Coto et al. [10]. Accurate predictions of the extraction yields, furfural content, composition and sulfur content of both phases were obtained by means of both models.

2. Experimental Section

Spindle Distillate (SPD) was obtained from light Arabia crude oil and provided by REPSOL-YPF from their refinery in Puertollano (Spain). The experimental characterization for this lubricating oil cut (sulfur content, pseudo-components composition and properties, and aromatics content obtained by HPLC analysis) is summarized in Table 1. Pseudo-components were obtained as fractions of the ASTM D2007 [7] standard test method which assumes petroleum mixtures to be formed by saturates, aromatics and polars. Such families were characterized by their average boiling point ($T_{50\%}$) obtained from the distillation curves (ASTM D1160 standard test

method [7]) shown in Figure 1. The average molecular weight (\bar{M}) of each pseudo-component was calculated from their $T_{50\%}$ using a correlation proposed by Riazi et al. [21]. Obtained values for $T_{50\%}$ and the calculated molecular weight for each pseudo-component are also included in Table 1.

Furfural was also supplied by REPSOL-YPF and distilled before use to remove the oxidation products formed due to air contact.

Experimental results of the extraction experiments for SPD (extraction yields, furfural content, composition in saturates, aromatics and polars and sulfur content) were previously reported by Coto et al. [10]. The quality of the experimental data was checked by mass balance [10] obtaining in all cases average absolute deviations within the limits of reproducibility indicated by the ASTM D2007 standard test method [7]: $X_S = \pm 4.0\%$, $X_A = \pm 3.3\%$; $X_P = \pm 1.3\%$ in weight.

In this work, polars were included in the aromatic fraction and only two families were considered: saturates and aromatics, thus considering polars as sulfur-containing aromatic compounds. Composition is given in terms of saturates (X_S) and aromatics (X_{AP}) as listed in Table 2. Additional HPLC analyses were carried out for the involved mixtures in order to distinguish several kinds of aromatic compounds (mono-, di- and poly-aromatic). Results for such characterization (X_{MA} , X_{DA} , X_{PA}) are also listed in Table 2.

Experimental characterization of the involved mixtures and the extraction conditions given elsewhere [10] were combined with HPLC characterization shown in Table 2 in order to determine the composition of the mixtures in equilibrium in terms of the four model molecules mentioned above (saturates, mono-aromatics, di-aromatics and sulfur-containing di-aromatics) and furfural. Obtained results are shown in Table 3.

In order to check the predictive capability of the model based on the equilibrium data discussed above, a second set of extraction experiments at different conditions was considered. Table 4 shows experimental conditions (temperature and furfural/feed ratio) and composition in saturates and aromatics for the involved mixtures.

3. Thermodynamic model

A new thermodynamic model was developed to predict the LLE in the system furfural+SPD lubricating oil based on the four model-molecules and the Dortmund modified UNIFAC model [20].

3.1. Model-molecules. The involved mixtures (feed, raffinates and extracts) present a very complex composition and a pseudo-component definition is needed. Different approaches have been reported to perform such definition. Van Grieken et al. [9] have reported the characterization of pseudo-components (saturates, aromatics and polars) through different physical properties (average boiling point, specific gravity, liquid density and refractive index at 343K and sulfur content). Ruzicka et al. [22] and Vakili-Nezhaad et al. [18] reported three families of model-molecules (saturates, naphthenics and aromatics) characterized by their molecular structure. In this work, a similar approach was used, considering four model-molecules (saturates, mono-aromatics, di-aromatics and sulfur-containing di-aromatics).

The chemical structure for saturate model-molecules was developed following the procedure reported by Vakili-Nezhaad et al. [18]. Several possibilities were tested for the branching of the main hydrocarbon chain and the structure shown in Figure 2 is that leading to the best results. The molecular structures for the different aromatic compounds were based on those reported by Al-Zaid et al. [19]. The structure of the mono-aromatic fraction was the same as reported by these authors. The di-aromatic fraction is considered to be formed by non-sulfur-containing and sulfur-containing

compounds. Different sulfur distributions were tested in the model-molecules, and the final structures shown in Figure 2 are those which provide the best results. The size of the model-molecules considered as shown in Figure 2 was calculated following a modification of the procedure developed elsewhere by Vakili-Nezhaad et al. [18]. These authors introduced several adjustable parameters for each model-molecule mainly related to the length of the hydrocarbon chain. In this work, n is proportional to the length of the saturate hydrocarbon chain of saturates and α and β are proportional to the length of the saturate hydrocarbon chain in mono- and di-aromatics, respectively). Parameter β was considered to be the same for both non sulfur-containing and sulfur-containing di-aromatic compounds. Parameters n , α and β can be calculated by solving simultaneously the equations for the molecular weight for each model-molecule:

$$M_S = (5 + n) \cdot M_{CH_2} + \left(\frac{n}{3}\right) \cdot M_{CH-CH_3} + M_{CH} + M_{CH_3} \quad (1)$$

$$M_{MA} = (6 + n\alpha) \cdot M_{CH_2} + 4M_C + 4M_{CH} + 2M_{CH_3} \quad (2)$$

$$M_{DA} = (6 + n\beta) \cdot M_{CH_2} + 6M_C + 6M_{CH} + 2M_{CH_3} \quad (3)$$

$$M_{S-DA} = (4 + n\beta) \cdot M_{CH_2} + 8M_C + 4M_{CH} + 2M_{CH_3} + M_S \quad (4)$$

Values for the molecular weight are taken from Table 1 and they were assumed to be the same for all aromatic compounds.

The obtained values for each parameter were the following:

$$n \approx 9.0$$

$$\alpha = 0.66$$

$$\beta = 0.27$$

3.2. Dortmund modified UNIFAC model. The UNIFAC model is a well known group contribution method which can be used to describe both VLE and LLE [15]. In this work, the Dortmund modified UNIFAC model (DMU) [20] was used to describe the LLE in the extraction operation with furfural. The DMU groups involved in the description of compounds (furfural+model-molecules) and most binary interaction

parameters were all available in DMU model [23, 24]. Only the binary parameters for the interaction between the solvent (furfural) and the sulfur containing group (2,5-dimethylthiophene) were not available.

Such parameters were fitted to the equilibrium data shown in Table 2 by means of a suitable algorithm provided in Aspen Plus[®], based on the generalized least squares method [25]. The temperature dependence for the binary parameters was:

$$a_{nm} = a_{nm1} + a_{nm2} \cdot T \quad (5)$$

where T is expressed in K.

Obtained values for the interaction furfural (f) and 2,5-dimethylthiophene (dmt) were:

$$a_{f-dmt1} = 659.0$$

$$a_{dmt-f1} = 2423.0$$

$$a_{f-dmt2} = -3.00$$

$$a_{dmt-f2} = -2.25$$

where subscripts 1 indicates the independent temperature parameter; and 2 the temperature dependent parameter according to expression (5).

4. Results and discussion

The developed model was applied both to experimental conditions shown in Tables 2 and 4 in order to show the accuracy of the correlation of equilibrium data and the predictive capabilities of the model, respectively.

4.1. Correlation of equilibrium data. The accuracy of the fit of the equilibrium data shown in Table 3 was checked by simulating the same experimental conditions. The simulation was performed with a commercial simulator, Aspen Plus[®], using the structure and the molecular weight of each model-molecule shown in Figure 2 and Table 1, respectively. The DMU model was used to calculate the activity coefficients using the reported group interaction parameters [24] and those calculated before.

Simulation results (extraction yields, furfural content, composition and sulfur content for each mixture) are summarized in Table 5.

Absolute average deviation ($\bar{\varepsilon}$) between experimental (P_{exp}) and calculated (P_{calc}) values was calculated as follows:

$$\bar{\varepsilon} = \frac{\sum |P_{exp} - P_{calc}|}{N} \quad (6)$$

where N represents the number of mixtures considered. These values are listed in Table 7 for the properties considered. Deviations obtained by applying the previously model developed by Coto et al. [10] are also included.

Figure 3 shows the comparison between experimental and calculated extraction yields and furfural content for the mixtures involved. Calculated yields are in good agreement with experimental values, confirming the expected distribution of phases. Absolute average deviations were similar to those obtained by the model developed by Coto et al. [10].

The predictions of the furfural content in raffinates and extracts show a slight overestimation of the furfural content in raffinates, which makes the absolute average deviations to be superior to those obtained by the model by Coto et al. [10].

Figure 4 shows the comparison between calculated and experimental compositions in saturates and the sum of aromatics and polars, (X_{AP}). As is shown, no remarkable deviations were found and similar results were obtained by both models. The absolute average deviations obtained by the model reported in this work are slightly lower than those obtained by applying the pseudo-components model. In all cases, the calculated deviations are within the limits of reproducibility indicated by the ASTM D2007 standard test method [7].

The sulfur content of the involved mixtures was calculated from the sulfur percent of the sulfur containing model-molecule shown in Figure 2, $\overline{S\%}_{S-DA}=10.7\%$ (w), and the calculated content of sulfur containing di-aromatics (X_{S-DA}) summarized in Table 5 according to:

$$S\%_{calc.} = \frac{X_{S-DA}}{100} \cdot \overline{S\%}_{S-DA} \quad (7)$$

where $S\%_{calc.}$ denotes the calculated sulfur content.

Figure 5 shows the comparison between calculated and experimental values for the sulfur content, and, as it can be observed no systematic deviations were obtained. Absolute average deviation (Table 7) was clearly lower to that obtained by Coto et al. [10], confirming the improvement in the description of the sulfur distribution in the model-molecules proposed in this work.

All these results confirm the accuracy in the correlation obtained for the equilibrium data.

The model reported in this work presents a limitation in the application to the experiments carried out at high temperature and high furfural/feed ratio. These conditions could not be simulated because the system is near the homogeneous region and not accurate predictions are obtained. This limitation was also reported in previously available models [9, 10], but it does not present a large problem for the model because these severe conditions are not of practical interest.

4.2. Prediction of equilibrium data. To check the predictive capability of the developed model, the experimental conditions for the second set of extraction experiments (Table 4) were simulated following the same procedure described above. The simulation results for such experiments (extraction yields, furfural content, composition and sulfur content for each mixture) are shown in Table 6.

Figure 6 shows the comparison between experimental and predicted values for yields and furfural content obtained from the pseudo-component model by Coto et al. [10] and from the model reported in this work. Predicted yields are in good agreement with experimental values and no remarkable differences were found. As it is shown in Table 6 no remarkable differences were found between the deviations for both sets of experiments, confirming the capability of the model for predicting different experimental conditions.

Figure 7 shows the comparison between experimental compositions (saturates and the sum of aromatics and polars) calculated from both models. As can be observed, calculated values are very similar to the experimental values, showing no systematic deviations. Table 7 shows similar deviations for both sets of experiments. All the calculated deviations are within the limits of reproducibility indicated by the ASTM D2007 standard test method [7].

The predictions of extraction yields and furfural content in raffinates and extracts are more accurate when applying the model developed by Coto et al. [10]. However, higher accuracy was obtained in the composition prediction using the developed model.

The sulfur content of the involved mixtures was calculated following the procedure described above. The comparison between experimental values for the sulfur content and those calculated from both models is shown in Figure 8. Good agreement was obtained between experimental and calculated values. As it can be observed, the systematic deviations predicted by the model by Coto et al. [10] were not found in the values predicted by the model developed in this work, thus improving the sulfur distribution description by means of the use of model-molecules. A value of 0.3% was obtained for the absolute average deviation, which is lower than the value obtained using the pseudo-components model (0.5%). As it is shown in Table 7 absolute average

deviations were similar for both sets of experiments (0.3%) thus showing the possibility to apply the developed model to accurately predict properties of the involved mixtures.

The experiments carried out at high temperature and furfural/feed ratio could not be simulated due to the limitations of the model mentioned before.

5. Conclusions

A new thermodynamic model, based on the model-molecules approach was developed to describe the LLE established in the extraction operation of light lubricating oils.

Four model-molecules (saturates, mono-aromatics, di-aromatics and sulfur-containing di-aromatics) were considered. The DMU model was used to determine the activity coefficients. Only not available UNIFAC group interaction parameters were fitted to experimental equilibrium data using AspenPlus[®].

The reported model provides accurate results and no remarkable deviations in the comparison with experimental values both in the correlation of equilibrium data and in the prediction of different experimental conditions.

The obtained results were compared with those obtained by means of a previously available model based on pseudo-components and the NRTL model [10]. The deviations for extraction yields, furfural content and composition are similar for both models.

The calculated sulfur content calculated from the developed model showed higher accuracy than that obtained by other models, providing smaller and no systematic deviations.

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Nomenclature

Symbols

a: UNIFAC group interaction parameter.

\bar{M} : Calculated average molecular weight

P: Studied property.

S%: Sulfur content, w%.

T: Temperature of extraction, K.

T_{50%}: Average boiling temperature of the feed lubricating oil, K

X: Mixture composition, w%.

Abbreviations

dmt: 2,5-dimethylthiophene.

DMU: Dortmund modified UNIFAC

E: Extract.

f: Furfural

R: Raffinate.

SPD: Spindle distillate.

vol/vol: volume/volume.

Subscripts

A: Aromatics

AP: Sum of aromatics and polars.

DA: Di-aromatics.

F: Furfural.

m, n: Compounds in expression (2).

MA: Mono-aromatics.

P: Polars

PA: Poly-aromatics.

S: Saturates

S-DA: Sulfur containing di-aromatic compounds

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Figure captions

Figure 1. ASTM D1160 distillation curves for the fractions obtained by ASTM D2007 standard test method: Saturates; --- Aromatics; — Polars.

Figure 2. Model-molecules structures for the proposed pseudo-components.

Figure 3. Comparison of experimental yields and furfural content (reference [10]) and calculated values listed in Table 5: ○ Raffinates; ● Extracts

Figure 4. Comparison of experimental compositions listed in Table 2 and calculated values listed in Table 5.

Saturates: □ Raffinates; ■ Extracts.

Aromatics: ▽ Raffinates; ▼ Extracts.

Figure 5. Comparison of experimental sulfur content (reference [10]) and calculated values listed in Table 5.

Figure 6. Comparison of experimental yields and furfural content (reference [10]) and predicted values by means of different models.

Pseudo-component model [10]: □ Raffinates; ■ Extracts.

This work: ○ Raffinates; ● Extracts

Figure 7. Comparison of experimental compositions listed in Table 4 and predicted values by means of different models.

Saturates: ■ Pseudo-component model [10]; □ This work.

Aromatics: ▼ Pseudo-component model [10]; ▽ This work.

Figure 8. Comparison of experimental sulfur content (reference [10]) with predicted values by means of different models: ▲ Pseudo-component model [10]; △ This work.