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Extraction of Aromatic Compounds from Heavy Neutral Distillate Lubricating Oils by Using Furfural

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ABSTRACT

Liquid–liquid equilibrium data for the furfural–refined oil system, considered to be pseudoternary, were obtained at different temperatures in the 335–402 K range. Type I isotherms were observed at all temperatures for the two crude oils used: Kirkuk and Light Arabia. Tie-line compositions were correlated by the reduced Eisen–Joffe equation. Reliability of data was ascertained through Othmer–Tobias plots. The binodal curves and the tie-lines were predicted using the NRTL model with an average error lower than 5%. The viability of the simulation of the industrial extraction process using our experimental data has been proved.

Key Words. Furfural; Heavy neutral distillate lubricating oils; Aromatic extraction

INTRODUCTION

One of the basic operations carried out in the process of obtaining lubricating oils is the extraction of aromatic components by using selective solvents to achieve low viscosity index products, i.e., low variations of the oil viscosity with temperature. Prior to the aromatic extraction, the

residue from the atmospheric distillation of the crude oil (long residue) is transferred to a vacuum distillation column and separated into four different lube oil cuts, depending of their boiling points: SPD (spindle distillate), LND (light neutral distillate), MND (medium neutral distillate), and HND (heavy neutral distillate).

Among the different solvents employed to extract aromatic compounds, furfural is the most commonly used because its selectivity is better and decreases less rapidly with increasing temperature than the selectivity of other reactants, having an acceptable light–heavy selectivity (1–3).

Although there are different empirical methods to predict, from a few data, the results achieved in the industrial process (4, 5), these equations are not accurate enough to simulate industrial extraction columns. These simulations are more and more used to develop the expert systems that are actually employed to operate in optimal conditions all the units for the treatment of crude oil in refineries. These expert systems require simulation programs for their different constituent elements.

The rigorous calculations concerning the extraction operations require the equilibrium data of the system employed in the process under study. However, when lubricating oil systems are used, it is difficult due to the high number of components in the mixture. The easier method to study these systems is to consider a pseudoternary system basically constituted by the solvent and two mixtures having the highest and the lowest values of the main component, as if it was a ternary mixture (6, 7). This simplification is especially adequate for aromatic compounds extraction because the objective of the process is to reduce not only one component but a complete group of components (the aromatics) responsible for the nondesired behavior of the viscosity versus the temperature.

The characterization and prediction of the equilibrium conditions between two liquid phases may be carried out by using such thermodynamic models as NRTL (8), UNIQUAC (9), and UNIFAC (10). However, these models were mainly developed for vapor–liquid equilibria and are not fully successful for liquid–liquid equilibria (LLE). Furthermore, the parameters of these models for LLE are more difficult to obtain than those for vapor–liquid equilibria. Therefore, in order to obtain sufficient accuracy for practical simulation of industrial extraction columns (11–13), different authors have proposed the use of empirical equations to correlate LLE data.

In this work we report liquid–liquid equilibria data in the 335–402 K range for two different pseudoternary systems constituted by furfural and two HND lubricating oils, Kirkuk and Light Arabia. These data are essential to simulate the industrial extraction of aromatic compounds from lubricating oils by obtaining better operation conditions to increase the effi-

ciency. However, this information does not appear in the literature for the systems mentioned above. In this paper, LLE data for the two systems are correlated by the NRTL model (8) whose parameters have been calculated.

EXPERIMENTAL SECTION

Materials

Lubricating Oils

To obtain the equilibrium data, two hydrocarbon mixtures, having the highest and the lowest values of the main component (aromatic compounds), were used. The mixtures were prepared in our laboratories according to the following procedures.

Hydrocarbon Mixture with the Highest Aromatic Concentration (HAC). A mixture of extracts from consecutive extractions at the minimum temperature allowed by the fluidity of the mixture (335 K) was obtained. The feed for the first equilibrium was the extract from the processing of HND bases in the lubricating oils unit of the Repsol Petroleo S.A. refinery in Puertollano, Spain.

$$n_D(335\ K) = 1.597\ (Kirkuk)$$
$$= 1.598\ (Light\ Arabia)$$

Hydrocarbon Mixture with the Lowest Aromatic Concentration (LAC). Raffinate was obtained after the consecutive extractive process was carried out at the minimum temperature allowed by the fluidity of the mixture (335 K). The feed used in the consecutive extraction steps was the raffinate obtained from the processing of HND bases in the lubricating oils unit of the Repsol Petroleo S.A. in Puertollano, Spain.

$$n_D(335\ K) = 1.463\ (Kirkuk)$$
$$= 1.469\ (Light\ Arabia)$$

Furfural

Furfural of guaranteed reagent grade and purity higher than 99.5% was used. Furfural was previously distilled to eliminate the oxidation products formed during air contact.

$$n_D(293\ K) = 1.526$$
$$n_D(335\ K) = 1.504$$

Apparatus and Procedure

The equilibrium experiments were carried out in a cylindrical stirred reactor of 2 L capacity, where the temperature was maintained within ± 0.05°C of the experimental temperature by using a thermostatic bath. Figure 1 shows a sketch of the experimental apparatus.

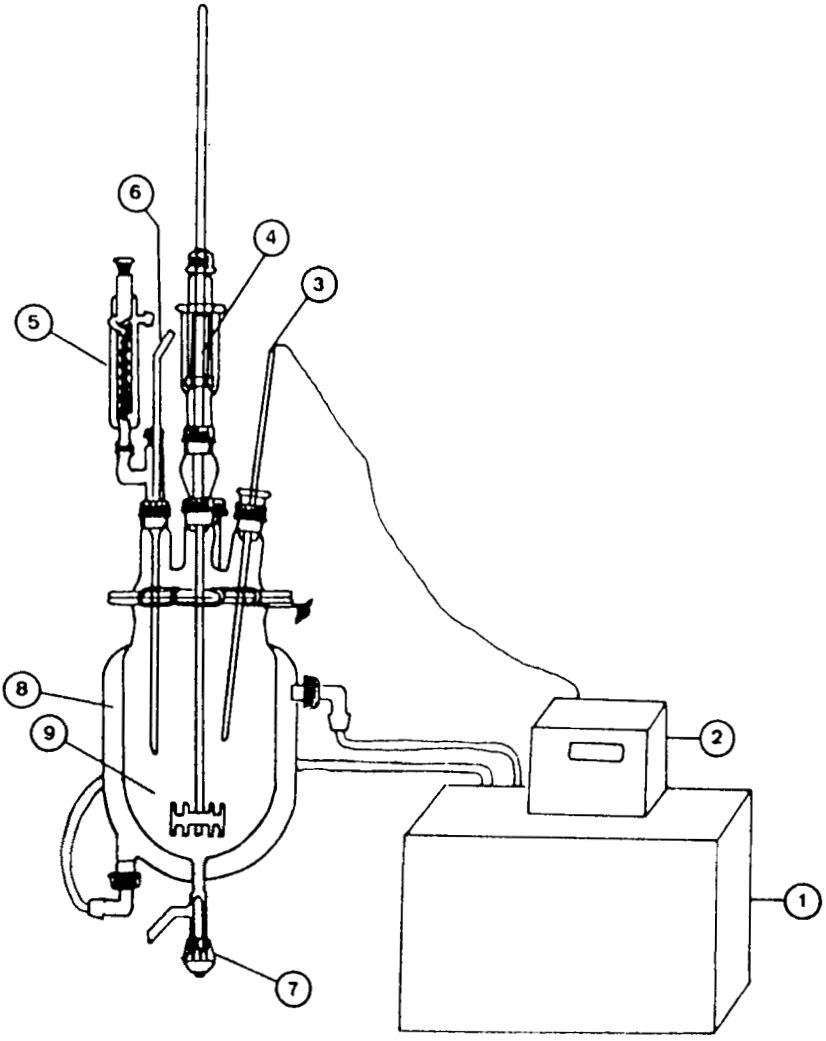

FIG. 1 Experimental set-up: (1) thermostatic bath; (2) temperature controller; (3) temperature probe; (4) agitation system; (5) cooler; (6) top sampling tube; (7) bottom sampling tube; (8) heating jacket; (9) experimental mixture.

The tie-lines and the binodal curves were determined by preparing pseudoternary mixtures from weighted amounts of furfural, HAC mixture, and LAC mixture. The experimental system was maintained under agitation (280 rpm) for at least 2 hours and then allowed to settle for 15 minutes to obtain a good separation of the two phases. Then furfural was eliminated from the extract and raffinate by vacuum distillation, and the amount of aromatic compounds in each phase was determined. This determination was carried out measuring the refractive index at 335 K by using a refractometer thermostated and previously calibrated with an accuracy of $\pm 0.0001 n_D$.

RESULTS AND DISCUSSION

Mixtures Characterization

Prior to studying the equilibrium, preliminary runs were carried out to obtain a property whose variation with the aromatic concentration was lineal. In order to consider the system as pseudoternary, this property was necessary. In these runs the following properties were measured: density, kinematic viscosity, refractive index, aniline point, sulfur concentration (wt%), and coke concentration (wt%).

The results from those preliminary experiments (14) showed that the refractive index (measured at 335 K) was the most appropriate property to determine the aromatic concentration. The data obtained may be fitted to a straight line through the following equations:

$$n_D(335\ \text{K}) = (1.4517 + 2.98 \times 10^{-3})(\text{aromatic concentration})\ (\text{wt\%})\ (\text{Kirkuk}) \quad (1)$$

$$r^2 = 0.999582$$

$$n_D(335\ \text{K}) = (1.4507 + 2.91 \times 10^{-3})(\text{aromatic concentration})\ (\text{wt\%})\ (\text{L. Arabia}) \quad (2)$$

$$r^2 = 0.999341$$

LLE Data

The experimental LLE data for the two pseudoternary mixtures (from Kirkuk and Light Arabia crude oils) at different temperatures in the 335–402 K range are plotted in Figs. 2 and 3. The temperature range for the experiments was selected by taking into account the temperatures usually employed in the industrial equipment we want to simulate.

It can be observed that type I isotherms with low slope tie-lines were obtained for the two systems at all temperatures. Moreover, the immiscibility region as well as the tine-lines slope decrease by increasing the temperature from 335 to 402 K. This fact explains the low efficiency

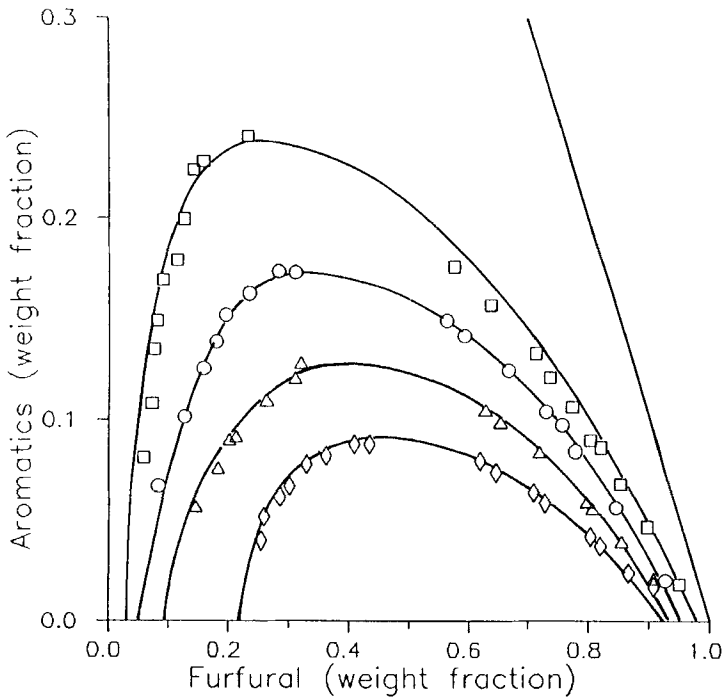

FIG. 2 Liquid–liquid equilibrium of furfural–aromatics–nonaromatics pseudoternary system from Kirkuk crude oil. Experimental data: (□) T = 335 K; (○) T = 363 K; (△) T = 385 K; (◇) T = 402 K. (——) Predicted binodal curves using the NRTL equation.

achieved in industrial extraction units where the main aim is to obtain a high quality raffinate.

On the other hand, it is important to note that the equilibrium data are similar for the two systems studied and that only a slight increase in the slope of the tie-lines is observed when HND from Kirkuk is used. This agreement between the two systems assayed may be explained by taking into account that the two crude oils have similar physical and chemical properties, as shown in Table 1.

The reliability of experimental measured tie-line compositions was ascertained by making Othmer–Tobias (15) plots at each temperature for the two feeds used. The linearity of the plots indicates the degree of consistency of the data. Figure 4 shows the plots obtained at 385 K when using the Kirkuk and Light Arabia crude oils. It can be seen that the experimental results give a good fit to a straight line with r^2 = 0.9968 for Kirkuk and r^2 = 0.9985 for Light Arabia. Similar results were obtained at the other temperatures assayed.

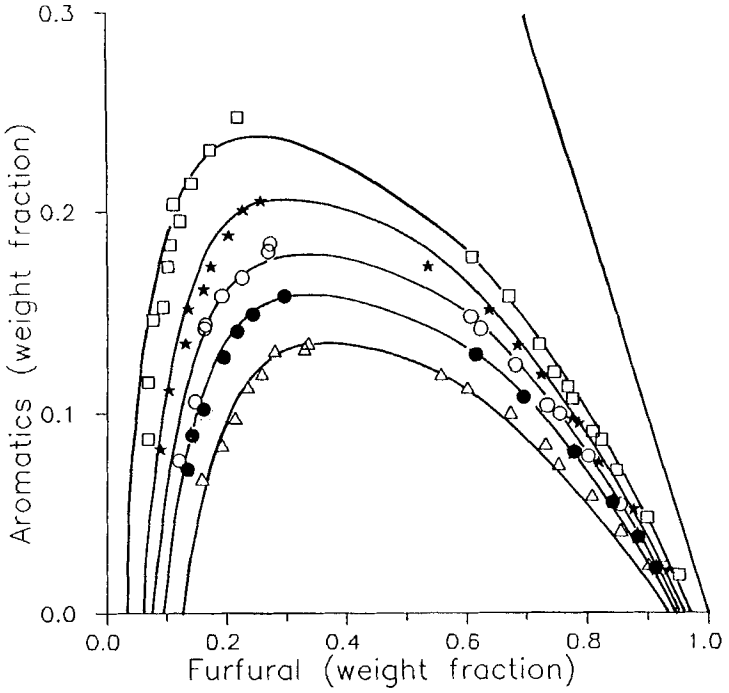

FIG. 3 Liquid–liquid equilibrium of furfural–aromatics–nonaromatics pseudoternary system from Light Arabia crude oil. Experimental data: (□) T = 335 K; (★) T = 353 K; (○) T = 363 K; (●) T = 373 K; (△) T = 385 K. (——) Predicted binodal curves using the NRTL equation.

TABLE 1
Characterization of Raffinate and Extract Streams from Repsol Petroleo S.A., Puertollano (U-E)

Property	Kirkuk		Light Arabia	
	Extract U-E	Raffinate U-E	Extract U-E	Raffinate U-E
Kinematic viscosity (cSt, 100°C)	29.2	9.2	27.0	10.17
Density (g/cm^3, 15°C)	1.0055	0.8710	1.0008	0.8836
Sulfur concentration (wt%)	5.0795	0.5888	4.3137	0.7976
Refractive index (62°C)	1.553	1.462	1.550	1.467
Color (ASTM P-526)	Black	2.5	Black	3.5
Aniline point (°C)	39.0	117.5	50.0	115.0
Coke concentration (wt%)	0.9779	0.0956	1.2072	0.0785

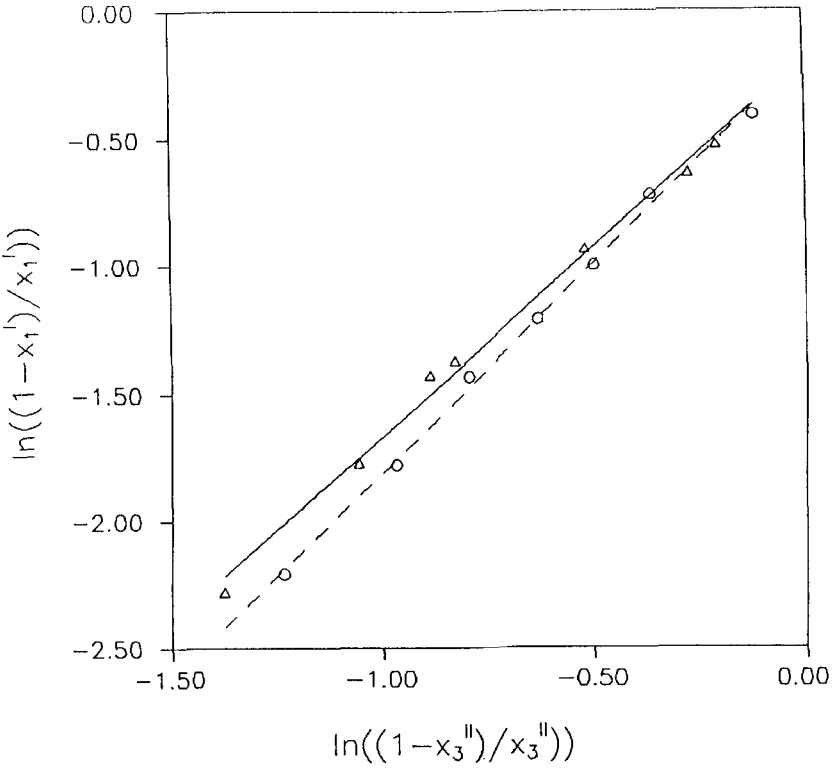

FIG. 4 Othmer–Tobias plots at 385 K: (△) Kirkuk; (○) Light Arabia.

Therefore, the experimental tie-line compositions were correlated with the reduced Eisen–Joffe equation (16):

$$\ln(x_2^{II}/x_3^{II}) = C_1 + C_2[\ln(x_2^{I}/x_1^{I})] \quad (3)$$

The coefficients C_1 and C_2 were estimated by least-squares regression, and the values obtained are summarized in Table 2. A high linearity has also been obtained, as can be seen from the correlation coefficients and standard deviations of all the experiments (Table 2).

Thermodynamic Correlation of the LLE Data

The prediction of equilibrium conditions between two liquid phases composed of dissimilar, polar species is one of the most difficult thermodynamic problems. The distribution coefficient for each specie i between

TABLE 2
Parameters of the Eisen–Joffe Reduced Equation
System: Furfural–Aromatics–Nonaromatics

	Kirkuk				Light Arabia			
T (K)	C_1	C_2	σ	r^2	C_1	C_2	σ	r^2
335	0.07415	0.72228	2.0×10^{-2}	0.9795	0.07102	0.70338	1.3×10^{-2}	0.9802
353	—	—	—	—	−0.21188	0.61390	1.1×10^{-2}	0.9901
363	−0.33861	0.59334	2.6×10^{-2}	0.9920	−0.35760	0.55332	3.1×10^{-2}	0.9882
373	—	—	—	—	−0.45070	0.53845	1.7×10^{-2}	0.9922
385	−0.43392	0.59840	0.7×10^{-2}	0.9966	−0.46715	0.55190	0.3×10^{-2}	0.9985
402	−0.47705	0.59732	0.5×10^{-2}	0.9976	—	—	—	—

phase I and phase II is defined as

$$K_i = \frac{x_i^{\mathrm{I}}}{x_i^{\mathrm{II}}} = \frac{\gamma_i^{\mathrm{II}}}{\gamma_i^{\mathrm{I}}} \tag{4}$$

Although there are many correlations for calculating the activity coefficients in the literature, different authors (17–19) have demonstrated that the nonrandom, two liquid (NRTL) equation of Renon and Prausnitz (8) is the most appropriate for the activity coefficients in a liquid–liquid system, especially when it is a type I system, as in this case. The NRTL equation considers the binary interactions between molecules i and j based on the local mole fraction concept. The NRTL expression for an i-component in any of the two phases is

$$\ln \gamma_i \frac{\sum_{j=1}^{c} (\tau_{ij} G_{ij} x_j)}{\sum_{k=1}^{c} (G_{ki} x_k)} + \sum_{j=1}^{c} \left[\frac{x_j G_{ij}}{\sum_{k=1}^{c} (G_{ki} x_k)} \left(\tau_{ij} - \frac{\sum_{k=1}^{c} (\tau_{kj} G_{kj} x_k)}{\sum_{k=1}^{c} (G_{kj} x_k)} \right) \right] \tag{5}$$

where

$$G_{ij} = \exp(-\alpha_{ij}\tau_{ij})$$

$$\tau_{ij} = A_{ij}/RT$$

$$\tau_{ii} = A_{ii} = 0$$

$$\alpha_{ij} = \alpha_{ji}$$

Then, for a ternary system, such as the one analyzed in this work, the NRTL model has nine parameters: the six binary parameters A_{ij} and the three $\alpha_{ij} = \alpha_{ji}$ coefficients. The A_{ij} parameters represent the differences between interaction energies between unlike and like molecule pairs. The

TABLE 3
Parameters of NRTL Equation Predicted from

Feed	$\alpha_{12} = \alpha_{21}$	$\alpha_{13} = \alpha_{31}$	$\alpha_{23} = \alpha_{32}$	$A_{12} \times 10^{-3}$ (J·mol^{-1})	$A_{21} \times 10^{-3}$ (J·mol^{-1})
Kirkuk	0.300	0.300	0.300	14.211	3.089
Kirkuk	0.395	0.426	0.313	11.918	9.809
Light Arabia	0.300	0.300	0.300	12.749	2.791
Light Arabia	0.366	0.426	0.291	11.902	7.018

[a] 1 = furfural, 2 = aromatics, 3 = nonaromatics.

α_{ij} coefficients represent the tendency of species i and j to be distributed in a random fashion. They can vary between 0.2 and 0.47 depending on the polarity of the molecular species (20).

In the literature there are several methods, more or less adequate, to correlate A_{ij} and α_{ij}, i.e., α_{ij} parameters are frequently set equal to constant, known values (dependent on the molecules species) without a great loss of accuracy, and A_{ij} values are estimated by making two experimental measurements at "infinite" dilution.

In this work, two different approximations have been made. The first was to assume that the α_{ij} parameters were constant and equal to 0.3, a value recommended by Henley and Seader (20) for hydrocarbon mixtures. With this approximation, the number of adjustable parameters was six. The second approximation was developed with nine adjustable parameters. In both cases the parameters were determined by fitting all the experimental data for both the crude oils used to Eq. (4), using the NRTL Eq. (3) to calculate the activity coefficients. A computer program based on the Marquardt algorithm (21) was used to obtain the values that minimized the objective function:

$$\phi = \sum [W_1^{\mathrm{I}}(x_{1,\mathrm{exp}}^{\mathrm{I}} - x_{1,\mathrm{calc}}^{\mathrm{I}}) + W_2^{\mathrm{I}}(x_{2,\mathrm{exp}}^{\mathrm{I}} - x_{2,\mathrm{calc}}^{\mathrm{I}}) + W_1^{\mathrm{II}}(x_{1,\mathrm{exp}}^{\mathrm{II}} - x_{1,\mathrm{calc}}^{\mathrm{II}}) + W_2^{\mathrm{II}}(x_{2,\mathrm{exp}}^{\mathrm{II}} - x_{2,\mathrm{calc}}^{\mathrm{II}})] \quad (6)$$

Table 3 summarizes the values obtained for the nine parameters as well as the values of the minimized objective function. The binodal curves predicted using the values of the parameters in Table 3 are plotted in Figs. 2 and 3. It can be observed that the predicted curves fit the experimental results with a maximum error of 5%.

By comparing the results obtained using the two different fitting methods (six and nine adjustable parameters), we can affirm that fitting the nonrandom parameters clearly reduces (by about 50%) the objective functions. That may be explained by taking into account the α_{ij} values, particu-

Experimental Equilibrium Data[a]

$A_{13} \times 10^{-3}$ (J·mol^{-1})	$A_{31} \times 10^{-3}$ (J·mol^{-1})	$A_{23} \times 10^{-3}$ (J·mol^{-1})	$A_{32} \times 10^{-3}$ (J·mol^{-1})	ϕ
1.978	7.807	8.579	11.985	15.07×10^{-3}
4.867	5.415	9.136	8.754	2.13×10^{-3}
2.257	11.262	8.721	8.720	7.19×10^{-3}
7.018	4.641	8.829	9.659	1.76×10^{-3}

larly the $\alpha_{13} = \alpha_{31}$ value. The second model predicts for this parameter a value of 0.426 [partial immiscibility of the 1–3 pair, furfural–nonaromatic compounds (20)]. However, the first model does not consider the immiscibility but rather the nature of the hydrocarbons, with 0.3 as the selected value (20).

There are also some differences between the two fittings related to the A_{ij} values, and these are especially significant for the 1–3 pair. Thus, the model with a constant value of $\alpha_{13} = 0.3$ leads to A_{13} and A_{31} values twofold higher than the nine parameters model. On the other hand, there are no significant differences between the parameters obtained for the two feeds used (Kirkuk and Light Arabia).

The equilibrium data presented in this work have been used to simulate the extraction column of the lubricating oil unit in the Repsol Petroleo S.A. refinery (Puertollano, Spain). The simulation carried out fits the operation results with an error of less than 10%. From this experience we conclude: 1) that the equilibrium data obtained in this work are good enough to simulate the process analyzed, and 2) that the supposition initially made about the pseudoternary system neither represents an important error in the data obtained nor in the thermodynamic reproduction of these data.

NOMENCLATURE

A_{ij}	difference between the interaction energies for the pair i–j (J·mol^{-1})
C_1, C_2	parameters of the Eisen–Joffe reduced equation
G_{ij}	parameter of the NRTL equation
HAC	mixture of hydrocarbons with the highest aromatic concentration
K_i	distribution coefficient between extract and raffinate for specie i

LAC	mixture of hydrocarbons with the lowest aromatic concentration
r^2	correlation coefficient
x_i^{I}	weight fraction of component i in the extract phase
x_i^{II}	weight fraction of component i in the raffinate phase
W	weighting factor
α_{ij}	nonrandomness parameter
ϕ	objective function
γ_i^{I}	activity coefficient of component i in the extract phase
γ_i^{II}	activity coefficient of component i in the raffinate phase
σ	standard deviation
τ_{ij}	parameter of the NRTL equation

Subscripts

1	furfural
2	aromatics
3	nonaromatics

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