Extraction of aromatic and polyaromatic compounds with NMP: experimental and model description

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ABSTRACT

Optimization of the extraction process for reducing aromatic and/or polyaromatic compounds is of primary interest in crude oil refining. Several solvents are described for carrying out such operations (furfural, N-methyl-pyrrolidone -NMP-, dimethyl-sulfoxide -DMSO-, …) and experimental data and model description are required for the correct design of the separation operations and the optimization of the conditions.

In this work, liquid-liquid equilibria (LLE) data were determined for oil multicomponent mixtures formed by n-dodecane + mono-aromatic + poly-aromatic with NMP at ambient temperature (298.15 K) and pressure and covering a wide range of the solvent/oil ratios.

A new analytical method based on NMR was developed, calibrated, and tested to fully determine the composition of equilibrium phases despite the high number of compounds.

Obtained values for distribution constants and selectivities are higher than one and ranging 1-15, respectively, for aromatic compounds and even higher for polyaromatic components. Thus NMP appears as a suitable solvent for carrying both separations.

The experimental data were predicted by several versions of the UNIFAC model, including the UNIFAC, modified UNIFAC (Dortmund), modified UNIFAC (NIST), and UNIFAC, including fitting parameters. Overall, modified UNIFAC (Dortmund) yields the best results, even when deviations obtained for some of the compositions are around 40% of the value, and simulations carried out with such models should be considered cautiously

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1. Introduction

During crude oil refining, the removal of aromatic hydrocarbons from vacuum distillates is required in manufacturing lubricating oil base stocks to improve several lubricating properties [1]. The aromatic extraction process requires a suitable solvent that maximizes differences in properties between the liquid phases, and furfural is one of the most widely used because its selectivity towards aromatic compounds is high enough, decreases slowly when increasing temperature, and is acceptable for light and heavy vacuum distillates [2].

During such a dearomatization process, the extract yields, as a by-product, oil with high aromatic content named DAE (distillate aromatic extract). Such aromatic process oils are traditionally and widely used as extender oils or plasticizers and rubber extenders

in many rubber products due to their excellent compatibility with natural and synthetic rubber [3], mainly in the tire industry [4]. Desired viscosity property is obtained by the high aromatic content fulfilled by the extract of the dearomatization process. The relatively low price of this group of products contributes to a given extension to the widespread application of these recipe ingredients, especially in tire compounds.

However, such DAE presents a high content of polycyclic aromatic compound (PCA) ranging 10-25%, which is responsible for their high carcinogenic potential [5,6] and has to be replaced with alternative eco-friendly low polyaromatic hydrocarbon content process oils [7]. More than 3 wt% of polycyclic aromatics (PCAs) in process oil are known to cause skin cancer, and such 3 wt% value is the criterion of distinguishing between low and high PCA oils. Distillate aromatic extracts (DAE) are considered high PCA and carcinogenic oils, while treated distillate aromatic extract (TDAE), mild extract solvates (MES), and paraffinic oil [8] are low PCA and safety oils.

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The global marketplace is increasingly demanding safe process oils to reduce the environmental impact of tires. The replacement of classified distillate aromatic extracts by non-carcinogenic MES, TDAE, or naphthenic process oils will reduce the PCA emissions from tires by more than 98 % [9].

Some studies have determined that the properties are strongly affected by oil contents but less by the oil types [10]. The sulfur in the natural rubber matrix leads to improved crosslink distribution and thus mechanical properties of the rubber vulcanizates. The results demonstrate that, to obtain a satisfactory degree of sulfur dispersion in the unfilled natural rubber, at least 20%wt. of TDAE oil is required as a dispersing agent [11]. Compounds made with naturally occurring oils showed better abrasion properties [12].

Between the several methods developed to reduce the PCA content of oil samples, the hydrogenation of aromatic compounds [13], the extraction with solvents, and the adsorption [3,14] are the most common methods.

Extraction with solvents is probably the most common process, and the effect of different solvents and extraction conditions have been studied [14–21], including ionic liquids as solvents. Some studies about the extraction of heavy aromatic compounds from crude oil fractions have shown that furfural and NMP are suitable solvents for such extraction with or without co-solvent [22–24]. Nowadays, extraction with furfural is the most common process and one of the most studied to reduce PCA content from crude oil fractions. The main topic is optimizing the process by adding a co-solvent, [25] analyzes the effect of water content ranging 0-15%, [26] uses formamide ranging 10%-15%.

Several patents described this process using different solvents with or without co-solvent and different extraction conditions. Most common solvents are furfural [27–30], dimethyl sulphoxide (DMSO) [31], or carbonates [32].

The design and simulation of solvent extraction processes, both in the production of lubricating basis and of TDAE, requires a rigorous model that reproduces the effect of changes in operating conditions or feed quality. Description of the extraction process requires a consistent thermodynamic model based on the liquid-liquid equilibrium (LLE) established. However, actual solvent + oil systems are very complex because of the high number of components in these mixtures, and simplified methods of characterization and calculation are used, usually in terms of only a few pseudo components [33]. For the same reason, oversimplified binary or ternary mixtures cannot represent the fundamental interactions occurring between involved compounds. Most experimental studies involving polyaromatic compounds are solubility [34] or solid-liquid equilibria [35] data, but the liquid-liquid equilibria data are relatively scarce [36–38].

Different thermodynamic models can be used to describe the LLE in this kind of system. NRTL [39] and UNIQUAC [40] models have been used to correlate LLE data for the system furfural + hydrocarbon systems [33] or NMP + hydrocarbon systems [34]. UNIFAC [41] has been widely used to describe the LLE for several solvent + hydrocarbon systems including sulfolane, aniline, furfural, and NMP [42–44].

In this work, LLE data for a multicomponent mixture representing a synthetic crude oil (SC) and NMP as solvent was studied. The SC was formed by 5 molecules of two families: saturates and aromatics. The aromatic fraction was formed by mono, di, and polyaromatic compounds. A quantitative characterization method based on NMR was developed to determine the composition of all the compounds simultaneously in a unique determination.

Several UNIFAC model versions were used to describe the LLE established in the extraction operation, and calculated values were compared with experimental values. Such comparison allowed to establish the accuracy of predicted values and the reliability of available models to carry on such predictions.

2. Experimental section

2.1. Materials

Chemicals used in this work are listed in Table 1 next to CAS Nº, supplier, and purity obtained from data specifications provided by the supplier. All chemicals were used without further purifications.

2.2. Experimental procedure

Synthetic crudes (SC) were formed by n-dodecane (1) + toluene (2) + 1,4-xylene (3) + 1-methylnaphthalene (4) + pyrene (5). Synthetic crudes of known composition were employed in carrying out calibration curves from the ^{1}H-NMR analysis and to obtain the equilibrium data referring to a liquid-liquid extraction process for different solvent/SC ratios.

Synthetic crudes were prepared as follows. All components were weighed by a balance (Sartorius Lab Balance) with an uncertainty of ± 0.0001 g and added to a glass vial with 100 mL of volume. Due to the low solubility of pyrene into the mixture at ambient temperature and high concentrations, firstly, pyrene was dissolved in 1-methylnaphthalene. After obtaining a homogeneous solution, the rest of the components of synthetic mixtures were added according to the composition detailed in Table 2. Mixtures were kept at 50 °C to 70 °C and 550 rpm for 24 h to ensure all components, particularly pyrene, were solubilized entirely. Table 2 lists the composition of synthetic mixtures employed in carrying out calibration curves from the ^{1}H-NMR analysis. Additionally, NMP/toluene mixtures at different compositions (79.88, 66.45, 49.87, 39.91, and 33.47 wt. % NMP in toluene) were prepared following the procedure described above. These mixtures were included in the calibration curve to consider the presence of solvent in raffinate and extract after phases separation. The standard deviation in the composition for the samples listed in Table 2 and those prepared with NMP/toluene is 0.1%.

Five of the mixtures shown in Table 2 were chosen to carry out liquid-liquid extraction experiments: Feed 1, Feed 5, Feed 6, Feed 7, and Feed 8. Liquid-liquid extractions were performed on 1-10 g of SC was added to a 40 ml glass vial. Several amounts of NMP were added at different NMP/SC (g/g) ratios: 0.25, 0.5, 1.0, 1.5, 2.5, and 3.0. Mixtures were vigorously stirred by a magnetic stirrer for 12 hours, and after this time, stirring was turned off, and phases were left separated by gravity for 12 hours. Phases were separated, avoiding contamination using a syringe, and the NMP-rich phase was transferred to a clean glass vial. Both solvent-rich and alkane-rich phases were analyzed by ^{1}H-NMR spectroscopy.

2.3. Analytical method

Several methods were recently proposed for the rapid determination of the composition of samples containing polyaromatic compounds involving the use of FTIR [46], gas chromatography (GC-MS) combined with NMR [47], or liquid chromatography [48,49].

Table 1
Chemicals used in this work.

Chemical [45]	CAS No.	Supplier	Purity
n-dodecane	112-40-3	Acros Organics	98.5 %
1,4-xylene	106-42-3	Acros Organics	98.5 %
1-methylnaphthalene	90-12-0	Acros Organics	95 %
toluene	108-88-3	Scharlau	99.9 %
1-methylpyrrolidin-2-one	872-50-4	Scharlau	99.5 %
pyrene	129-00-0	Alfa Aesar	99 %
dichloro(^{2}H$_2$)methane	1665-00-5	Eurositop®	99.8%

Table 2
Composition[a] of mixtures used in this work.

Mixture	n-dodecane mass fraction, %	toluene mass fraction, %	1,4-xylene mass fraction, %	1-methylnaphthalene mass fraction, %	pyrene mass fraction, %
Feed 1	50.0	25.0	-	15.0	10.0
Feed 2	50.0	19.0	-	19.0	12.0
Feed 3	50.0	17.5	-	17.5	15.0
Feed 4	49.9	16.0	-	16.0	18.1
Feed 5	50.0	-	27.5	17.5	5.0
Feed 6	50.1	-	25.0	15.0	9.9
Feed 7	49.8	-	24.2	13.9	12.1
Feed 8	49.8	-	22.4	12.8	15.0

[a] Standard uncertainties (u), are: u(mass fraction, %)=0.1%.

In this work, characterization and quantification of solvent-rich and alkane-rich phases were performed by ^{1}H-NMR spectroscopy. Once separated raffinate and extract, 0.2 ml of each phase was dissolved into 0.7 ml of dichloro(2H2)methane and placed in a 5 mm NMR sample tube. The spectra were recorded on a Bruker DRX 500 spectrometer operating at 75.4 MHz at 25°C.

3. Calculation section

3.1. Determination of liquid-liquid equilibrium (LLE)

Equilibrium condition is given by:

$$\gamma_i^r x_i^r = \gamma_i^e x_i^e \tag{1}$$

Where γ_i and x_i are the activity coefficient and mole fraction of component i in the phase indicated by the subscript, r and e refer to raffinate and extract phases, respectively.

Distribution constant, K_i, and selectivity, α_i, are defined as

$$K_i = \frac{x_i^e}{x_i^r}$$

$$\alpha_i = \frac{K_i}{K_j} \tag{2}$$

Where subscript i refer to aromatic compounds (x_i being obtained as the sum over all the aromatic compounds, $x_i = x_2+x_3+x_4+x_5$), polyaromatic (x_i being obtained as the sum over naphthalene and pyrene, $x_i = x_3+x_5$), or pyrene ($x_i=x_5$), and j to aliphatic compounds, in this case, n-dodecane ($x_j=x_1$, $K_j=K_1$).

In this work, an iterative method following a procedure similar to the well-known Rachford-Rice algorithm [50] solves the Eq. (1) by using thermodynamic models for computing the activity coefficient.

Agreement of model description was quantified through standard deviation σ for mole fractions:

$$\sigma = \left(\sum_k \sum_j \sum_i \frac{\left(x_{exp,i}^j - x_{c,i}^j\right)^2}{n-1} \right)^{0.5} \tag{3}$$

Where subscripts exp and c indicate experimental values and those calculated from Eq. (1), respectively, the index i sums over all the components, j sums over phases r and e, and k sums over experimental data, n is the total number of compositions involved in the determination of σ. When parameters were fitted, the minimization of such standard deviation, σ, between experimental and calculated values according to Eq. (3) was attempted.

3.2. UNIFAC models

UNIFAC model versions are widely used and are well-known thermodynamic models: UNIFAC model [41], Modified UNIFAC (Lyngby) [51], Modified UNIFAC (Dortmund) [52,53], and Modified

UNIFAC (NIST) [54]. Expressions for activity coefficient, γ_i, of component i in the liquid phase are described elsewhere and not included in this work. The main differences between the several versions are the parameter temperature dependence and the revision of the interaction parameters according to new experimental information.

In the several UNIFAC versions, the group interaction parameters between groups n and m, a_{nm}, are given by:

UNIFAC : $\quad a_{nm} = a_{nm,1}$

Mod.UNIFAC (Lyngby) : $\quad a_{nm} = a_{nm,1} + a_{nm,2}(T - T_0)$
$$+ a_{nm,3}\left(T\ln\frac{T_0}{T} + T - T_0\right)$$

Mod.UNIFAC (Dortmund) : $\quad a_{nm} = a_{nm,1} + a_{nm,2}T + a_{nm,3}T^2$

Mod.UNIFAC (NIST) : $\quad a_{nm} = a_{nm,1} + a_{nm,2}T + a_{nm,3}T^2 \tag{4}$

4. Results and discussion

4.1. ^{1}H-NMR spectra processing, characterization, and quantification of mixtures

Characterization and quantification of each liquid phase once separated were performed by ^{1}H-NMR analysis. The NMR spectra were processed by Mnova NMR software. Firstly, the signals of each pure compound were identified individually by recording NMR spectra.

Fig. 1 shows an example of the NMR spectrum of the synthetic crude, which precisely corresponds to Feed 4. The composition of this mixture is specified in Table 2. Molecular structures of each compound that form Feed 4 are represented in the graph, and red stands out proton numbering in the molecule and the signal assigned to each different proton. Generally, in the left region appear signals corresponding to protons in the rings of polyaromatic compound (a. pyrene) in the shifting range (8.4 to 7.9) ppm. Particularly for Feed 4 shown in Fig 1. the H shift range of pyrene corresponds (8.4 to 8.1) ppm. Due to the differences in the concentration of each component in the synthetic mixtures, small displacements in the H shift ranges may be given. The shifting range from (7.9 to 7.3) ppm corresponds to proton signals in diaromatic compound (b. 1-methylnaphthalene), and the end of the aromatic region of spectrum shifting range from (7.3 to 7.0) ppm corresponds to signals of aromatic H of toluene (c) or, in this case, 1,4-xylene. On the contrary, signals of the aliphatic part of molecules appear in the region on the right of the spectrum. First, CH_3- of 1-methylnaphthalene from (2.75 to 2.60) ppm followed by CH_3- of toluene from (2.40 to 2.30 ppm) and ending CH_2- from (1.40 to 1.15) ppm and CH_3- from (1.00 to 0.80) ppm of dodecane.

Once all the signals have been assigned, the area of every compound was determined, integrating each peak manually and expressing as a relation among absolute areas of peaks assigned to
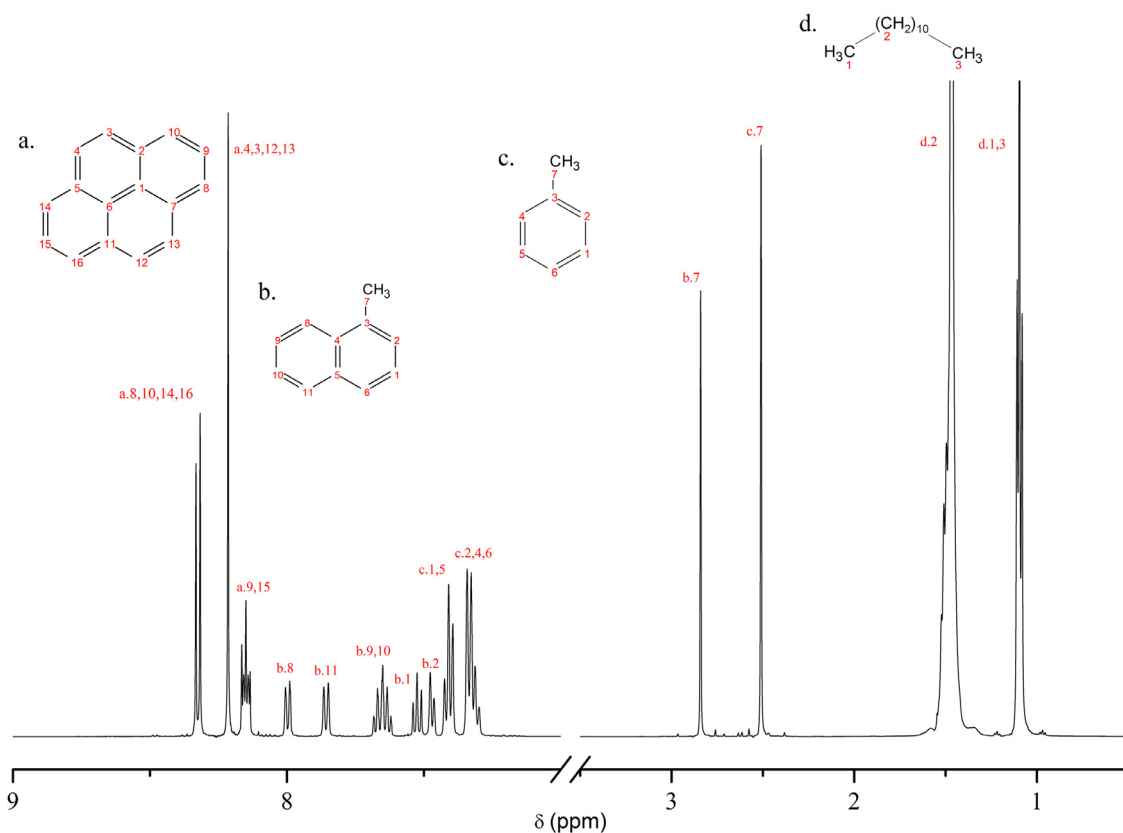
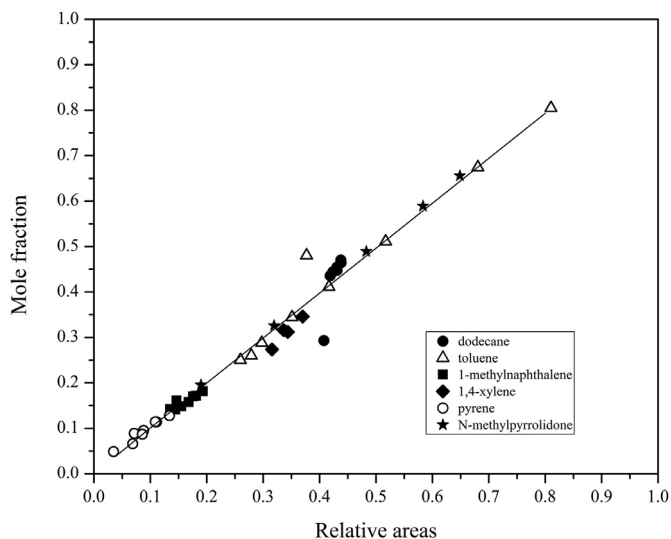**Fig. 1.** The assignments of the signals of Feed 4 obtained by ^{1}H-NMR.

Fig. 2. Calibration curve showing the linear range between relative NMR areas vs. mole fraction of each compound in synthetic mixtures (slope=0.989, y-intercept=0.00185, R^2=0.990).

that compound and signals assigned to polyaromatic compound. In this way, the area obtained by analysis of ^{1}H-NMR for pyrene in the synthetic mixture was given the value of 1.

Fig.2 shows the analytical curve obtained by correlating the mole fraction compositions of all synthetic mixture components against their relative areas. Relative areas are the ratio of component area and the area of all the peaks appearing in the NMR spectrum. Component area sums the contributions of each type of

proton and their number, including a response factor determined in the calibration process.

The analytical curve shows a linear relationship between relative areas and mole composition. The standard deviation for mole fractions is 0.3 %. The equation obtained by the least square method allows quantifying the compounds in both phases after extractions by simple H-NMR analysis and interpolation of values of NMR areas to the equation. This method has been developed time for the study of these mixtures.

4.2. Liquid-liquid equilibria

Experimental compositions for the liquid phases in equilibrium conditions are reported in Table 3. All the experiments were carried out at 298.15 K and atmospheric pressure. Table 3 lists values for the ratio NMP/SC (mol/mol) and the mole fraction for the six involved compounds in both raffinate and extract phases.

As expected, the x_1 mole fraction of n-dodecane in the raffinate phase increases as solvent/oil ratio, r, increases because of the higher aromatic compound extraction, the opposite occurs for x_1 in the extract phase mainly due to the increase in the amount of solvent in such phase.

Similar analysis can be made for the sum of aromatic compounds ($x_{ar}= x_2 + x_3 + x_4 + x_5$) and for the sum of poly-aromatic compounds ($x_{par}= x_3 + x_5$, in this work, naphthalene was considered part of polyaromatic compounds despite only two aromatic rings) in both phases. As expected, aromatic and polyaromatic mole fraction in the raffinate phase decreases as r increases because of the higher aromatic compound extraction, but also a decrease can be analyzed in the extract phase related to the increase in the solvent amount present in such phase.

From experimental information, the selectivity of NMP to aromatic compounds related to that of the n-dodecane, α, was calcu-

Table 3

Experimental LLE data[a] in mole fractions at 298.15 K and atmospheric pressure (101.6 kPa, u(P) = 0.5 kPa) for the multicomponent system n-dodecane (1) + toluene (2) + 1,4-xylene (3) + 1-methylnaphtalene (4) + pyrene (5) +NMP (6)

r	Raffinate						Extract					
(mol/mol)	x_1	x_2	x_3	x_4	x_5	x_6	x_1	x_2	x_3	x_4	x_5	x_6
2.2	0.860	-	0.068	0.018	0.004	0.050	0.158	-	0.104	0.058	0.014	0.666
0.7	0.641	-	0.131	0.050	0.020	0.158	0.392	-	0.142	0.077	0.038	0.351
1.5	0.822	-	0.085	0.022	0.006	0.065	0.240	-	0.124	0.069	0.017	0.550
2.2	0.858	-	0.067	0.015	0.005	0.055	0.157	-	0.098	0.052	0.026	0.667
0.7	0.651	-	0.134	0.047	0.021	0.147	0.320	-	0.150	0.081	0.050	0.399
1.5	0.800	-	0.092	0.022	0.008	0.078	0.206	-	0.113	0.062	0.036	0.583
2.2	0.857	-	0.062	0.015	0.005	0.061	0.181	-	0.094	0.057	0.024	0.644
3.0	0.877	-	0.050	0.011	0.005	0.057	0.174	-	0.093	0.038	0.021	0.674
0.4	0.664	-	0.136	0.055	0.035	0.110	0.250	-	0.162	0.105	0.095	0.388
0.8	0.725	-	0.109	0.037	0.018	0.111	0.252	-	0.141	0.080	0.064	0.463
1.4	0.813	-	0.082	0.020	0.009	0.076	0.190	-	0.113	0.063	0.048	0.586
2.3	0.863	-	0.058	0.013	0.005	0.061	0.150	-	0.085	0.045	0.033	0.687
3.0	0.878	-	0.048	0.010	0.004	0.060	0.135	-	0.073	0.037	0.027	0.728
0.7	0.645	0.106	-	0.048	0.020	0.181	0.397	0.142	-	0.072	0.032	0.357
1.4	0.783	0.080	-	0.025	0.007	0.105	0.210	0.113	-	0.061	0.028	0.588
2.1	0.861	0.053	-	0.016	0.005	0.065	0.177	0.088	-	0.049	0.022	0.664
4.2	0.894	0.032	-	0.009	0.003	0.062	0.145	0.054	-	0.030	0.013	0.758

[a] Standard uncertainties (u), are: u(T)=0.05 K, u(x)=0.003.
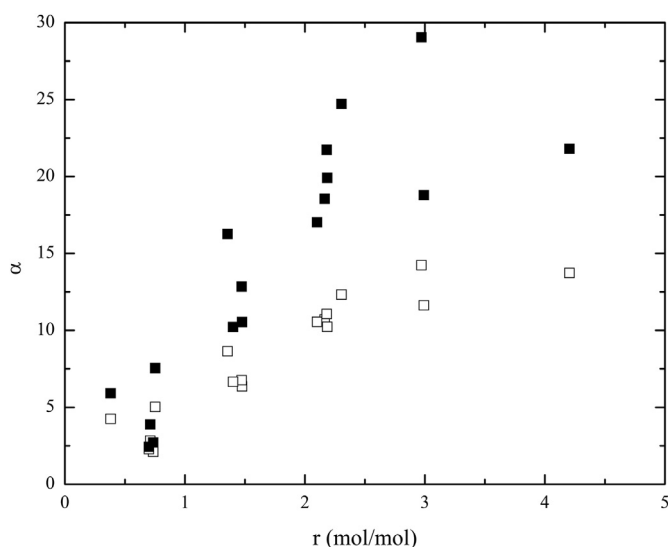
Fig. 3. Evolution of selectivity for aromatic (□) and polyaromatic (■) compounds with the solvent/oil ratio.

Fig. 4. Selectivity for aromatic (open symbol) and polyaromatic (fill symbol) compounds vs. distribution constant for extraction with NMP (square) and furfural (circle).

lated. Fig. 3 plots the selectivity of aromatic and polyaromatic compounds to n-dodecane vs. solvent/oil ratio. Although dispersion is higher due to involved errors in the determination of the composition of all compounds, it is clearly stated how NMP present high selectivity values (most of them > 5) and consequently is an adequate solvent for aromatic extraction. Even more, selectivity values are even higher when polyaromatic compounds are considered.

Simultaneous values of α and K have to be analyzed to determine the quality of the solvent. Fig. 4 plots values of α vs. K for all the experimental data presented in this paper. For comparison purposes, similar information for furfural solvent is presented in Fig. 4 [37], even when it is necessary to note that mixtures are not exactly the same. α values for aromatics cover a similar range between 2 and 14 for NMP and furfural, thus showing similar selectivity to extract such compounds. However, K values for furfural are lower (ranging 0.6-0.8) than those for NMP (ranging 1.2-2.3) and, consequently, higher extraction efficiencies are expected for NMP.

As selectivity for polyaromatics appears higher than that for aromatic in Figs. 3 and 4, it can check the option to selectively
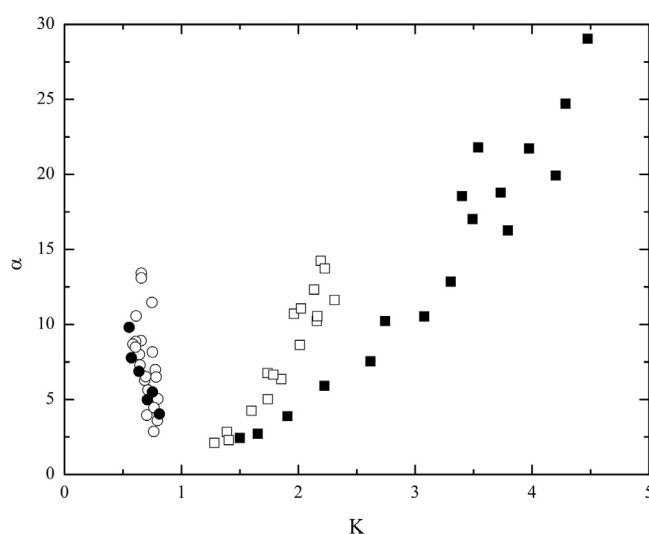
separate the polyaromatic compounds from the mixture of saturates and mono aromatics. Selectivity for such separation can be computed by Eq. 3 when j refers to the sum of aliphatic and mono aromatic compounds. Such selectivity is plotted in Fig. 5 and shows high values (most of them > 5), thus confirming NMP as solvent adequate for polyaromatic extraction.

4.3. Modeling results

The objective of this study is to check the predictive capacity of several UNIFAC versions. Calculated LLE values were performed with classical UNIFAC [34], modified UNIFAC (Dortmund) [52,53] and modified UNIFAC (NIST) [54] model versions.

Experimental and predicted compositions were compared in terms of the standard deviation as defined in Eq. (3). Eq. (3) was applied to all the compositions (σ), to compositions of the raffinate and extract phases separately (σ^r and σ^e respectively), to compositions of saturates in each phase (σ^r_1 and σ^e_1 respectively), and to compositions of aromatics and polyaromatics in each phase (σ^r_{ar}, σ^e_{ar}, σ^r_{par}, and σ^e_{par}, respectively) to check specific calculations.

Table 4

Standard deviations for LLE resulting from calculations using three UNIFAC versions

Property	Max. value	Deviation	UNIFAC	Mod.UNIFAC (Dortmund)	Mod.UNIFAC (NIST)	UNIFAC a (AC-NMP) = -145 a (NMP-AC) =-10
x^r_1	0.893	σ^r_1	0.31	0.19	0.33	0.11
x^e_1	0.397	σ^e_1	0.14	0.17	0.17	0.16
x^r_{ar}	0.226	σ^r_{ar}	0.12	0.09	0.13	0.05
x^e_{ar}	0.361	σ^e_{ar}	0.04	0.05	0.04	0.06
x^r_{par}	0.090	σ^r_{par}	0.05	0.02	0.04	0.009
x^e_{par}	0.200	σ^e_{par}	0.01	0.02	0.02	0.02
x^r	0.893	σ^r	0.15	0.09	0.16	0.06
x^e	0.756	σ^e	0.07	0.08	0.09	0.08
x	0.893	σ	0.12	0.09	0.13	0.07
K_1	0.617	$\sigma_{K,1}$	0.23	0.20	0.20	0.21
K_{ar}	1,855	$\sigma_{K,ar}$	0.60	0.58	0.79	0.18
K_{par}	4.475	$\sigma_{K,apr}$	2.1	1.4	1.9	0.86
α_{ar}	14.23	$\sigma_{\alpha,ar}$	2.7	3.6	1.8	16
α_{par}	29.04	$\sigma_{\alpha,par}$	7.0	6.6	3.4	41

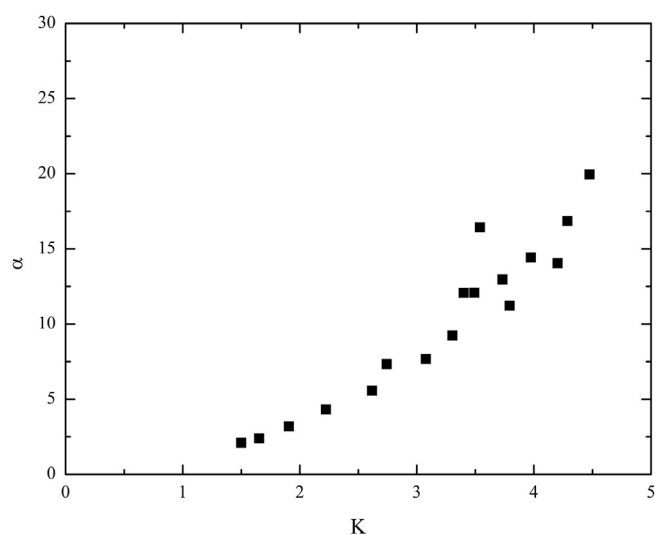**Fig. 5.** Selectivity for polyaromatic compounds to the rest of compounds (saturates + mono aromatics) vs. distribution constant (■).

Fig. 6. Evolution of experimental (▲: raffinate, △: extract) and calculated by modified UNIFAC (Dortmund) (●: raffinate, ○: extract) mole fractions of n-dodecane with the solvent/oil ratio.

Comparison is also carried out in terms of extraction coefficient (σ_K) and selectivity (σ_α) defined in Eq. (2).

Values for such deviations are listed in Table 4. Maximum values of the corresponding compositions (x^r_1, x^e_1, x^r_{ar}, x^e_{ar}, x^r_{par}, x^e_{par}, x^r, x^e, x) are also listed to set as a reference,

Overall, the most accurate predictions are obtained with modified UNIFAC (Dortmund), whose values $\sigma=0.09$, $\sigma^r=0.09$, and $\sigma^e=0.08$, represent around 10% when related to the maximum values and can be considered reasonably accurate predictions taking into account the complexity of the sample. Results for UNIFAC and Modified UNIFAC (NIST) are less accurate, mainly those for the raffinate phase (deviations higher than 15%).

The same conclusion can be stated about specific calculations. Similar accuracy is obtained for compositions of the extract phase (x^e_1, x^e_{ar}, x^e_{par}) for the three models, however, compositions of the raffinate phase (x^r_1, x^r_{ar}, x^r_{par}) are better described by modified UNIFAC (Dortmund).

In general, models fail to predict x^r_1 and x^e_1 with deviations higher than 30%. Only Modified UNIFAC (Dortmund) yielded slightly better results for x^r_1, with a deviation of around 20%. Fig. 6 plots experimental and modified UNIFAC (Dortmund) calculated mol fractions of n-dodecane in raffinate and extract phases vs. solvent/oil ratio. The experimental trend is correctly described despite high deviation.
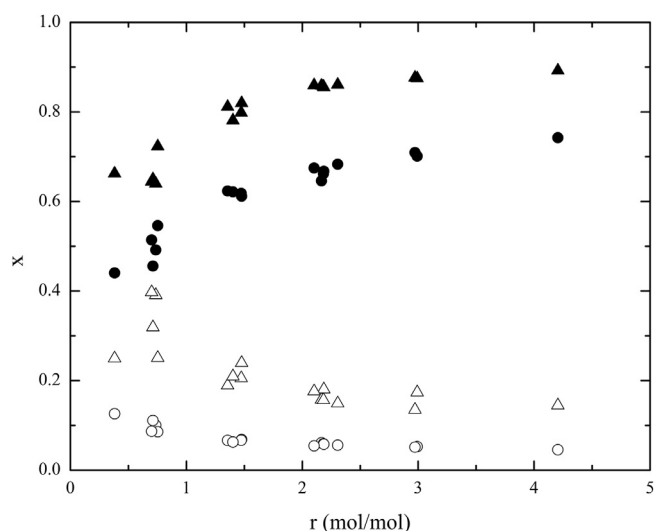
Predicted values for x^e_{ar} and x^e_{par} agree within 10% and can be considered reasonably accurate for the three model versions. However, x^r_{ar} and x^r_{par} are poorly described with deviations higher than 50%, except for modified UNIFAC (Dortmund) whose predictions for x^r_{ar} and x^r_{par} were slightly better with deviation around 40% and 25%, respectively. Fig. 7 plots experimental and modified UNIFAC (Dortmund) calculated mole fractions of the sum of aromatic and poly-aromatic compounds in both phases vs. ratio solvent/oil mixture. The experimental trend is correctly described despite high percent deviation, which has to be considered with precaution because of low values of mol fractions.

Distribution coefficients and selectivity of NMP to aromatic compounds related to that of the n-dodecane, α, were also estimated by UNIFAC models. K values are underestimated, and deviations higher than 30% show poor agreement. However, better results are obtained for α values, probably due to error compensation. In this case, lower deviations are obtained by the modified UNIFAC (NIST) model, with deviations around 10%.

Fig. 8 plots experimental and calculated by modified UNIFAC (Dortmund) selectivity of aromatic and polyaromatic compounds to n-dodecane ratio solvent/oil mixture. Despite predicted values for K property appearing too low when compared to experimental
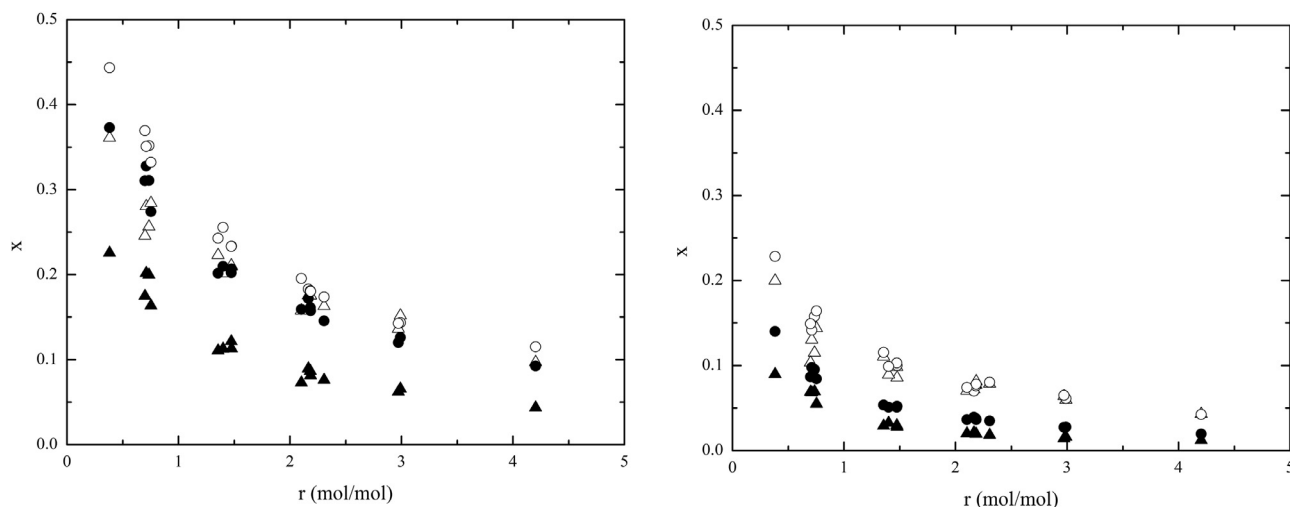
Fig. 7. Evolution of experimental (▲: raffinate, △: extract) and calculated by modified UNIFAC (Dortmund) (●: raffinate, ○: extract) mole fractions of aromatic (left) and polyaromatic (right) compounds with the solvent/oil ratio.
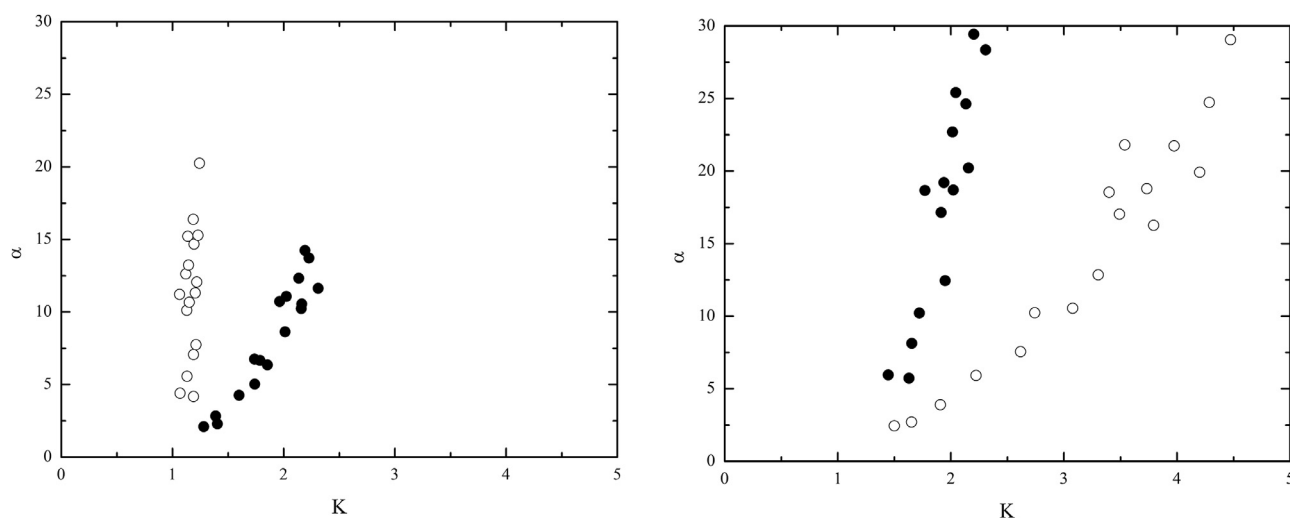

Fig. 8. Experimental (●) and calculated by modified UNIFAC (Dortmund) (○) selectivities for aromatic (left) and polyaromatic (right) compounds vs. distribution constant.

values, selectivity ranges are correctly estimated both for aromatic and polyaromatic compounds.

A readjustment of some of the interaction parameters was attempted to check if studied models have the flexibility to improve predicted values. Classical UNIFAC was used, and binary interaction parameters for the interaction between the aromatic group (AC) and the solvent (NMP) group were assumed to have the main effect in these systems. Alternative parameter values for the UNIFAC model were obtained in the present work. Parameter optimization was carried out by minimizing the standard deviation defined by Eq. 4. Alternative values for interaction parameters are listed in Table 4 as well as the deviations obtained for the several variables above analyzed.

It is important to point out, as a consequence of the high number of variables involved, that parameters that yield lower overall deviation do not usually lead to the best raffinate nor extract phases composition. Consequently, depending on the desired application, specific parameters could be obtained to assure the best description of one phase or another. The same could be stated about the deviations for the several kinds of compounds.

New UNIFAC parameters allow improving predictions of the properties poorly described by the original version without drawback in the description of the properties correctly predicted by the previous version. Consequently, comparison of deviations in Table 4 allows us to conclude that predictions with the UNIFAC model with the new parameter values are even better than those obtained by Modified UNIFAC (Dortmund) both for mole fraction and for K values. Unfortunately, predicted α values are not accurate and deviations for such property are the highest, probably due to high errors in single points with very low K values leading to extremely high α values and very far from experimental values.

5. Conclusions

Oil mixture with NMP solvent presents liquid-liquid equilibria for solvent/oil ratios ranging 0.4 to 4 at ambient temperature. An NMR procedure was developed and calibrated to fully determine the composition of samples formed by up to 6 compounds. The method showed good accuracy as checked by several synthetic samples, and was fully used to analyze the samples obtained in the extraction experiments.

The amount of saturates and aromatic compounds increase and decrease, respectively, in the raffinate phase and the difference is higher as the solvent/oil ratio increases, however, such a trend is not so clear in the extract phase because the increase of solvent leads to a full dilution effect. Distribution constants higher

than 1 and selectivities ranging 1-15 were obtained for aromatic compounds and even higher for polyaromatic compounds, thus confirming the ability of NMP for selective extraction of such compounds. Comparison with similar experiments with furfural showed better distribution constants values for NMP.

LLE data were predicted by original UNIFAC, Mod. UNIFAC (Dortmund) and Mod. UNIFAC (NIST). The best predictions were obtained by Mod. UNIFAC (Dortmund) for compositions and selectivities; however, some predicted compositions can not be considered accurate, and, consequently, utilization of such models in the simulation of the dearomatization process should be considered with caution. UNIFAC models have flexibility enough to improve such results, and more accurate values can be predicted by readjustment of some of the interaction parameters.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

Baudilio Coto: Conceptualization, Data curation, Software, Funding acquisition, Writing – original draft, Writing – review & editing. **Inmaculada Suárez:** Conceptualization, Methodology, Formal analysis, Writing – original draft. **Maria José Tenorio:** Methodology, Validation, Investigation, Writing – original draft. **Isabel Huerga:** Methodology, Investigation.

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