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Thermodynamic Modeling and Experimental Studies of Dearomatization Process from a Complex Petroleum Fraction

G. R. Vakili-Nezhaad[a]; H. Modarress[a]; G. A. Mansoori[b]
[a] DEPARTMENT OF CHEMICAL ENGINEERING, AMIRKABIR (POLYTECHNIC) UNIVERSITY OF TECHNOLOGY, TEHRAN, IRAN [b] DEPARTMENT OF CHEMICAL ENGINEERING, THE UNIVERSITY OF ILLINOIS AT CHICAGO, CHICAGO, ILLINOIS, USA

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Thermodynamic Modeling and Experimental Studies of Dearomatization Process from a Complex Petroleum Fraction

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G. R. VAKILI-NEZHAAD and H. MODARRESS*
DEPARTMENT OF CHEMICAL ENGINEERING
AMIRKABIR (POLYTECHNIC) UNIVERSITY OF TECHNOLOGY
HAFEZ AVE., NO. 424, TEHRAN, IRAN

G. A. MANSOORI
DEPARTMENT OF CHEMICAL ENGINEERING
THE UNIVERSITY OF ILLINOIS AT CHICAGO
810 SOUTH CLINTON STREET, CHICAGO, ILLINOIS 60607-7000, USA

ABSTRACT

Experimental studies and thermodynamic modeling for the separation of aromatic compounds from a complex mixture of hydrocarbons have been carried out. The sample used in this work is the main material for producing lubricating oils, and the solvent used for extraction of aromatic components is a new selective solvent which has unique specifications in comparison with conventional solvents such as furfural. This modeling is based on the method of Ruzicka for making model molecules. The parameters required for modeling were obtained, and then liquid–liquid equilibrium calculations were done and compared with the experimental data. These calculations were also carried out using published parameters for the vapor–liquid equilibria of the components involved in the mixture. The results have been compared with the previous calculations as well as with the experimental data, and good agreement was found.

INTRODUCTION

Many mixtures used in chemical industries have a complex nature because of the large number of various species they contain. Their compositions can not be represented by such conventional quantities as mole or

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* To whom correspondence should be addressed. E-mail: hmodares@cic.aku.ac.ir

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weight fractions. Examples of such mixtures are petroleum fluid fractions and polymer solutions. To define the composition of these complex mixtures, three methods have been published in the literature: pseudocomponent (10, 13), continuous (4, 15), and the method of Ruzicka (18). In this work the third method is developed and applied to the petroleum fluid considered, and a complex mixture consisting of several homologous series is modeled. The procedure is as follows (23, 24): The molecular distribution functions of the different homologous series in the mixture are obtained. Then the average molecular weights of the different homologous series are calculated by using these distribution functions. Next, model molecules of the different types of hydrocarbons are made by using the method of Ruzicka (18). Finally, the conservation of mass law is applied to obtain a system of equations which must be solved.

The sample used here to illustrate the above-mentioned method is lube-oil cut SAE 10 (on the scale of the Society of Automative Engineers) of the Tehran Refinery.

For many years a great deal of attention has been paid to the selective solvents used to extract aromatic compounds from hydrocarbon mixtures. One of the solvents used extensively for this purpose is furfural (8, 9, 11). Due to some difficulties in using furfural, attempts have been made to replace it with other solvents such as *N*-methylpyrrolidone (2, 19). The advantages of using this solvent (NMP) instead of furfural for the extraction of aromatic compounds from hydrocarbon mixtures (lube-oil cut) are as follows:

1. Lower energy consumption in the lube-oil extraction units
2. Lower solvent-to-oil ratio in the lube-oil extraction units
3. Lower toxicity
4. Lower fouling of rotating disk contractors used in the extraction equipment

To replace furfural with NMP in the separation processes, equilibrium data are required to design the needed equipment. Equilibrium data can be deduced by using the model molecules proposed here along with such thermodynamic models as the UNIFAC [Universal Functional Groups Activity Coefficient (12)]. To use the UNIFAC model, van der Waals surface and volume size parameters as well as interaction parameters between different functional groups are required. These parameters are available in the revision and extension of the UNIFAC model (6, 21), but they have been fitted to vapor–liquid equilibrium data. In this work the interaction parameters of the NMP/CH_2 and NMP/ACH pairs have been fitted by liquid–liquid equilibrium data.

EXPERIMENTS

In order to study the extraction of aromatic components from the lube-oil cut by using a solvent, several experiments have been carried out using different oil/solvent ratios. These experiments have been done in the batch mixer-settler shown in Fig. 1. The temperature and pressure were 50°C and 1 atm, respectively. The temperature of the extraction process was held constant by a controller with an accuracy of ±0.01°C. The solvent used was NMP, and the petroleum fraction was the lube-oil cut SAE 10 of the Tehran Refinery. The properties of the lube-oil cut as well as the accuracy of the measured quantities are given in Table 1. The true boiling point (TBP) data of the lube oil cut were obtained by using a Simdis GC Chrompac Model 438 by the standard method of ASTM-D2887 (1). The results are shown in Table 2.

Following the extraction process, the resultant phases (raffinate and the extract phases) were separated. After evaporating the solvent from these phases

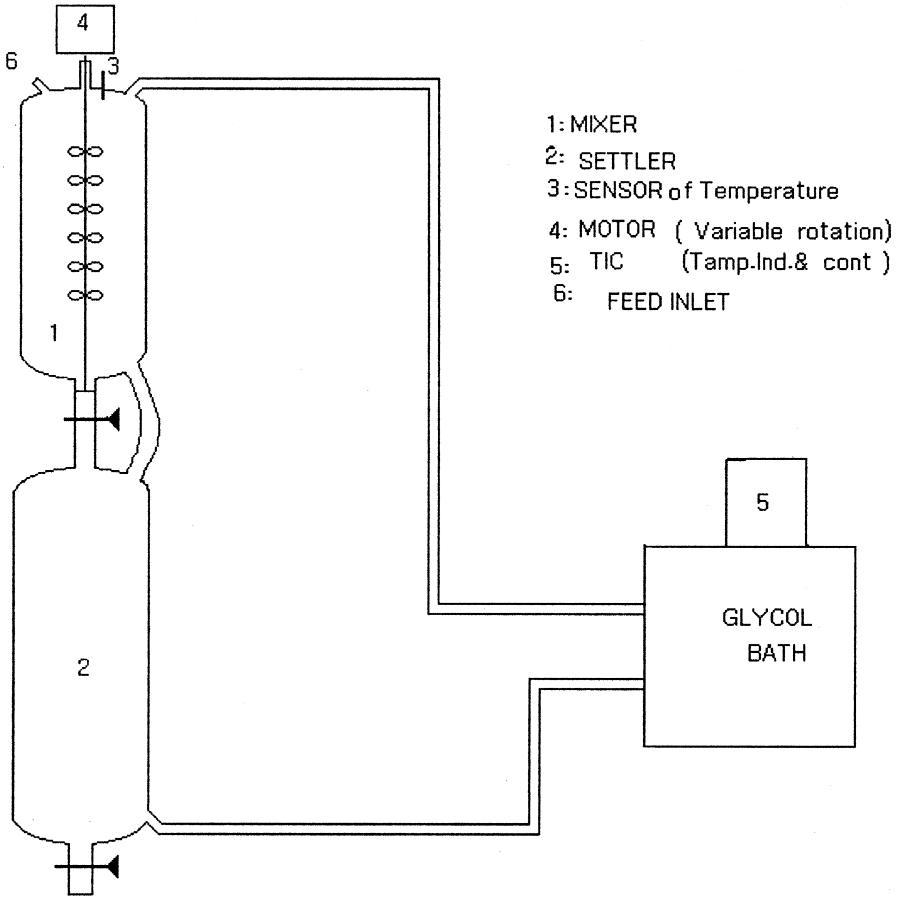


FIG. 1 Liquid–liquid extractor (batch mixer-settler).

TABLE 1
The Properties of the Lube-Oil Cut SAE 10 of Tehran Refinery and NMP

Property	Measured value
Viscosity (40ºC)	32.19 ± 0.01 (centistokes)
Viscosity (100ºC)	4.93 ± 0.01 (centistokes)
Specific gravity (60ºF/60ºF)	0.9134 ± 0.00003
Refractive index (1 atm and 20ºC)	1.5058 ± 0.00006

in a rotary evaporator system, the equilibrium compositions were determined by using the reliable equations of Riazi (16) with less than 5% average absolute deviation (AAD). The results are given below in Table 7.

MODELING AND CALCULATIONS

In this section we describe the details of the modeling for two cases. In Case One the calculation results are based on the parameters obtained in this work (from liquid–liquid equilibrium, LLE, data), and in Case Two similar calcula-

TABLE 2
True Boiling Point (TBP) vs Weight Percent of Distilled Lube-Oil Cut SAE 10 of Tehran Refinery Produced by the Simdis GC Chrompac System Model 438

Wt% distilled	TBP (°C)	Wt% distilled	TBP (°C)
0	281.3	40	390.7
2	308.3	44	393.8
4	324.7	46	395.2
6	335.8	50	398.3
8	344.8	54	401.3
10	350.6	58	404.0
12	356.0	60	405.3
14	359.8	64	408.2
16	363.7	68	411.2
18	367.3	70	412.5
20	370.2	74	415.4
22	372.4	78	418.6
24	375.1	80	420.2
26	377.6	86	425.3
28	379.9	90	429.4
30	381.7	94	435.0
32	383.5	96	438.6
34	385.3	98	444.5
36	387.3	100	464.7

tions were made by using published parameters fitted to vapor–liquid equilibrium (VLE) data (21).

Case One: Calculations with LLE Parameters

It is evident that a complex mixture such as the lube-oil cut used here can not be directly introduced into the equilibrium calculations but must be modeled to several representative molecules. Therefore, the data of Table 2 were analyzed in order to determine the distribution functions of the lube-oil cut. The experimental methods for determining the composition of petroleum fluids are expensive and time-consuming and are not proper for engineering applications (7, 17, 25).

By using the data of Table 2 and the general form of a proper distribution function (15), the molecular weight distribution functions of the three main homologous series in the lube-oil cut, i.e., paraffins, naphthenes, and aromatics, can be presented in the following general form (22):

$$W_i(N) = a_{1i}(a_{2i}N - a_{3i})^{a_{4i}} \exp\left[-\left(\frac{a_{5i}N - a_{6i}}{a_{7i}}\right)^{a_{8i}}\right] \tag{1}$$

where subscript i refers to the paraffinic, naphthenic, and aromatic homologous series. The constants of Eq. (1) are given in Table 3. The average molecular weights of the different homologous series existing in the lube-oil cut were calculated from Eq. (1). A table of gamma function must be used to calculate the average molecular weights of different homologues series. The average molecular weights obtained after using this mathematical table (20) are given in Table 4.

TABLE 3
Constants of the Distribution Function (Eq. 1)

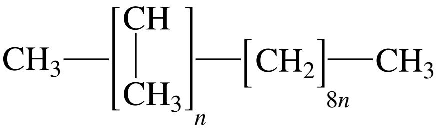
	Homologue series (i)		
Constant	Paraffins	Naphthenes	Aromatics
a_{1i}	3.78E-7	5.54E-7	7.42E-7
a_{2i}	14.0268	14.0268	14.0268
a_{3i}	223.8	209.7	201.047
a_{4i}	2.4662	2.47	2.4575
a_{5i}	14.0268	14.0268	14.0268
a_{6i}	223.8	209.7	201.047
a_{7i}	102	91.43	85
a_{8i}	3.4662	3.47	3.4575

TABLE 4
Average Molecular Weights of Different Homologous Series and the Parameters of the Model Molecules

$MW_{av,p}$	$MW_{av,n}$	$MW_{av,a}$	α	β	n
328.18	291.84	271.16	0.6407	0.5834	2.1298

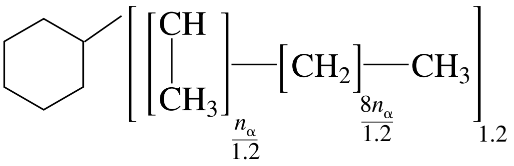
Here we use the method of Ruzicka (18) to obtain the model molecules. The general molecular structures used for this purpose are as follows:

Paraffins:

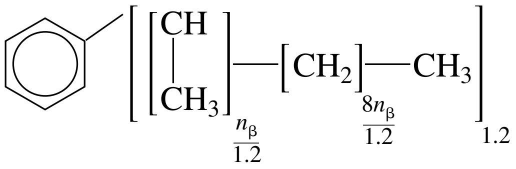


$$CH_3-\left[\begin{matrix}CH\\ |\\ CH_3\end{matrix}\right]_n-[CH_2]_{8n}-CH_3$$

Naphthenes:



Aromatics:



The last step is to determine parameters n, α, and β in the above model molecules. To calculate these parameters, the following system for the conservation of mass must be solved:

$$(n+2)MW_{CH_3} + 8nMW_{CH_2} + nMW_{CH} = MW_{av,p} \tag{2}$$

$$4.8MW_{CH_2} + 1.2MW_{CH} + n\alpha MW_{CH\text{-}CH_3} + 8n\alpha MW_{CH_2} + 1.2MW_{CH_3} = MW_{av,n} \tag{3}$$

$$4.8MW_{CH} + 1.2MW_{CH_2} + n\beta MW_{CH\text{-}CH_3} + 8n\beta MW_{CH_2} + 1.2MW_{CH_3} = MW_{av,a} \tag{4}$$

The calculated parameters obtained by using the average molecular weights are given in Table 4. It is worth noting that in this method the model molecules may have a noninteger number of groups in different hydrocarbon families.

The complex mixture is considered to consist of these three model molecules. Therefore, the liquid–liquid equilibrium can be obtained. However, as can be seen from the structures of the model molecules, we must apply a group contribution method to calculate the activity coefficients of these molecules. In this work the UNIFAC model was chosen. To use this activity coefficient model, van der Waals surface and volume size parameters as well as the interaction parameters between different functional groups are required. These parameters have not been reported for the groups involved in NMP (14), hence application of the UNIFAC model for a mixture containing NMP is not possible. To overcome this difficulty, the size and energy parameters related to NMP were calculated as follows.

We first used Bondi's method (3) of functional groups to calculate the van der Waals surface and volume size parameters of NMP, and then the interaction parameters of NMP with the other groups in heptane and benzene were obtained. The idea of taking NMP as a functional group for obtaining the interaction parameters is based on similar work done by several researchers (10, 13).

In the *n*-heptane/benzene/NMP system, two liquid phases are in equilibrium. The benzene-rich phase is named the extract and the benzene-lean phase is named the raffinate. The condition for the equilibrium of these phases is

$$x_i^{(\mathrm{I})}\gamma_i^{(\mathrm{I})} = x_i^{(\mathrm{II})}\gamma_i^{(\mathrm{II})} \tag{5}$$

in which superscripts I and II refers to the first and second phases in equilibrium. In the UNIFAC model the activity coefficient is represented as having two parts, i.e., combinatorial and residual activity coefficients:

$$\ln \gamma_i = \ln \gamma_i^{(C)} + \ln \gamma_i^{(R)} \tag{6}$$

The combinatorial part is given by

$$\ln \gamma_i^{(C)} = (\ln \phi_i/x_i + 1 - \phi_i/x_i) - zq_i/2[\ln \phi_i/\theta_i + 1 - \phi_i/\theta_i] \tag{7}$$

where

$$\phi_i = \frac{x_i r_i}{\sum_{j=1}^{M} x_j r_i} \tag{8}$$

$$\theta_i = \frac{x_i q_i}{\sum_{j=1}^{M} x_j q_i} \tag{9}$$

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$$r_i = \sum_{k=1}^{N} \nu_k^{(i)} R_k \tag{10}$$

$$q_i = \sum_{k=1}^{N} \nu_k^{(i)} Q_k \tag{11}$$

where R_k is the volume parameter and Q_k is the surface area parameter of the group k. The residual part of the activity coefficient is given in the following form:

$$\ln \gamma_i^R = \sum_{k=1}^{N} \nu_k^{(i)} (\ln \Gamma_k - \ln \Gamma_k^{(i)}) \tag{12}$$

where Γ_k is the activity coefficient of group k, which is written in the following form:

$$\ln \Gamma_k = Q_k \left[1 - \ln\left(\sum_{m=1}^{N} \theta_m \Psi_{mk} \right) - \sum_{m=1}^{N} \left(\frac{\theta_m \Psi_{km}}{\sum_{p=1}^{N} \theta_p \Psi_{pm}} \right) \right] \tag{13}$$

where

$$\Psi_{mn} = \exp(-a_{nm}/T) \tag{14}$$

and

$$\theta_m = Q_m X_m / \sum_{n-1}^{N} Q_n X_n \tag{15}$$

where

$$X_m = \frac{\sum_{j=1}^{M} \nu_m^{(j)} x_i}{\sum_{j=1}^{M} \sum_{n=1}^{N} \nu_n^{(j)} x_j} \tag{16}$$

In Eq. (14) the parameter a is the interaction parameter between different functional groups. It can be seen from Eq. (7) that for calculating the combinatorial part of the activity coefficient, we need the surface and volume size parameters of different functional groups (R and Q) in the solution. These parameters can be calculated by using the table of Bondi (3) and the method of Prausnitz, and the related values are given in Table 5. For calculating the residual part of activity coefficient we need to determine the interaction parameters between different functional groups in the solution. The NMP

TABLE 5
Van der Waals Surface Area (*Q*) and Volume (*R*) Size Parameters of the Functional Groups

Groups	*R*	*Q*
CH_2	0.6744	0.5400
CH_3	0.9011	0.8480
ACH	0.5313	0.4000
NMP	3.9810	3.2000

TABLE 6
UNIFAC Interaction Parameters of Different Functional Groups in the Ternary System of Heptane/Benzene/NMP

Groups	CH_2	CH_3	ACH	NMP
CH_2	0	0	61.13	4833
CH_3	0	0	61.13	4833
ACH	−11.12	−11.12	0	1262.5
NMP	−123.19	−123.19	−567.98	0

TABLE 7
Calculated and Experimental Values of the Composition of the Extract and Raffinate Phases with LLE and VLE Parameters

		Raffinate composition			Extract composition		
			Calculated			Calculated	
Experiments	Feed composition	Experimental	LLE	VLE	Experimental	LLE	VLE
No. 1:							
x_p	.117	.451	.473	.482	.0396	.0412	.0423
x_n	.079	.175	.186	.193	.0254	.0264	.0284
x_a	.042	.0561	.0591	.060	.0349	.0359	.0406
x_{NMP}	.762	.317	.281	.265	.900	.896	.8887
No. 2:							
x_p	.102	.492	.501	.513	.0373	.0394	.0409
x_n	.0688	.117	.120	.131	.0199	.0211	.0221
x_a	.0369	.0697	.070	.0722	.0297	.0301	.0311
x_{NMP}	.793	.321	.309	.284	.913	.909	.9059
No. 3:							
x_p	.0661	.520	.531	.553	.0282	.0299	.0313
x_n	.0448	.0553	.0563	.0580	.0150	.0162	.0182
x_a	.0240	.0818	.0830	.0855	.0205	.0216	.0237
x_{NMP}	.865	.343	.330	.3035	.936	.932	.9268

molecule is considered to be a functional group, so by using the equilibrium condition of Eq. (5) and the experimental data (5) the interaction parameters can be obtained by solving a nonlinear system of equations. The results are given in Table 6. The precision of the calculated parameters in this table has been adjusted with an accuracy of ±0.01. Therefore the problem is reduced to an ordinary liquid–liquid equilibrium calculation in a multicomponent mixture, and this can be handled by standard algorithms. The calculated values and the experimental data are given in Table 7.

Case Two: Calculation with VLE Parameters

Although the previous published parameters (21) for the groups involved in our system have been fitted to vapor–liquid equilibrium data, we have made calculations similar to Case One with these parameters for Case Two, and a comparison is made with the ones obtained with the proposed parameters (Table 6) in Table 7.

CONCLUSION

A new approach in modeling complex hydrocarbon mixtures has been presented which is appropriate to phase equilibrium calculations of such mixtures as the lube-oil cut. The results of this modeling and the related liquid–liquid equilibrium calculations are in good agreement with the experimental data which were carefully obtained from the batch mixer-settler by standard measurements.

NOMENCLATURE

a_{mn}	interaction parameter between m and n groups
MW	molecular weight
N	carbon number
q_i	parameter in Eq. (7), defined in Eq. (11)
Q_k	surface area parameter of the group k
r_i	parameter in Eq. (7), defined in Eq. (10)
R	volume parameter
T	absolute temperature
$W(N)$	molecular distribution function
x_i	mole fraction of component i
X_m	parameter defined in Eq. (16)
z	coordination number
α	parameter of the model molecules
β	parameter of the model molecules

γ_i	activity coefficient of component i
Γ_k	group activity coefficient
θ_i	parameter in Eq. (7), defined in Eq. (9)
ϕ_i	parameter in Eq. (7), defined in Eq. (8)
Ψ_{mn}	parameter defined in Eq. (14)
ν_k	number of group k

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