$$x_i^{I} = \frac{\gamma_i^{II} x_i^{II}}{\gamma_i^{I}} \qquad (33)$$

5. If $\Sigma x_i^{II} = 1$ not satisfied, φ is adjusted and Eqs. (32) and (33) are used again for x_i^{II} and x_i^{I}, respectively, until the equation $\Sigma x_i^{II} = 1$ is satisfied.

Table 3. van der Waals surface area (Q) and volume (R) size parameters of the functional groups.

Groups	R	Q
CH₂	0.6744	0.5400
CH₃	0.9011	0.8480
ACH	0.5313	0.4000
NMP	3.9810	3.2000

**Table 4.** Functions (f_i) and constants (C_i) of the system of Eqs. (27–30).

$C_1 = 0.3115$ $C_2 = 0.1894$
$C_3 = 0.1683$ $C_4 = 0.1447$

$f_1 = \dfrac{0.3346 + 0.6684\Psi_{41}}{0.8715 + 0.306\Psi_{41}}$

$f_2 = \dfrac{0.2503}{0.3346 + 0.6684\Psi_{41}}$

$f_3 = \dfrac{-0.8151}{0.8715 + 0.1306\Psi_{41}}$

$f_4 = \dfrac{0.06619}{0.2851 + 0.6684\Psi_{43}}$

$f_5 = -\dfrac{0.04427}{0.7183 + 0.1306\Psi_{43}}$

$f_6 = \dfrac{0.6684\Psi_{14}}{0.6684 + 0.2503\Psi_{14} + 0.8125\Psi_{34}}$

$f_7 = \dfrac{-0.1306\Psi_{14}}{0.1306 + 0.8151\Psi_{14} + 0.05435\Psi_{34}}$

$f_8 = \dfrac{0.4725 + 0.5321\Psi_{41}}{0.8047 + 0.1987\Psi_{41}}$

$f_9 = \dfrac{0.3481}{0.4725 + 0.5321\Psi_{41}}$

$f_{10} = \dfrac{-0.7082}{0.8047 + 0.1987\Psi_{41}}$

$f_{11} = \dfrac{.09759}{0.4034 + 0.5321\Psi_{43}}$

$f_{12} = \dfrac{-0.07576}{0.6699 + 0.1987\Psi_{43}}$

$f_{13} = \dfrac{0.5321\Psi_{14}}{0.5321 + 0.3481\Psi_{14} + 0.1198\Psi_{34}}$

$f_{14} = \dfrac{-0.1987\Psi_{14}}{0.1987 + 0.8395\Psi_{14} + 0.093\Psi_{34}}$

$f_{15} = \dfrac{0.4917 + 0.5128\Psi_{41}}{0.7873 + 0.2163\Psi_{41}}$

$f_{16} = \dfrac{0.3658}{0.4917 + 0.5128\Psi_{41}}$

$f_{17} = \dfrac{-0.6873}{0.7873 + 0.2163\Psi_{41}}$

$f_{18} = \dfrac{0.09881}{0.4193 + 0.5128\Psi_{43}}$

$f_{19} = -\dfrac{0.07849}{0.6562 + 0.2163\Psi_{43}}$

$f_{20} = \dfrac{0.5128\Psi_{14}}{0.5128 + 0.3658\Psi_{14} + 0.1213\Psi_{34}}$

$f_{21} = \dfrac{-0.2163\Psi_{14}}{0.2163 + 0.6873\Psi_{14} + 0.09635\Psi_{34}}$

$f_{22} = \dfrac{0.5198 + 0.4849\Psi_{41}}{0.78 + 0.2237\Psi_{41}}$

$f_{23} = \dfrac{0.3925}{0.5198 + 0.4849\Psi_{41}}$

$f_{24} = \dfrac{-0.6741}{0.78 + 0.2237\Psi_{41}}$

$f_{25} = \dfrac{0.09987}{0.4423 + 0.4849\Psi_{43}}$

$f_{26} = \dfrac{-0.0831}{0.6511 + 0.2237\Psi_{43}}$

$f_{27} = \dfrac{0.4849\Psi_{14}}{0.4849 + 0.3925\Psi_{14} + 0.1226\Psi_{34}}$

$f_{28} = \dfrac{-0.1987\Psi_{14}}{0.1987 + 0.8395\Psi_{14} + 0.093\Psi_{34}}$

Table 5. UNIFAC interaction parameters of different functional groups in ternary system of heptane/benzene/NMP.
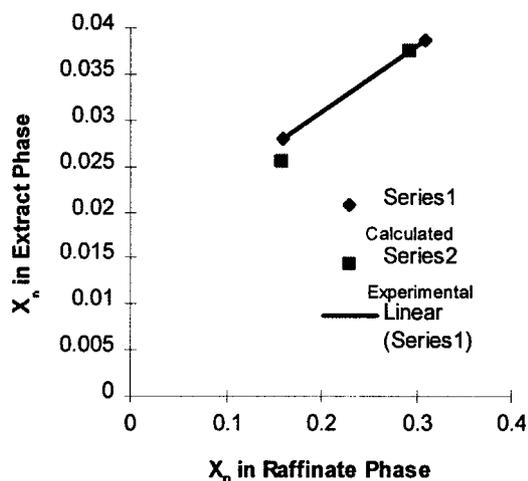
Groups	CH₂	CH₃	ACH	NMP
CH₂	0	0	61.13	4833
CH₃	0	0	61.13	4833
ACH	-11.12	-11.12	0	1262.5
NMP	-123.19	-123.19	-567.98	0

Calculated values for composition of liquid phases (extract and raffinate phases) and their experimental values have been given in Tabs. 6 and 7 and their related ternary diagrams are shown in Figs. 2 and 3, respectively. As it can be shown in these figures the results of the calculations are in good agreement with the experimental data.
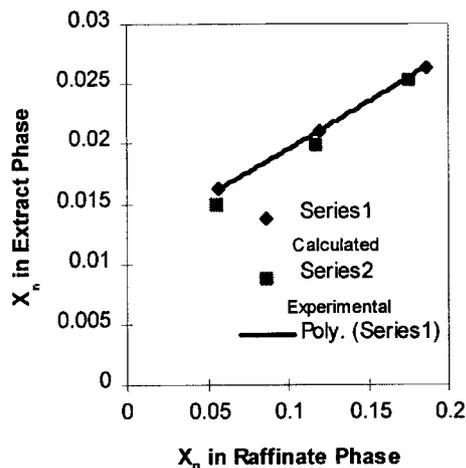
Figure 2. Distributioin curve for the naphthenic components between the raffinate and extract phases at 1 atm and 50 °C.

Figure 3. Distribution curve for the naphthenic components between the raffinate and extract phases at 1 atm and 42 °C.

4 Conclusion

Although two well-known methods for characterization of complex hydrocarbon mixtures namely pseudocomponent and continuous methods have several important advantages such as simplicity for the first and time saving for the later, each of these methods have special deficiencies for the application to those thermodynamic calculations requiring the molecular characteristics of the different species in the complex multicomponent mixture. For example, in phase equilibrium calculations where the non-ideal behavior of components in the liquid phase must account for the activity coefficient. The properties such as the interaction parameters between different molecules in the mixture are needed which

Table 6. Calculated and experimental values of the composition of the extract and raffinate phases at 1 atm and 50 °C.

Experiments	Feed composition	Raffinate composition			Extract composition		
		Exp.	Calc.	AD	Exp.	Calc.	AD
No. 1							
x_p	.117	.451	.473	.022	.0396	.0412	.0016
x_n	.079	.175	.186	.011	.0254	.0264	.001
x_a	.042	.0561	.0591	.003	.0349	.0359	.001
x_{NMP}	.762	.317	.281	.036	.900	.896	.004
No. 2							
x_p	.102	.492	.501	.009	.0373	.0394	.0021
x_n	.0688	.117	.120	.003	.0199	.0211	.0012
x_a	.0369	.0697	.070	.0003	.0297	.0301	.0004
x_{NMP}	.793	.321	.309	.012	.913	.909	.004
No. 3							
x_p	.0661	.520	.531	.011	.0282	.0299	.0017
x_n	.0448	.0553	.0563	.001	.0150	.0162	.0012
x_a	.0240	.0818	.0830	.0012	.0205	.0216	.0011
x_{NMP}	.865	.343	.330	.013	.936	.932	.004
				AAD[2] =.0102			AAD=.0019

1) AD =Absolute Deviation 2) AAD= Average Absolute Deviation

Table 7. Calculated and experimental values of the composition of the extract and raffinate phases at 1 atm and 42 °C.

Experiments	Feed composition	Raffinate composition			Extract composition		
		Exp.	Calc.	AD	Exp.	Calc.	AD
No. 1							
x_p	.117	.442	.454	.012	.0361	.0389	.0028
x_n	.079	.158	.160	.002	.0255	.0280	.0025
x_a	.042	.0532	.0549	.0017	.0322	.0344	.0022
x_{NMP}	.762	.346	.331	.015	.906	.899	.007
No. 2							
x_p	.101	.319	.334	.015	.0178	.0188	.001
x_n	.0685	.293	.310	.017	.0376	.0387	.0011
x_a	.0367	.0541	.0551	.001	.0301	.0314	.0013
x_{NMP}	.794	.334	.301	.033	.915	.911	.004
				AAD=.012			AAD=.0027

is directly related to the molecular characteristics of the well-defined molecules in the mixture. To overcome the drawbacks of these methods from the molecular point of view, in this work the method of Ruzicka for modeling the complex mixture of hydrocarbons has been developed. In this method, the complex mixture of hydrocarbons which is comprised of the main homolog series of paraffins, naphthenes, and aromatics is modeled with the three representative molecules. Therefore, in this method a complex mixture is equivalent to a ternary mixture with defined molecules. Hence, we deal with a multicomponent mixture with a few components and the time for the calculation is less than the pseudocomponent method. On the other hand, the continuous method is not good enough to represent the mixtures which contain several homolog series. For examination of the proposed method, the lube-oil cut SAE 10 of the Tehran Refinery is modeled and the results of this modeling along with the related liquid-liquid equilibrium calculations are in good agreement with the experimental data which are carefully obtained from the batch system of mixer-settler by the standard experimental measurements.

Symbols used

a_{mn}	interaction parameter between m and n groups
MW	molecular weight
N	carbon number
q_i	parameter in Eq. (15), defined in Eq. (19)
Q_k	surface area parameter of the group k
r_i	parameter in Eq. (15), defined in Eq. (18)
R	volume parameter
T	absolute temperature
$W(N)$	molecular distribution function
x_i	mole fraction of the component "i"
X_m	parameter defined in Eq. (24)
z	coordination number
α	parameter of the model molecules
β	parameter of the model molecules
γ_i	activity coefficient of the component "i"
Γ_k	group activity coefficient
θ_i	parameter in the Eq. (15), defined in Eq. (17)
ϕ_i	parameter in the Eq. (15), defined in Eq. (16)
Ψ_{mn}	parameter defined in Eq. (22)
v_k	number of group k

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