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Experiments and modelling of liquid–liquid equilibria in the mineral oil + N,N-dimethylformamide system

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Abstract

Description of phase behaviour of a highly nonideal system mineral oil + DMF is a rather complex task, because hydrocarbon feed, which has to be separated into aromatic and nonaromatic fractions, consists of large number of compounds that differ significantly in molecular weight and chemical structure. Such a complex mixture was substituted by two pseudo-components, aromatic and nonaromatic in order to simplify the procedure. They were represented by adequate model compounds, whose thermodynamic behaviour was similar to the original one. The chosen model system simulates properly the real one in the sense of the mutual solubility of aromatic and nonaromatic components. However, this simplification of description of strongly nonideal mixtures should be considered as the first approximation.

Keywords: mineral oil; extraction; liquid-liquid equilibria; binodal curve; pseudo-component approach

1. Introduction

An extraction of aromatic hydrocarbons from a complex multicomponent hydrocarbon mixture, such as mineral oil, is of great commercial importance in the petroleum refining industry. Mineral oil is derived from crude oil, however the properties of product depend on degree of refinement. It comprises of paraffins, cycloparaffins, and naphthenes along with aromatics. The mineral oil samples used in this work are of rare type from the Croatian oil field Ivanić located 70 km from Zagreb. This oil in its raw form is used for therapeutic baths known as balneo treatment in Ivanić Grad spa resort. In its purified form (such as white oil when aromates are removed) the product is efficient for different kinds of medical treatment, especially for healing dermatological diseases, and also for applications in cosmetic industry. The aromatic components must be selectively removed by means of extraction using industrial solvents like triethylene glycol, sulfolane, dimethylsulphoxide, N,N-dimethylformamide, etc.

Liquid–liquid equilibrium (LLE) data are essential for proper understanding the extraction process for selection of solvents as well as for the engineering design of extraction unit. In the absence of experimental data on multicomponent LLE of such highly nonideal systems, data should be predicted with sufficient accuracy using a suitable thermodynamic model supported by all available experimental information.

This work describes experiments and modelling of the phase equilibria in a

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multicomponent aromatic extraction system, using the UNIFAC group contribution model [1, 2] designed for prediction of LLE.

2. Experimental part

2.1. Materials

Chemicals were purchased mainly from Fluka (Buchs, Switzerland) with declared initial purity by manufacturer. All chemicals were stored above 4A molecular sieve and used without further purification. The specifications are summarized in Table 1.

Table 1. Sample description

Compound	Source	Purity (GC ^a by supplier)
n-Heptane	Fluka	≥97.0%
Benzene	Fluka	puriss. p.a., ≥99.7%
Toluene	Fluka	anhydrous, 99.8%
Dodecyl benzene	Aldrich	puriss, 97%
N,N-dimethylformamide	Fluka	anhydrous, 99.8%

^a Gas liquid chromatography

2.2. Extraction

Raw mineral oil (boiling point 550 – 700 K) can be considered as a mixture consisting of two groups of kindred substances, i.e. mixture of aromatics (AR) to be extracted and nonaromatics (NAR) as the final product. The aromatic compounds were extracted using N,N-dimethylformamide (DMF) and subsequently separated from the solvents by distillation. The final purifications of nonaromatic fractions from aromatics were completed by sulfonation. LLE data for the real aromatics + nonaromatics + DMF system were determined at 298.2 K both by titration method [2] and by IR analysis [3].

2.3. Binodal curve determination

A titration technique was used for binodal curve determination. Heterogeneous samples of NAR + DMF were titrated with AR in a thermostated glass-stoppered bottle to the single phase solution. The glass-stoppered bottle was maintained at temperature within 298.2 ± 0.1 K. The addition of appropriate amount of AR to heterogeneous mixture of NAR+DMF rendered the miscible system. The titrant was added in small increments from a jacked microburet held at constant temperature, and the content of the glass-stoppered bottle was shaken vigorously. The weight amount of added titrant was evaluated from measured volume. The composition of the ternary mixture at the transition point from a turbid to clear solution determines the experimental point of binodal curve. The binodal curve for AR + NAR + DMF is shown in Figure 1.

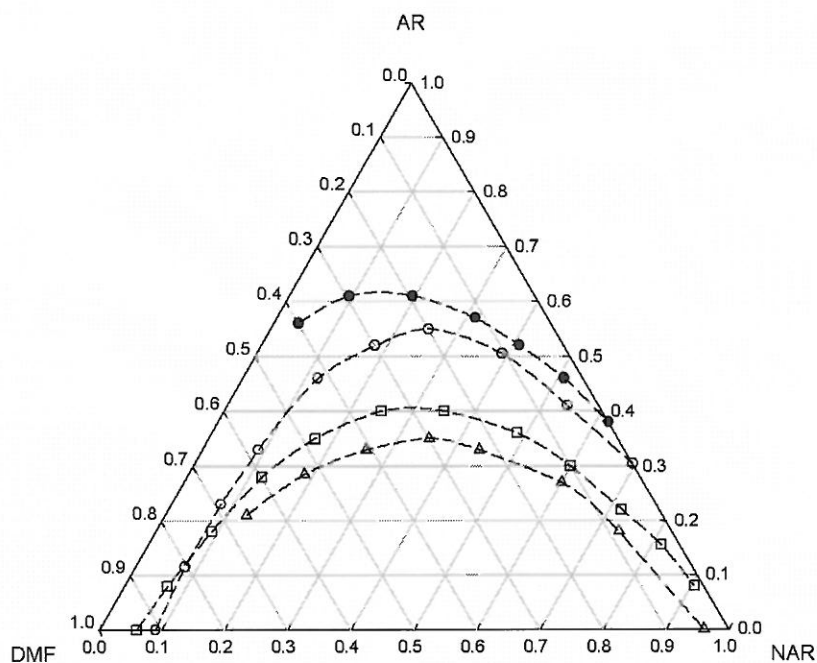


Figure 1. Experimental binodal curves at 298.2 K for the AR + NAR + DMF system

- the real system; AR (extracted from mineral oil) + NAR (extracted from mineral oil)
- ▲ the model system; AR (benzene) + NAR (n-heptane)
- the model system; AR (toluene) + NAR (n-heptane)
- the model system; AR (dodecyl benzene) + NAR (n-heptane)

3. Results

3.1. Modelling of the extractant

Description of LLE of highly nonideal mineral oil + DMF system is a rather complex task. Hydrocarbon feed, which has to be separated into aromatic and nonaromatic fractions consists of a large number of compounds that differ in molecular weight and chemical structure. A simplified method is used here for the simulation of mineral oil fractions based on our recent work [4].

The procedure is as follows: each mineral oil can be divided into two pseudo-components, aromatic and nonaromatic. They could be represented by adequate model compounds: aromatic and paraffinic, bearing in mind that the thermodynamic behaviour of the model system should be similar to the original one. Nonaromatics are represented by n-heptane, while aromatics are represented by benzene and/or toluene and/or dodecyl benzene. DMF was used as the only solvent. Binodal curves were determined as described above. Experiments with model compounds are shown in Figure 1. It can be seen that dodecyl benzene represents aromatics quite well. Thermodynamic behaviour of dodecyl benzene + n-heptane + DMF is similar as the behaviour of the real multicomponent system AR + NAR + DMF and it can be used as a model system to describe extraction of complex hydrocarbon mixture to simplify further calculations.

3.2. Prediction of LLE using the UNIFAC model

Prediction of LLE for the model system dodecyl benzene + n-heptane + DMF was carried out using the UNIFAC model with original Magnusen parameters [5] without any new parameter adjustment or re-estimations. The equations of the model are listed in Figure 2. The calculation procedure and the necessary LLE parameters can be found in reference [5]. Predicted binodal curve for the AR (dodecyl benzene) + NAR (n-heptane) + DMF model system is shown in Figure 3.

$$\ln \gamma_i = \ln \gamma_i^C + \ln \gamma_i^R$$

where C and R refer to the combinatorial and residual contribution, respectively

$$\ln \gamma_i^C = \left(\frac{\ln \phi_i}{x_i} + 1 + \frac{\phi_i}{x_i} \right) - \frac{1}{2} z q_i \left(\frac{\ln \phi_i}{\theta_i} + 1 - \frac{\phi_i}{\theta_i} \right)$$

$$\phi_i = \frac{x_i r_i}{\sum_j x_j r_j} \quad \theta_i = \frac{x_i q_i}{\sum_j x_j q_j}$$

where the summation is over all components

$$r_i = \sum_k v_{ki} R_k \quad q_i = \sum_k v_{ki} Q_k$$

R_k = volume parameter for group k
 Q_k = surface area parameter for group k
 v_{ki} = number of groups of type k in molecule i
 x_i = liquid mole fraction of component i
 Z = coordination number = 10

$$\ln \gamma_i^R = \sum_k v_{ki} (\ln \Gamma_k - \ln \Gamma_k^{(i)})$$

where the summation is over all groups

$$\ln \Gamma_k = Q_k \left[1 - \ln \left(\sum_m \theta_m \psi_{mk} \right) - \sum_m \frac{\theta_m \psi_{km}}{\sum_n \theta_n \psi_{nm}} \right]$$

$$\psi_{nm} = \exp \left(-\frac{a_{nm}}{T} \right)$$

$$\theta_m = \frac{Q_m X_m}{\sum_n Q_n X_n} \quad x_m = \frac{\sum_j v_{mj} x_j}{\sum_j \sum_n v_{nj} x_j}$$

a_{nm} = group interaction parameter for the interaction between groups m and n
 $\Gamma_k^{(i)}$ = the residual activity coefficient of group k in a reference solution containing only molecules of type i

Figure 2. The original UNIFAC equations

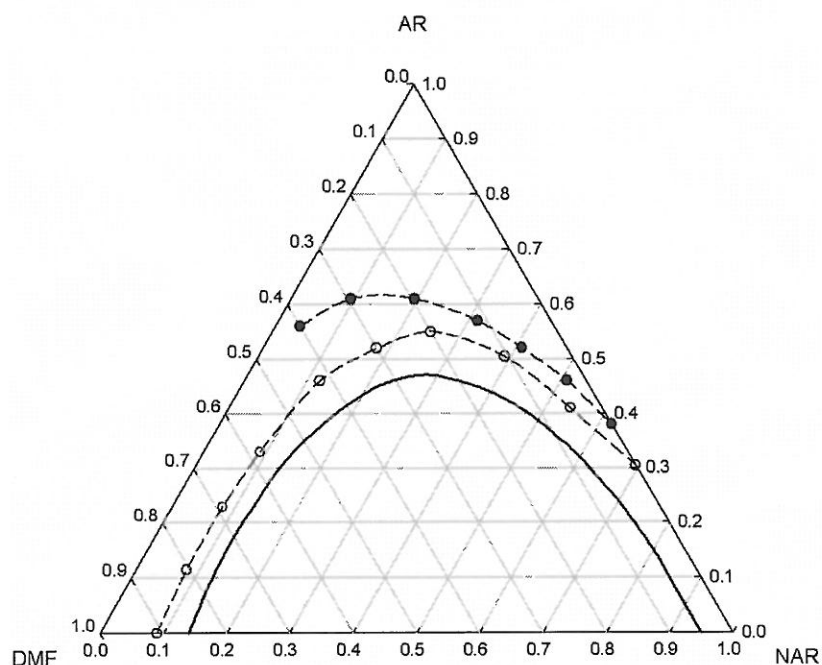


Figure 3. Experimental and predicted binodal curves at 298.2 K for the AR + NAR + DMF system

- experimental data for the real system; AR (extracted from mineral oil) + NAR (extracted from mineral oil)
- experimental data the model system; AR (dodecyl benzene) + NAR (n-heptane)
- prediction by the UNIFAC for the model system; AR (dodecyl benzene) + NAR (n-heptane)

4. Conclusion

The method proposed in this work is a large simplification of the complex problem. Petroleum fraction as a blend of many hydrocarbon stocks was simulated as the system composed of the two types of pseudo-components, aromatic and nonaromatic. It was found that dodecyl benzene represents the aromatics, as well as n-heptane characterizes nonaromatics. The model system behaves similarly as the real one in the sense of the mutual solubility of AR and NAR components. Group interaction parameters for the UNIFAC modes were not specially adjusted for predicting LLE for mentioned systems, therefore the obtained results are underestimated. This simplification of LLE without any other pretence in strongly nonideal mixtures should be considered as the first approximation, and as the starting point for future development.

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