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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

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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 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