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Quaternary (liquid + liquid) equilibria for (methanol + 2,2,4-trimethylpentane + toluene + 1,1-dimethylpropyl methyl ether or 1,1-dimethylethyl methyl ether) at $T = 298.15$ K

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Abstract

The experimental equilibrium tie-lines of two quaternary mixtures for (methanol + 1,1-dimethylpropyl methyl ether + toluene + 2,2,4-trimethylpentane) and (methanol + 1,1-dimethylethyl methyl ether + toluene + 2,2,4-trimethylpentane) were measured at the temperature 298.15 K and ambient pressure. The quaternary experimental results and their constituent ternaries have been satisfactorily predicted using binary parameters alone obtained by an associated-solution model that takes into account association of methanol molecules and solvation between (methanol + polar molecules) with allowance for a non-polar interaction given by an extended form of the UNIQUAC model. The results are further compared with those correlated by modified and extended forms of the UNIQUAC models that include multi-body interaction parameters in addition to binary ones.

Keywords: (liquid + liquid) equilibria; Fuel additive; Alkyl methyl ether; Quaternary mixtures; UNIQUAC models

1. Introduction

In a modern gasoline reformulation, alkyl methyl ethers such as 1,1-dimethylpropyl methyl ether (TAME, *tert*-amyl methyl ether) and 1,1-dimethylethyl methyl ether (MTBE, methyl *tert*-butyl ether) have been concerned from viewpoints of a reduction of toxic substances in automotive exhaust fumes as well as an octane enhancer in the improvement of gasoline performance. To understand phase behavior for the oxygenate mixtures, we continue to measure the multicomponent (liquid + liquid) equilibrium for these oxygenate mixtures and further to develop an accurate representation of the experimental (liquid + liquid) equilibrium data for the multicomponent mixtures.

In this paper we report the quaternary (liquid + liquid) equilibrium data for (methanol + toluene + TMP + TAME or MTBE) measured at $T = 298.15$ K as fuel oxygenate additives including methanol and isooctane (TMP, 2,2,4-trimethylpentane). The experimental results are predicted by using an associated-solution model [1] having binary parameters obtained from binary phase equilibria and are reproduced by modified and extended forms of the UNIQUAC models [2,3] including ternary and quaternary parameters obtained from the ternary and quaternary (liquid + liquid) equilibria in addition to binary ones. The binary (vapour + liquid) equilibria, mutual solubility and ternary (liquid + liquid) equilibria relevant to the quaternaries have been available from the literatures: (vapour + liquid) equilibria, (methanol + TAME) [4], (methanol + MTBE) [4], (methanol + toluene) [5], (TAME + MTBE) [6], (TAME + toluene) [7], (MTBE + toluene) [8],

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(TMP + toluene) [9], (TAME + TMP) [7] and (MTBE + TMP) [10]; mutual solubilities, (methanol + TMP) [1]; ternary (liquid + liquid) equilibria, (methanol + TAME + TMP) [1], (methanol + MTBE + TMP) [1] and (methanol + toluene + TMP) [1].

2. Experimental

Methanol, MTBE, TAME, toluene and TMP with minimum mass purities of 0.998, 0.998, 0.989, 0.998, and 0.998 mass fraction were supplied by Aldrich Chemical. Densities of the pure chemicals were determined by a densimeter (Anton Paar, DMA58) with a resolution accuracy of 1×10^{-5} g · cm^{-3} and the values measured at $T = 298.15$ K were in good agreement with the literatures [11] as shown in table 1. A g.l.c analysis detected no any noticeable peak for impurities. All chemicals were used without further purification.

The quaternary (liquid + liquid) measurements were carried out at the temperature (298.15 ± 0.01) K. The experimental apparatus was the same that reported in detail previously [12]. The experimental procedure in the present work was performed as follows. The quaternary mixtures whose volume is about 70 cm^3 were loaded in a glass equilibrium cell and the headspace of the cell was filled with dry nitrogen gas to prevent contamination of moisture. The mixtures were stirred vigorously by using a magnetic stirrer for 5 h and then settled more than 5 h that is sufficient for separation to liquid two layers. The liquid samples about 4 cm^3, withdrawn from upper and lower phases in the cell by using a microliter syringe without changing the equilibria between two layers, were analyzed by a gas chromatograph (Shimadzu, GC-8A) equipped with a thermal conductivity detector. The oven temperatures of the injection port and detector were set at 363 K. The helium flow rates for the separation and reference columns were set at 0.5 ml · s^{-1}. The columns packed with a Shimalite 80/100 (Shinwakakou) coated by 1,2,3-tri(2-cyanothoxypropane) was used for the separation of the quaternary components. The peak area of the every components, analyzed with a chromatopac (Shimadzu, C-R6A), was calibrated by gravimetrically weighted mixtures. A digital electronic balance (Shimadzu, AEX-180) with an accuracy of ±0.1 mg was used to prepare the mixtures in a vial. Three analyses at least for each sample were made to obtain a mean value. The accuracy of the experimental measurements was estimated to be within ±0.001 in mole fraction.

TABLE 1
Densities, ρ, of pure components at $T = 298.15$ K

Component	ρ(298.15 K)/g · cm^{-3}	
	Exptl.	Lit.
Methanol	0.78652	0.78637[a]
1,1-Dimethylethyl methyl ether (MTBE, methyl *tert*-butyl ether)	0.73540	0.73528[b]
1,1-Dimethylpropyl methyl ether (TAME, *tert*-amyl methyl ether)	0.76587	0.76577[b]
Tsoluene	0.86235	0.8629[a]
2,4-Trimethylpentane (TMP, isooctane)	0.68777	0.68781[a]

[a] Ref. [11].
[b] Ref. [6].

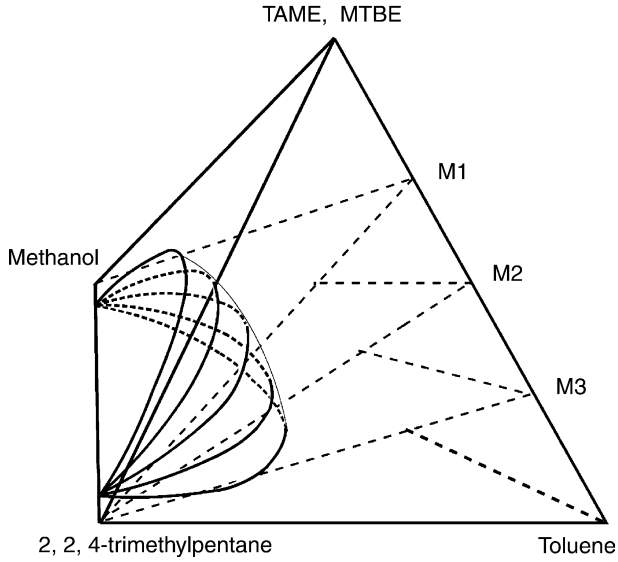

FIGURE 1. Phase equilibria of (methanol + 2,2,4-trimethylpentane + toluene + 1,1-dimethylethyl methyl ether or 1,1-dimethylpropyl methyl ether). M1, M2 and M3 denote quaternary sectional planes.

The quaternary mixtures for (methanol + MTBE + toluene + TMP) and (methanol + TAME + toluene + TMP) were prepared by mixing the binary mixtures of (alkyl ether + toluene) whose compositions are M1, M2 and M3 with methanol then TMP stepwise to cover the two-phase region. Figure 1 shows schematically a tetrahedron to depict three planes of the quaternary mixtures of (methanol + TMP + toluene + MTBE or TAME). The values of M1, M2 and M3 are approximately 0.25, 0.50 and 0.75, respectively, indicating the mole fraction of TAME or MTBE in TMP. Tables 2 and 3 list the experimental equilibrium tie-line compositions for the quaternary mixtures of (methanol + TAME + toluene + TMP) and (methanol + MTBE + toluene + TMP) at $T = 298.15$ K.

3. Results of analysis

For an accurate description of the experimental quaternary (liquid + liquid) equilibrium data, we used the associated-solution model having only binary parameters, and the modified UNIQUAC and extended UNIQUAC models with additional ternary and quaternary