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Phase equilibrium properties of the ternary mixture dibutyl ether + toluene + heptane at 313.15 K

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ABSTRACT

New accurate vapour liquid equilibrium data for the ternary mixture formed by dibutyl ether (DBE), toluene and heptane at 313.15 K have been measured. A static method using an isothermal total pressure cell (Van Ness' technique) has been employed. The system studied presented a slight deviation from ideal behaviour. Reduction of the experimental data has been done by Barker's method using Wohl expansion, NRTL, Wilson and UNIQUAC equations. Moreover, experimental results have been compared to predictions for the ternary system obtained from the Wilson, NRTL, UNIQUAC and UNIFAC (Dortmund) models.

1. Introduction

Oxygenated additives, as ethers and alcohols have been traditionally used as a blending agent in the formulation of the new gasoline to enhance octane number in substitution of the traditional leaded products. A comprehensive review of the thermophysical property measurements of these mixtures was presented by Marsh et al. [1]. To better understand and model the new formulated gasoline, we have started many years ago a research programme on the thermodynamic characterization of ternary mixtures, as the simplest multicomponent system, containing oxygenated additives (ethers and alcohols) and different type of hydrocarbons (paraffins, cycloparaffins, aromatics, oleffins). As result of this programme, we have characterized mixtures of hydrocarbons with methyl tert-butyl ether (MTBE) [2–11], tert-amyl methyl ether (TAME) [4,12–16], di-isopropyl ether (DIPE) [4,17–27] and ethyl tert-butyl ether (ETBE) [28–33] and dibutyl ether (DBE)[34,35]. Here, the ternary (DBE + toluene + heptane) and the binary (toluene + heptane) systems at 313.15 K are presented. In previous work [34,35], experimental data at the same temperature for the other constituent binaries, (DBE + toluene) and (DBE + heptane), have been reported.

Dibutyl ether has been proposed as well as a promising butanol-derived oxygenated diesel fuel product to be used in blends of diesel and butanol [36]. Experimental results suggest that the combustion properties of the resulting oxygenated fuels improve fuel conversion efficiency [36].

2. Materials

All the chemicals used were purchased from Fluka Chemie AG and were of the highest purity available, chromatography quality reagents (of the series puriss. p.a.) with a stated purity >99.5% (GC) for dibutyl ether and heptane and >99.7% (GC) for toluene. Only dibutyl ether was additionally distilled at vacuum in a packed column. The first and last portions of the distillate were discarded and the intermediate fraction distilling at constant temperature was collected; the purity was improved up to 99.7% (GC). All reagents were thoroughly degassed. The purity of the products after degassing was checked by gas chromatography, and the values were >99.8% (GC) for all the compounds. Table 1 shows a complete description of the purity of the products used in this work.

3. Experimental method

A static VLE apparatus consisting of an isothermal total pressure cell has been employed. The apparatus and measuring technique

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Table 1
Description of pure compounds used in this work. Purity has been checked by gas chromatography (GC).

	CAS-no.	Purity (GC)	Purity (GC) after purification and degassing
DBE (i = 1)	(142-96-1)	99.5%	>99.8%
Toluene (i = 2)	(108-88-3)	99.7%	>99.8%
Heptane (i = 3)	(142-82-5)	99.5%	>99.8%

are based on those of Van Ness and co-workers [37,38] and whose performance has been described previously [4,5,11,16].

Experimental values of total vapour pressure for the binary mixture were obtained in two overlapping runs starting from opposite ends of the composition range. For the ternary mixture, data were obtained by addition of a pure species to a mixture of the other two at a fixed temperature. Six runs (dilution lines) were made starting from the corresponding binary system at mole fractions close to 0.3 or 0.7 and adding the third component up to a mole fraction of 0.5.

The equilibrium properties were measured directly and their uncertainties were: injected volume ±0.03 ml, temperature ±10 mK and total pressure ±5 Pa. The overall mole fraction is determined accurately from volumetric displacement of the pistons, the temperature of the injectors and the densities of the pure compounds. The uncertainty in mole fraction is ±0.0005. The composition of the liquid phase is close to the overall composition but is corrected taken into account the vapour space of the cell and using the virial equation for the vapour phase [5]. The estimation of the measurement uncertainty has been made using the most extended framework for assessing uncertainty, the law of propagation of uncertainties described in the Guide to the Expression of Uncertainty in Measurement (GUM) [39].

4. Experimental results and correlations

The use of the static measurement technique described above allows a condition of true thermodynamic equilibrium to be established. As a consequence of Duhem's theorem, sampling of the phases is not necessary. Given a set of isothermal pressure and total composition data, thermodynamics allows calculation of the coexisting liquid and vapour phases. Thus, the equilibrium vapour does not need to be sampled for analysis and the data are thermodynamically consistent "per se" [40,41]. Data reduction for the binary and ternary mixtures was done by Barker's method [42], according to well-established procedures [43,44].

The non-ideality of the vapour phase was taken into account with the virial equation of state, truncated after the second term. The pure component and interaction second virial coefficient (B_{ii}, B_{ij}) are given in Table 2. They were calculated by the Hayden and O'Connell method [45] using the experimental parameters given by Dymond and Smith [46].

The ternary system (DBE + toluene + heptane) and the binary system (toluene + heptane) have been measured at 313.15 K. The remaining binary systems involved in the ternary, (DBE + heptane) and (DBE + toluene), were published previously [34,35]. The experimental data of the vapour liquid equilibrium of the binary (toluene + heptane) are reported in Table 3. These experimental data agree with those reported by our research group in a previous work [30] and those published by Góral [47] at the same temperature. Table 4 reports the experimental data for the ternary system.

Data for this ternary system are adequately correlated by the Wohl equation [48]:

$$g_{123} = \frac{g^E}{RT} = g_{12} + g_{13} + g_{23} + (C_0 + C_1x_1 + C_2x_2)x_1x_2x_3 \tag{1}$$

Table 2
Average values of experimental vapour pressures (P_i^{sat}) for the pure compounds measured in this work and literature values (P_i^{sat}) (lit.), molar volumes of pure liquids (V_i^L), second virial coefficients (B_{ii}, B_{ij}) and van der Waals molecular volumes (r_i) and surfaces (q_i) at 313.15 K used for the reduction of the systems.

	DBE (i = 1)	Toluene (i = 2)	Heptane (i = 3)
P_i^{sat} (kPa)	2.068	7.886	12.337
P_i^{sat} (lit.) (kPa)	2.236[a]	7.894[a]	12.335[a]
	2.101[b]	7.861[b]	12.300[b]
		7.871[c]	12.335[c]
		7.894[d]	12.334[d]
V_i^L (cm^3 mol^{-1})[e]	173	109	150
B_{i1} (cm^3 mol^{-1})[f]	−4328	−3024	−3249
B_{i2} (cm^3 mol^{-1})[f]	−3024	−2106	−2298
B_{i3} (cm^3 mol^{-1})[f]	−3249	−2298	−2521
r_i[g]	5.5709	2.7915	4.4275
q_i[g]	6.9116	3.1095	5.6621

[a] Calculated from Antoine equation with parameters taken from Ref. [54].
[b] Calculated from Antoine equation with parameters taken from Ref. [55].
[c] Calculated from Antoine equation with parameters taken from Ref. [56].
[d] Reported in Ref. [47].
[e] Reported in Ref. [57].
[f] Calculated by Hayden and O'Connell [45] from Dymond and Smith [46].
[g] Calculated from parameters from Gmehling et al. [53].

Here, g^E is the excess mol Gibbs free energy and the parameters C_0, C_1 and C_2 were found by regression of the ternary data. The parameters g_{ij} of the constituent binary systems were represented by the three parameters Margules equation [49]:

$$g_{ij} = \frac{g^E}{RT} = [A_{ji}x_i + A_{ij}x_j - \lambda x_i x_j]x_i x_j \tag{2}$$

Binary and ternary systems have also been correlated using Wilson [50], NRTL [51] and UNIQUAC [52] models. VLE data may be calculated through the activity coefficients with the help of a group-contribution model such as modified UNIFAC (Dortmund) model [53]. Results of data correlation and UNIFAC prediction for binary systems are summarized in Table 5. Table 6 reports the results of the correlation and UNIFAC predictions for the ternary system. We have also made the prediction of the fluid phase equilibrium behaviour of the ternary system using the correlation parameters of the binary systems included in Table 5. These tables contain the root mean square of the differences between experimental and calculated pressures (rms(ΔP)) and the maximum value of these pressures residuals (max.|ΔP|), both indicators of the quality of the agreement with data.

Table 3
Total pressure, P, for the binary system toluene + heptane, at 313.15 K[a] and at various compositions of the liquid phase, x_1, and the calculated composition of the vapour phase, y_1, using three parameters Margules equation.

Toluene (1) + heptane (2)					
x_1 [c]	$y_{1,calc}$ [d]	P (kPa)[b]	x_1 [c]	$y_{1,calc}$ [d]	P (kPa)[b]
0.0000	0.0000	12.329	0.5449	0.4330	10.999
0.0510	0.0460	12.277	0.5453	0.4334	10.999
0.1019	0.0899	12.206	0.5979	0.4756	10.775
0.1508	0.1303	12.125	0.5982	0.4758	10.782
0.1978	0.1680	12.032	0.6453	0.5154	10.563
0.2476	0.2070	11.915	0.6924	0.5574	10.326
0.2973	0.2451	11.802	0.7469	0.6101	10.025
0.3508	0.2855	11.657	0.7959	0.6627	9.716
0.4017	0.3237	11.503	0.8428	0.7197	9.373
0.4458	0.3569	11.364	0.8956	0.7945	8.960
0.4488	0.3592	11.348	0.9455	0.8804	8.491
0.4987	0.3971	11.179	1.0000	1.0000	7.893
0.4988	0.3972	11.179			

[a] $u(T)$ = 0.01 K.
[b] $u(P)$ = 5 Pa.
[c] $u(x_1)$ = 0.0005.
[d] $u(y_{1,calc})$ = 0.0005.