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Phase equilibrium for the systems diisopropyl ether, isopropyl alcohol + 2,2,4-trimethylpentane and +n-heptane at 101.3 kPa

Estela Lladosa[1], Juan B. Montón*, MªCruz Burguet[2]

Departamento de Ingeniería Química, Escuela Técnica Superior de Ingeniería, Universitat de València, Dr. Moliner, 50, 46100 Burjassot, Valencia, Spain

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ABSTRACT

Consistent vapour–liquid equilibrium data for the ternary systems diisopropyl ether + isopropyl alcohol + 2,2,4-trimethylpentane and diisopropyl ether + isopropyl alcohol + n-heptane are reported at 101.3 kPa. The vapour–liquid equilibrium data have been correlated by Wilson, NRTL and UNIQUAC equations. The ternary systems do not present ternary azeotropes.

1. Introduction

The addition of oxygenated compounds, such as ethers and alcohols, to gasoline has been of interest owing to their pollution-reducing and octane-enhancing capabilities. Therefore, phase equilibrium data of oxygenated mixtures are important for predicting the vapour-phase composition that would be in equilibrium with hydrocarbon mixtures, and the systems reported here constitute examples of such mixtures.

Methyl 1,1-dimethylethyl ether (MTBE) is the primary oxygenated compound being used to reformulate gasolines to improve their octane rating and pollution-reducing capability. However, potential and documented contamination of water resources by MTBE has become a major public issue over the past few years and restrictions in its use as additive are expected. This fact promotes further research with other ethers as potential additives. Diisopropyl ether shows good characteristics as a gasoline additive including: low volatility, low water solubility, high octane value and large reductions in carbon monoxide and hydrocarbon emissions.

For binary systems there is a large amount of information about this kind of compounds, however, experimental measurements of vapour–liquid equilibrium (VLE) for ternary or higher mixtures are quite scarce due to the effort necessary to obtain a complete description of the system.

Therefore, in this work, to improve the knowledge of the phase behaviour we report VLE data for the ternary systems with oxygenated compounds and some hydrocarbons in gasoline. The oxygenated compounds that have been considered are diisopropyl ether and isopropyl alcohol, due to both products are obtained from propylene in the same reactive process. With regard to the third component, 2,2,4-trimethylpentane has been chosen as a branched paraffin representative of the gasoline and n-heptane as a linear paraffin.

In a recent literature review only isothermal VLE data for the diisopropyl ether (1) + isopropyl alcohol (2) + 2,2,4 trimethylpentane (3) and diisopropyl ether (1) + isopropyl alcohol (2) + n-heptane (4) have been found [1,2].

VLE data of ternary systems, studied in this work, were found to be thermodynamically consistent. Data reduction was carried out using the Wilson, NRTL and UNIQUAC equations to relate activity coefficients with compositions.

2. Experimental

2.1. Chemicals

Diisopropyl ether (>99.0 mass%, *analytical grade*) was purchased from Fluka, isopropyl alcohol (>99.5 mass%, *HPLC grade*), 2,2,4-

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* Corresponding author. Tel.: +34 96 35 44317; fax: +34 96 35 44898.
E-mail addresses: estela.lladosa@uv.es (E. Lladosa), juan.b.monton@uv.es (J.B. Montón), cruz.burguet@uv.es (M. Burguet).

[1] Tel.: +34 96 35 44325.

[2] Tel.: +34 96 35 44318.

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Table 1
Density d, refractive index n_D, and normal boiling point T_b of pure components.

Component	d (kg m^{-3}) (298.15 K)		n_D (298.15 K)		T_b (K)	
	Exptl.	Lit.[a]	Exptl.	Lit.[a]	Exptl.	Lit.[b]
Diisopropyl ether (1)	0.7183	0.7182	1.3652	1.3655	341.49	341.45
Isopropyl alcohol (2)	0.7827	0.7813	1.3754	1.3752	355.35	355.41
2,2,4-Trimethylpentane (3)	0.6876	0.6878	1.3889	1.3890	372.33	372.39
n-Heptane (4)	0.6796	0.6795	1.3858	1.3851	371.35	371.58

[a] Taken from TRC tables [3].
[b] Taken from Daubert and Danner[4].

trimethylpentane (99.8 mass%, *analytical grade*) and n-heptane (>99.0 mass%, *HPLC grade*) were purchased from Aldrich Ltd. The reagents were used without further purification, since impurities are smaller than detection limit of analytical method used. The water content, determined using a Karl Fischer volumetric automatic titrator (Metrohm, 701 KF Titrino), was small in all chemicals (<0.05 mass%). Before measurements, the liquids were degassed and subsequently dried over molecular sieves (Union Carbide, type 4 Å, 1/16 in. pellets). The refractive indexes of the pure components were measured at 298.15 K using an Abbe refractometer Atago 3T, and the densities were measured at 298.15 K using an Anton Paar DMA 58 densimeter. Temperature was controlled to ±0.01 K with a thermostated bath. The accuracy in refractive index and density measurements are ±0.0002 and ±0.01 kg m^{-3}, respectively. The experimental values of these properties and the boiling points are given in Table 1 together with those given in the literature. Appropriate precautions were taken when handling the reagents in order to avoid hydration.

2.2. Apparatus and procedure

The equilibrium vessel used in the measurements (Labodest VLE 602/D) was an all-glass dynamic-recirculating still equipped with a Cottrell circulation pump, manufactured by Fischer Labor und Verfahrenstechnik (Germany). The apparatus is capable of handling pressures from 0.25 to 130 kPa, and temperatures up to 523.15 K. The Cottrell pump ensures that both liquid and vapour phases are in intimate contact during boiling and also in contact with the temperature sensing element. The equilibrium temperature was measured with a digital Hart Scientific thermometer model 1502A and a Pt 100 probe Hart Scientific model 5622 calibrated at the ENAC-Spanish Instituto Nacional de Técnica Aeroespacial. The uncertainty is estimated to be ±0.01 K. To guarantee the correct operation of the temperature probe, the boiling and the ice points of nanopure water were measured. A Fisher M101 pressure control system was used to measure and control the pressure and the heating power. The measured pressure in the still was 101.3 ± 0.1 kPa. The manometer was calibrated using the vapour pressure of ultrapure water.

In each experiment, the pressure was fixed and the heating and stirring system of the liquid mixture was turned on. The still was operated at constant pressure until equilibrium was reached. Equilibrium conditions were assumed when constant temperature and pressure were obtained for 45 min or longer, and moreover to verifying the equilibrium conditions, we analyze the vapour and liquid until the variation of the mole fraction of the both compositions is less than 0.001. The sampling was carried out with special syringes that allowed withdrawal of small volume samples.

2.3. Analysis

The composition of the sampled liquid and condensed vapour phase were determined using a TRACE GC Ultra Thermo Scientific gas chromatograph (GC), after calibration with gravimetrically prepared standard solutions. A flame ionization detector was used together with a 30 m, 0.454 mm i.d., capillary column, (DB-MTBE, J & Scientific). The GC response peaks were treated with Chrom-Card for Windows. Column, injector and detector temperatures were 373, 473, and 498 K, respectively, for all systems. Very good peak separation was achieved under these conditions and calibration analyses were carried out to convert the peak area ratio to the mass composition of the sample. In general, two analyses were made of each liquid and vapour composition. The standard deviation in the mole fraction was usually less than 0.001.

3. Results and discussion

The VLE data for the ternary systems are shown in Tables 2 and 3 and in Figs. 1 and 2. We have included in these figures, as a represen-

Table 2
Experimental vapour–liquid equilibrium data for diisopropyl ether (1) + isopropyl alcohol (2) + 2,2,4-trimethylpentane (3) at 101.3 kPa.

T (K)	x_1	x_2	y_1	y_2	γ_1	γ_2	γ_3
340.34	0.708	0.252	0.736	0.252	1.083	1.889	0.788
340.98	0.732	0.168	0.748	0.211	1.043	2.305	1.087
341.05	0.630	0.270	0.678	0.275	1.096	1.860	1.257
341.48	0.821	0.085	0.834	0.130	1.020	2.756	0.983
341.53	0.480	0.487	0.614	0.365	1.281	1.342	1.676
341.54	0.902	0.054	0.908	0.082	1.008	2.713	0.646
341.68	0.514	0.383	0.607	0.334	1.178	1.554	1.484
342.46	0.596	0.198	0.637	0.258	1.040	2.244	1.291
342.65	0.399	0.498	0.533	0.393	1.293	1.344	1.814
342.67	0.488	0.307	0.557	0.323	1.103	1.792	1.481
343.20	0.699	0.091	0.747	0.155	1.015	2.845	1.158
343.43	0.383	0.414	0.479	0.382	1.181	1.519	1.684
343.50	0.306	0.649	0.508	0.451	1.563	1.141	2.245
344.06	0.294	0.603	0.447	0.456	1.404	1.215	2.263
344.21	0.509	0.178	0.560	0.274	1.012	2.452	1.267
344.49	0.398	0.289	0.460	0.353	1.054	1.926	1.416
344.50	0.281	0.517	0.394	0.442	1.281	1.346	1.921
345.29	0.292	0.398	0.367	0.420	1.117	1.608	1.587
345.60	0.398	0.206	0.455	0.326	1.008	2.384	1.257
345.85	0.293	0.324	0.356	0.405	1.061	1.861	1.411
345.92	0.191	0.704	0.337	0.532	1.539	1.121	2.817
346.06	0.643	0.051	0.750	0.095	1.013	2.752	1.135
346.34	0.499	0.103	0.580	0.212	0.998	2.990	1.168
346.62	0.179	0.505	0.254	0.495	1.209	1.411	1.757
346.71	0.191	0.428	0.253	0.476	1.128	1.596	1.564
346.86	0.136	0.658	0.232	0.551	1.445	1.195	2.303
347.47	0.326	0.160	0.391	0.330	0.997	2.863	1.163
347.64	0.211	0.266	0.262	0.430	1.028	2.237	1.252
348.09	0.085	0.600	0.134	0.571	1.280	1.289	1.971
348.32	0.099	0.810	0.238	0.629	1.947	1.041	3.050
348.59	0.098	0.379	0.134	0.519	1.102	1.819	1.369
348.86	0.049	0.567	0.071	0.588	1.159	1.360	1.820
349.13	0.204	0.170	0.264	0.394	1.022	3.006	1.107
349.41	0.034	0.740	0.064	0.654	1.480	1.133	2.514
350.08	0.041	0.320	0.057	0.540	1.081	2.110	1.238
350.26	0.298	0.094	0.398	0.269	1.018	3.562	1.071
350.50	0.451	0.052	0.606	0.113	1.018	2.701	1.093
350.77	0.053	0.902	0.163	0.751	2.307	1.011	3.674
350.97	0.085	0.172	0.121	0.462	1.063	3.234	1.072
354.61	0.094	0.074	0.156	0.348	1.108	4.921	1.014
354.79	0.236	0.052	0.379	0.189	1.070	3.751	1.025
359.63	0.049	0.039	0.095	0.266	1.125	5.829	1.019