

Phase equilibria properties of binary and ternary systems containing di-isopropyl ether + isobutanol + benzene at 313.15 K

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Abstract

Isothermal vapour–liquid equilibrium data have been measured for the ternary system (di-isopropyl ether + isobutanol + benzene) and two of the binary systems involved (di-isopropyl ether + isobutanol) and (isobutanol + benzene) at 313.15 K. A static technique consisting of an isothermal total pressure cell was used for the measurements. Data reduction by Barker's method provides correlations for G^E using the Margules equation for the binary systems and the Wohl expansion for the ternary system. Wilson, NRTL and UNIQUAC models have been applied successfully to both the binary and the ternary systems.

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1. Introduction

Ethers and alcohols have been traditionally used as blending agents in the formulation of new gasolines for enhancing the octane number. To better understand and model these unleaded gasolines we started many years ago a research program 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, olefins). Methyl *tert*-butyl ether (MTBE), *tert*-amylmethyl ether (TAME) and di-isopropyl ether (DIPE) were chosen as representative ethers; methanol, isopropanol, 1-propanol and *tert*-amyl alcohol as alcohol additives.

Now, we continued studying ternary mixtures containing DIPE, benzene and different butanol isomers. Here, we report vapour–liquid equilibrium data concerning the ternary mixture DIPE + isobutanol + benzene at 313.15 K. The experimental technique used is a static type of high accuracy.

These highest quality of vapour–liquid equilibrium data are required to improve the interaction parameters of the predictive models which are used in process simulation packages. The accuracy of a process simulation depends strongly on the thermodynamic models used to describe the physical behaviour of the involved components. This purpose could be carried out with these measurements.

2. Experimental

Di-isopropyl ether and benzene 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 purity >0.99 and >0.995 (GC), respectively. Isobutanol used was anhydrous Aldrich product with a purity >0.999 (GC). All liquids degassed prior to measurements using a modified distillation method based on the technique of Van Ness and Abbott [1], under vacuum. The purities of the chemicals were checked by gas chromatography and were found to be >99.5 for all the compounds. In Table 1, the vapour pressures of the pure constituents measured in this work are compared with those reported in the literature as a check for complete degassing.

An isothermal total pressure cell has been employed for measuring the vapour–liquid equilibrium of binary and ternary mixtures. The apparatus and static measuring technique are based

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Table 1

Average values of experimental vapour pressures (p_i^s) for the pure compounds measured in this work, and literature values (p_i^s) (lit.) at $T = 313.15$ K

	DIPE ($i = 1$)	Isobutanol ($i = 2$)	Benzene ($i = 3$)
p_i^s (kPa)	37.108	4.008	24.386
p_i^s (lit.) (kPa)	37.128 ^a	3.988 ^d	24.398 ^{a,g}
	37.090 ^b	4.014 ^e	24.367 ^h
	37.081 ^c	4.026 ^f	24.378 ⁱ
V_i^L (cm ³ mol ⁻¹) ^j	145	94	91
B_{i1} (cm ³ mol ⁻¹) ^k	-1687.8	-1610.0	-1701.0
B_{i2} (cm ³ mol ⁻¹) ^k	-1610.0	-3773.4	-1056.0
B_{i3} (cm ³ mol ⁻¹) ^k	-1701.0	-1056.0	-1310.5

Molar volumes of pure liquids (V_i^L) and the second virial coefficients (B_{ii} , B_{ij}) at $T = 313.15$ K used for the calculations.^a Reported by Chamorro et al. [4].^b Reported by Ambrose et al. [13].^c Calculated from the Antoine equation using constants reported by Riddick et al. [14].^d Reported by Ambrose and Ghassee [15].^e Reported by Garriga et al. [16].^f Reported by Garriga et al. [17].^g Reported by Garriga et al. [18].^h Reported by Oracz [19].ⁱ Reported by Ambrose [20].^j Reported in TRC [21].^k Calculated by Hayden and Connell [7] from Dymond and Smith [8].

on that by Van Ness and has been described in detail in the literature [2,3]. The equilibrium properties measured directly and their uncertainties are: injected volume ± 0.03 mL, temperature ± 10 mK and total pressure ± 5 Pa.

Experimental values of the total vapour pressure for the binary mixtures are obtained in two overlapping runs starting from opposite ends of the composition range. For the ternary mixture they are obtained by adding a third component up to a mole fraction of $x = 0.5$ to a binary mixture with a mole fraction of one component close to $x = (0.3 \text{ or } 0.7)$. Six dilution lines were carried out.

3. Results and discussion

In this work, experimental isothermal p - x - y data for the ternary system di-isopropyl ether (DIPE) + isobutanol + benzene and two of the binary systems involved DIPE + isobutanol and benzene + isobutanol at 313.15 K are reported. The other binary system has been measured and published before [4].

Data reduction for the binary and ternary mixtures was done by Barker's method according to well established procedures [5,6]. The non-ideality of the vapour phase was taken into account with the virial equation of state, truncated after the second term. The second virial coefficients are calculated by Hayden O'Connell method [7] using the coefficients given by Dymond and Smith [8], these values are given in Table 1.

Data for the ternary system is adequately correlated by the three-parameter Wohl equation [9]:

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

which also includes the parameters of the corresponding binaries g_{ij} , according to equation (2). The adjustable parameters C_0 , C_1 and C_2 are found by regression of the ternary data.

Correlations for g_{ij} are given by a five-parameter Margules equation of the following form:

$$g_{ij} = \frac{G^E}{RT} = \{A_{ji}x_i + A_{ij}x_j - (\lambda_{ji}x_i + \lambda_{ij}x_j)x_ix_j + \eta x_i^2x_j^2\}x_ix_j \quad (2)$$

The binary and ternary systems have also been correlated using Wilson [10], NRTL [11] and UNIQUAC [12] models. The dimensionless adjustable parameters are given by $A_{ij} = (V_j^L/V_i^L) \exp[-(\lambda_{ij} - \lambda_{ii})/RT]$; $A_{ij} = (g_{ij} - g_{jj})/RT$ and $A_{ij} = \exp[-(u_{ij} - u_{ii})/RT]$, respectively.

Tables 2 and 3 give experimental values of total pressure and the corresponding compositions of the liquid and vapour phases for the binary systems and the ternary system where the vapour phase compositions have been calculated by Margules equation and Wohl expansion, respectively.

The data correlation results for the binary systems reported here are summarized in Table 4, including, for convenience, those of (DIPE + benzene), which have been published previously [4].

All the models fit quite good both binary systems however slight better results are obtained for the five-parameter Margules equation. The root mean square deviation between experimental and calculated pressure is 9 Pa with a maximum deviation of 16 Pa for (DIPE + isobutanol) and they are 12 and 18 Pa, respectively, for (benzene + isobutanol). Both binary systems present a large positive deviation from the ideality with a maximum value of the excess molar Gibbs energy of 950 J mol⁻¹ for (benzene + isobutanol) and 585 J mol⁻¹ for (DIPE + isobutanol), which are located near isobutanol liquid mole fraction of 0.45.

Experimental p - x data for the binary systems are shown in Fig. 1, the vapour compositions have been calculated by the Margules equation. As an example of the fits of models to the

Table 2

Total pressure p for the binary systems at $T = 313.15$ K, and at various compositions of the liquid phase x_1 and the calculated composition of the vapour phase y_1 using the Margules equation

x_1	y_1	p (kPa)	x_1	y_1	p (kPa)
Di-isopropyl ether (1) + isobutanol (2)					
0.0000	0.0000	3.999	0.5013	0.9068	26.341
0.0582	0.5286	8.047	0.5492	0.9155	27.449
0.1047	0.6694	10.983	0.5516	0.9159	27.518
0.1562	0.7513	13.887	0.5998	0.9238	28.563
0.2026	0.7962	16.204	0.6037	0.9244	28.650
0.2497	0.8274	18.305	0.6484	0.9313	29.567
0.3012	0.8521	20.327	0.7004	0.9391	30.592
0.3486	0.8694	21.985	0.7506	0.9468	31.587
0.3998	0.8843	23.592	0.8008	0.9549	32.584
0.4041	0.8854	23.737	0.8502	0.9637	33.592
0.4445	0.8951	24.849	0.9006	0.9740	34.682
0.4511	0.8966	25.059	0.9505	0.9859	35.849
0.4993	0.9065	26.265	1.0000	1.0000	37.111
Benzene (1) + isobutanol (2)					
0.0000	0.0000	3.996	0.4995	0.8742	21.452
0.0584	0.5361	8.181	0.5492	0.8817	21.990
0.0982	0.6519	10.540	0.5495	0.8818	22.001
0.1500	0.7322	13.099	0.5990	0.8887	22.465
0.2072	0.7825	15.356	0.6013	0.8890	22.476
0.2539	0.8090	16.881	0.6488	0.8953	22.879
0.2995	0.8280	18.060	0.6995	0.9018	23.248
0.3496	0.8436	19.157	0.7491	0.9083	23.570
0.3991	0.8557	20.053	0.8001	0.9153	23.875
0.3996	0.8558	20.077	0.8553	0.9245	24.145
0.4488	0.8656	20.808	0.8990	0.9347	24.341
0.4495	0.8657	20.827	0.9518	0.9565	24.518
0.4994	0.8742	21.458	1.0000	1.0000	24.380

data, in Fig. 2 it is plotted of the pressure residuals versus liquid composition for both binary systems using the five-parameters Margules equation. It shows how the model fits the data and also, the good agreement of experimental pressure measured twice for compositions $0.4 \leq x_1 \leq 0.6$.

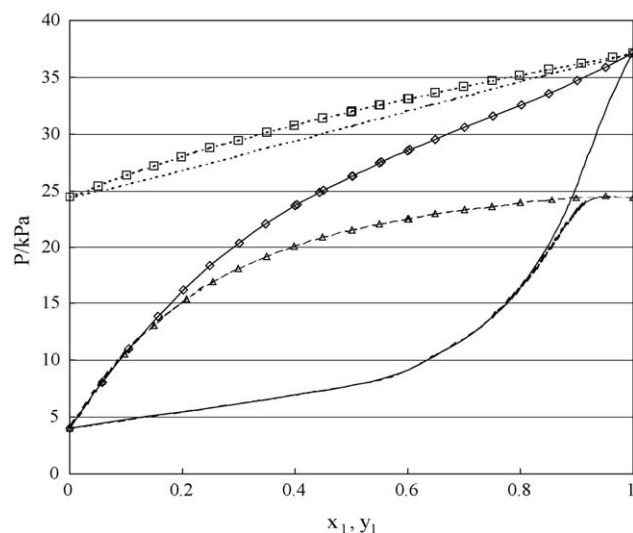


Fig. 1. Total vapour pressure for binary systems as a function of the liquid, x_1 , and vapour compositions, y_1 : (◇) di-isopropyl ether (1) + isobutanol (2); (△) benzene (1) + isobutanol (2) and (□) di-isopropyl ether (1) + benzene (2).

Table 3

Total pressure p for the ternary system di-isopropyl ether (1) + isobutanol (2) + benzene (3) at $T = 313.15$ K, and at various compositions of the liquid x_1 , x_2 and the vapour phases y_1 , y_2 , calculated using the Wohl expansion

x_1	x_2	y_1	y_2	p (kPa)
1.0000	0.0000	1.0000	0.0000	37.093
0.6870	0.3130	0.9371	0.0629	30.321
0.6699	0.3052	0.9101	0.0623	30.242
0.6534	0.2976	0.8844	0.0617	30.191
0.6192	0.2821	0.8323	0.0606	30.029
0.5850	0.2664	0.7813	0.0595	29.859
0.5513	0.2511	0.7326	0.0584	29.684
0.5163	0.2351	0.6831	0.0574	29.501
0.4812	0.2191	0.6347	0.0563	29.304
0.4458	0.2030	0.5872	0.0551	29.092
0.4128	0.1879	0.5438	0.0541	28.886
0.3781	0.1721	0.4992	0.0528	28.653
0.3440	0.1566	0.4563	0.0516	28.420
0.0000	1.0000	0.0000	1.0000	4.015
0.3027	0.6973	0.8527	0.1473	20.388
0.2924	0.6735	0.7796	0.1410	20.886
0.2855	0.6576	0.7346	0.1370	21.206
0.2728	0.6281	0.6586	0.1302	21.748
0.2553	0.5876	0.5684	0.1220	22.398
0.2409	0.5545	0.5050	0.1162	22.861
0.2276	0.5238	0.4531	0.1114	23.231
0.2124	0.4886	0.4009	0.1065	23.597
0.1959	0.4506	0.3514	0.1018	23.942
0.1811	0.4164	0.3121	0.0980	24.194
0.1670	0.3841	0.2784	0.0946	24.393
0.1518	0.3490	0.2453	0.0911	24.580
0.0000	0.0000	0.0000	0.0000	24.381
0.3015	0.0000	0.4071	0.0000	29.498
0.2941	0.0246	0.3940	0.0141	29.150
0.2865	0.0498	0.3828	0.0256	28.770
0.2714	0.1000	0.3651	0.0426	28.084
0.2565	0.1495	0.3517	0.0547	27.472
0.2447	0.1884	0.3430	0.0624	27.005
0.2261	0.2501	0.3310	0.0729	26.273
0.2109	0.3007	0.3223	0.0807	25.654
0.1959	0.3504	0.3141	0.0881	25.012
0.1807	0.4009	0.3060	0.0959	24.337
0.1658	0.4504	0.2981	0.1040	23.610
0.1506	0.5005	0.2900	0.1129	22.807
1.0000	0.0000	1.0000	0.0000	37.137
0.7004	0.0000	0.7657	0.0000	34.207
0.6815	0.0271	0.7555	0.0099	33.605
0.6476	0.0754	0.7401	0.0244	32.601
0.6251	0.1075	0.7315	0.0324	31.989
0.5959	0.1492	0.7217	0.0414	31.217
0.5610	0.1990	0.7116	0.0507	30.352
0.5252	0.2502	0.7023	0.0591	29.480
0.4899	0.3006	0.6937	0.0670	28.613
0.4553	0.3500	0.6856	0.0745	27.747
0.4199	0.4006	0.6773	0.0825	26.818
0.3847	0.4508	0.6686	0.0909	25.836
0.3499	0.5005	0.6594	0.1002	24.787
0.0000	1.0000	0.0000	1.0000	4.016
0.0000	0.6935	0.0000	0.1696	18.247
0.0317	0.6715	0.0800	0.1606	18.873
0.0585	0.6529	0.1441	0.1532	19.427
0.1051	0.6205	0.2470	0.1409	20.423
0.1546	0.5862	0.3430	0.1290	21.495
0.2026	0.5528	0.4241	0.1185	22.526
0.2514	0.5189	0.4956	0.1090	23.544
0.3023	0.4836	0.5600	0.1001	24.579
0.3500	0.4505	0.6126	0.0926	25.511

Table 3 (Continued)

x_1	x_2	y_1	y_2	p (kPa)
0.4003	0.4156	0.6612	0.0853	26.461
0.4516	0.3801	0.7048	0.0785	27.391
0.5001	0.3464	0.7416	0.0724	28.238
0.0000	0.0000	0.0000	0.0000	24.365
0.0000	0.3009	0.0000	0.0982	23.226
0.0296	0.2920	0.0472	0.0940	23.639
0.0517	0.2853	0.0817	0.0911	23.955
0.1013	0.2704	0.1565	0.0847	24.655
0.1546	0.2543	0.2324	0.0783	25.420
0.2029	0.2398	0.2973	0.0729	26.106
0.2504	0.2255	0.3577	0.0679	26.779
0.3007	0.2103	0.4179	0.0628	27.482
0.3511	0.1952	0.4747	0.0579	28.178
0.4007	0.1802	0.5274	0.0533	28.861
0.4509	0.1651	0.5779	0.0487	29.547
0.5013	0.1499	0.6259	0.0442	30.235

The binary system benzene (1) + isobutanol (2) exhibits a maximum pressure azeotrope. The pressure and the composition of the azeotrope have been estimated using all the models and they are summarized in Table 4.

Table 4

Determined parameters of the models used for the binary subsystems of ternary system di-isopropyl ether (1) + isobutanol (2) + benzene (3) at $T = 313.15$ K, together with the root mean square deviation of pressure (R.M.S.D. Δp) and the maximum value of the deviation (max $|\Delta p|$)

	Margules	Wilson	NRTL	UNIQUAC
Di-isopropyl ether (1) + isobutanol (2)				
A_{12}	0.7426	0.8125	1.7284	0.4799
A_{21}	1.0429	0.4075	−0.6261	1.3749
λ_{12}	−0.1483			
λ_{21}	−0.0589			
η	−0.3775			
α_{12}			0.1217	
R.M.S.D. Δp (kPa)	0.009	0.051	0.017	0.017
max $ \Delta p $ (kPa)	0.016	0.120	0.048	0.050
Benzene (1) + isobutanol (2)				
A_{12}	1.2579	0.6505	1.6028	0.5683
A_{21}	2.1115	0.1768	0.6457	1.0065
λ_{12}	0.6985			
λ_{21}	1.8268			
η	1.2086			
α_{12}			0.5694	
R.M.S.D. Δp (kPa)	0.012	0.044	0.053	0.173
max $ \Delta p $ (kPa)	0.018	0.092	0.098	0.310
$x_{\text{azeotrope}}$	0.9656	0.9688	0.9693	0.9862
$p_{\text{azeotrope}}$ (kPa)	24.513	24.490	24.478	24.400
Di-isopropyl ether (1) + benzene (2)^a				
A_{12}	0.2134	0.5515	−0.4967	0.9014
A_{21}	0.1277	1.3762	0.7905	1.0698
$\lambda_{12} = \lambda_{21}$	0.0282			
α_{12}			0.3	
R.M.S.D. Δp (kPa)	0.005	0.006	0.005	0.006
max $ \Delta p $ (kPa)	0.009	0.013	0.008	0.013

The Δp term is defined as the difference between the experimental and calculated pressure.

^a Data published in ref. [4].

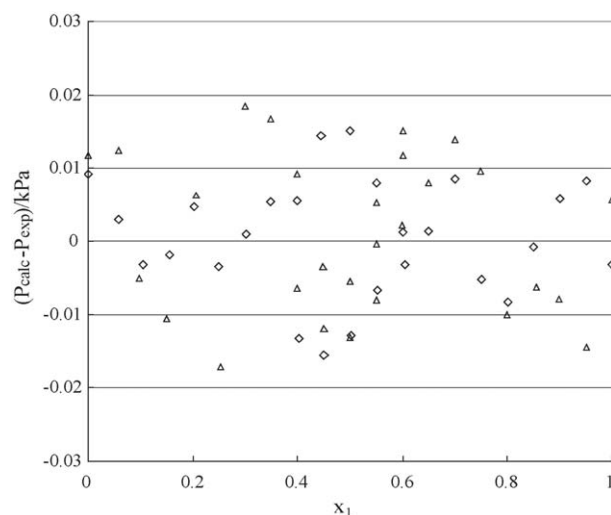


Fig. 2. Pressure residuals as a function of the liquid composition, x_1 : (◇) di-isopropyl ether (1) + isobutanol (2); (△) benzene (1) + isobutanol (2).

Table 5

Summary of the data reduction results obtained for the ternary system (DIPE (1) + isobutanol (2) + benzene (3)) at 313.15 K

	Wilson	NRTL	UNIQUAC	Wohl
A_{12}	0.8279	1.8293	0.4662	$C_0 = 2.1822$
A_{21}	0.3996	−0.6995	1.3989	$C_1 = 0.6538$
A_{13}	0.3788	−0.6234	1.2626	$C_2 = −0.4358$
A_{31}	1.6794	0.9980	0.7328	
A_{23}	0.1966	0.6878	1.1095	
A_{32}	0.6249	1.5279	0.4950	
α_{12}		0.1217		
α_{13}		0.3000		
α_{23}		0.5694		
R.M.S.D. Δp (kPa)	0.051	0.036	0.042	0.023
max $ \Delta p $ (kPa)	0.174	0.109	0.146	0.040

For the ternary system, correlation results are summarized in Table 5. It contains the correlations parameters, the root mean square pressure deviation and the maximum value of this deviation. The good results of the fits for all the models are shown in

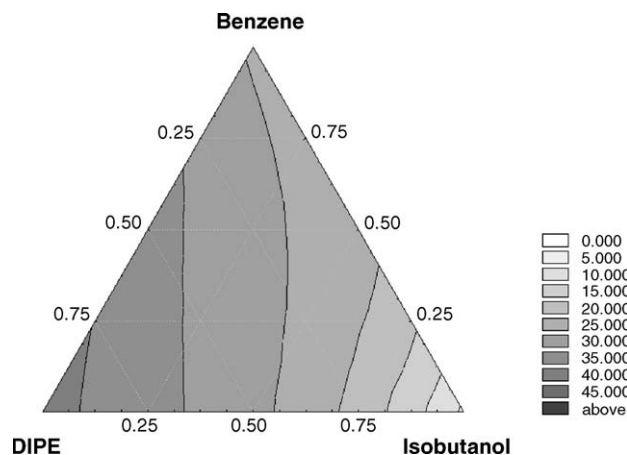


Fig. 3. Isobar lines in kPa for the ternary system di-isopropyl ether (1) + isobutanol (2) + benzene (3) at 313.15 K as a function of liquid composition x_i .

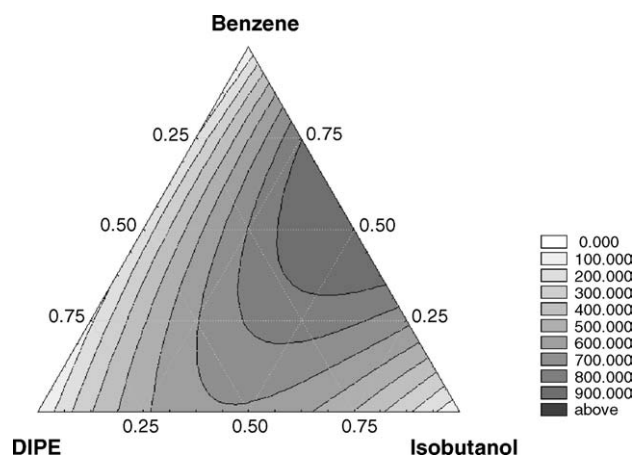


Fig. 4. Iso- G^E lines in J mol^{-1} for the ternary system di-isopropyl ether (1) + isobutanol (2) + benzene (3) at 313.15 K, calculated using the Wohl expansion, as a function of liquid composition x_i .

the table, the root mean square pressure deviation varies between 23 Pa for the Wohl expansion and 51 Pa for the Wilson equation and the maximum value of the deviation is 174 Pa for the Wilson equation.

Results for the ternary system are also shown graphically in Figs. 3 and 4. Lines of constant total pressure and lines of constant excess molar Gibbs energy are plotted for the ternary system calculated with the Wohl expansion. The total pressure of the ternary system varies from the vapour pressure of the least volatile pure component (isobutanol) to the vapour pressure of the pure component (DIPE) with the highest volatility. On the other hand, the maximum value of the excess molar Gibbs energy corresponds to the least ideal binary system.

List of symbols

A_{ij}, A_{ji}	adjustable parameters of the correlation models
C_0, C_1, C_2	parameters in Eq. (1)
G^E	molar excess Gibbs energy (J mol^{-1})
i, j	constituent identification: 1, 2 or 3
p	total pressure (kPa)
p_i^s	vapour pressure of pure constituent i (kPa)
R.M.S.D.	root mean square pressure deviation
x	mole fraction, liquid phase
y	mole fraction, vapour phase

Greek letters

Δ	signifies difference
α_{ij}	parameter for NRTL model
λ_{ij}	parameter for Margules equation
η	parameter for Margules equation

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