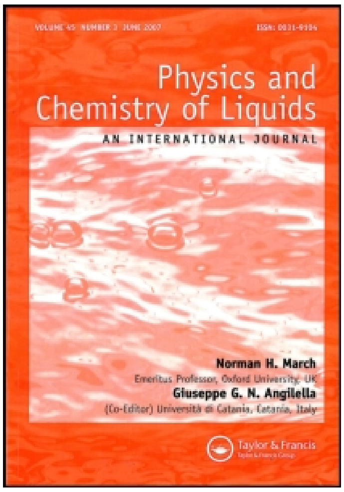

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Isobaric vapour–liquid equilibria for the binary systems of fuel oxygenates with aromatic hydrocarbons

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Isobaric vapour–liquid equilibrium data at 720 mm Hg for the binary systems of diisopropyl ether with *o*-xylene and *m*-xylene and dimethoxymethane with benzene and toluene are determined. A Swietoslawski type ebulliometer is used for the measurements. The experimental $T-x$ data are used to estimate Wilson parameters and the parameters in turn are used to calculate the vapour compositions and activity coefficients. The activity coefficients are used to calculate molar excess Gibbs free energy (G^E). All the systems studied here do not exhibit azeotropes. Excess Gibbs free energy values are positive over the entire range of composition for all the systems.

Keywords: Phase equilibria; Oxygenates; Aromatic hydrocarbons; Wilson model

1. Introduction

To meet the stringent environmental regulations fuel oxygenates are added to unleaded gasoline. Thermophysical properties of fuel oxygenates with hydrocarbons are essential to have a better understanding of fuel oxygenate mixtures. Because of this, recently several articles have been published on methyl *tert*-butyl ether (MTBE), diisopropyl ether (DIPE) and ethyl *tert*-butyl ether (ETBE). MTBE has been used extensively as gasoline additive, because of ease of manufacture, blending and transportation. MTBE, highly soluble in water, has become a very controversial gasoline additive as it can cause health risks by contaminating drinking water [1]. In addition it is resistant to microbial decomposition. These facts have promoted research on the possible use of several oxygenates that have low solubility in water and have harmless to the environment. The isomeric ethers, ETBE and DIPE have some advantages

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over MTBE, such as being chemically more similar to hydrocarbons and having a lower solubility in water [2–4]. Finally, the higher boiling points of ETBE and DIPE allow incorporation of more light feed stocks in gasoline [5]. Recently dimethoxymethane (DMM) has also used as octane-enhancing additive in diesel fuel [6]. Test results indicate that addition of 30% DMM to diesel fuel results in reduction of particulate matter [7]. Phase equilibrium data of these oxygenated mixtures are important for predicting the vapour phase composition that would be in equilibrium with hydrocarbons. In continuation of our work on thermodynamic and transport properties of octane-enhancing additives [8–10], this article reports isobaric vapour equilibrium data for the binary systems of diisopropyl ether with *o*-xylene and *m*-xylene, DMM with benzene and toluene at 720 mm Hg. A search of literature indicates that no vapour liquid equilibrium data have been reported for the above systems.

2. Experimental

The chemicals diisopropyl ether and DMM were supplied by E. Merck Ltd (India) with a guaranteed purity of 99.5%. These two chemicals were used without further purification after gas chromatography failed to show any significant impurities. Benzene, toluene, *o*-xylene and *m*-xylene were supplied by S. D. Fine Chemicals (India). The aromatic compounds were made thiophene-free as described in Vogel [11], dried over calcium chloride and finally fractionally distilled over metallic sodium. The purity of the chemicals was checked by comparing the measured densities and boiling points with those reported in literature [12]. The values are included in table 1. The densities were determined with a bicapillary pycnometer described by Rao and Naidu [13].

A Swietoslawski ebulliometer [14] was used for the measurements of the boiling points of the pure components and mixtures. The ebulliometer was connected to a pressure controlling system. The pressure was controlled by a Cartesian diver and was measured with an accuracy of ±1 mm Hg. The equilibrium temperatures were measured with an accuracy of ±0.1 K by means of a resistance thermometer carefully calibrated by means of point-to-point comparison with standard platinum resistance thermometer certified by the National Institute of Standards Technology (NIST). The liquid mixtures of required composition were prepared gravimetrically, with the use of an electronic balance that was precise to ±0.0001 g. The ebulliometer was charged with the mixture of desired composition and the boiler was heated up

Table 1. Densities (ρ) at 298.15 K and boiling points of pure components.

	Density ($kg\,m^{-3}$)		Boiling point (K)	
Component	Present work	Literature	Present work	Literature
DIPE	718.14	718.20	341.35	341.45
DMM	847.51	847.45	315.25	315.45
Benzene	873.64	873.70	353.15	353.25
Toluene	862.48	862.31	383.85	383.77
o-Xylene	875.83	875.96	417.45	417.56
m-Xylene	859.72	859.90	412.35	412.25

by nichrome wire wound on the boiler. The heating rate was adjusted to the desired condensate drop rate that was 30 drops per minute following the suggestions of Hala *et al.* [14]. The equilibrium temperatures were noted after a steady drop rate and constant temperature was maintained for at least 30 min. All the precautions were taken to minimize the loss of components due to evaporation during the preparation and subsequent measurements.

3. Results and discussion

The experimental liquid phase composition (x_1) of oxygenate *versus* temperature (T) data, summarized in tables 2 and 3, are fitted to the Wilson model [15] using the equations,

$$\ln\gamma_1 = -\ln(x_1 + \Lambda_{12}x_2) + x_2\left[\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{x_2 + \Lambda_{21}x_1}\right] \tag{1}$$

$$\ln\gamma_2 = -\ln(x_2 + \Lambda_{21}x_1) + x_1\left[\frac{\Lambda_{21}}{x_2 + \Lambda_{21}x_1} - \frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2}\right] \tag{2}$$

Table 2. $T - x_1 - y_1$ data, activity coefficients (γ_1 and γ_2) and molar excess Gibbs free energy (G^{E}) for the binary systems of dimethoxymethane (DMM) at 720 mm Hg.

x_1	T_{exp} (K)	T_{cal} (K)	$y_{1,\mathrm{cal}}$	γ_1	γ_2	G^{E} (J mol^{-1})
DMM (**1**) + benzene (**2**)						
0.0000	350.85	350.85	0.0000	2.7074	1.0000	0.0
0.0615	339.75	339.75	0.3423	2.3867	1.0050	164.3
0.1456	331.75	331.75	0.5359	2.0146	1.0271	344.3
0.2135	327.95	327.95	0.6163	1.7820	1.0569	455.0
0.3003	324.75	324.75	0.6816	1.5559	1.1100	555.6
0.4071	322.05	322.05	0.7369	1.3575	1.1985	620.6
0.4785	320.65	320.65	0.7669	1.2603	1.2732	630.9
0.5617	319.25	319.25	0.7992	1.1731	1.3782	611.2
0.6384	318.15	318.15	0.828	1.1127	1.4942	564.4
0.7555	316.65	316.55	0.8749	1.0489	1.7150	442.1
0.8607	315.25	315.25	0.9221	1.0154	1.9703	282.1
1.0000	313.75	313.75	1.0000	1.0000	2.4211	0.0
DMM (**1**) + toluene (**2**)						
0.0000	381.85	381.85	0.0000	2.1697	1.0000	0.0
0.0713	357.25	357.25	0.5668	2.0786	1.0019	160.2
0.1713	340.25	340.25	0.7873	1.9428	1.0121	350.0
0.2504	332.35	332.35	0.8559	1.8357	1.0282	477.8
0.3828	324.25	324.25	0.9109	1.6615	1.0785	649.7
0.4819	320.35	320.35	0.9325	1.5364	1.1462	739.5
0.5522	318.35	318.45	0.9431	1.4507	1.2199	779.3
0.5981	317.35	317.35	0.9486	1.3962	1.2855	793.0
0.6801	315.85	315.95	0.9565	1.3018	1.4575	787.5
0.7888	314.75	314.65	0.9644	1.1831	1.9112	705.0
0.8815	314.15	314.05	0.9700	1.0890	2.9514	531.2
1.0000	313.75	313.75	1.0000	1.0000	21.2171	0.0

Table 3. $T-x_1-y_1$ data, activity coefficients (γ_1 and γ_2) and molar excess Gibbs free energy (G^E) for the binary systems of diisopropyl ether (DIPE) at 720 mm Hg.

x_1	T_{exp} (K)	T_{cal} (K)	$y_{1,cal}$	γ_1	γ_2	G^E (J mol^{-1})
DIPE (**1**) + *o*-xylene (**2**)						
0.0000	415.65	415.65	0.0000	2.2702	1.0000	0.0
0.0662	389.45	389.45	0.5602	2.1817	1.0022	173.8
0.1755	368.25	368.15	0.8049	2.0022	1.0167	414.8
0.2618	359.45	359.35	0.8713	1.8570	1.0406	572.0
0.3620	352.75	352.75	0.9099	1.6957	1.0873	717.2
0.4382	349.25	349.35	0.9273	1.5804	1.1417	798.5
0.5608	345.65	345.65	0.9451	1.4101	1.2842	869.5
0.6299	344.15	344.15	0.9520	1.3225	1.4139	870.5
0.7186	342.85	342.85	0.9591	1.2195	1.6776	821.4
0.8362	341.55	341.55	0.9674	1.1008	2.4273	640.5
0.9092	340.85	340.85	0.9740	1.0409	3.5993	432.8
1.0000	339.95	339.95	1.0000	1.0000	9.7045	0.0
DIPE (**1**) + *m*-xylene (**2**)						
0.0000	410.25	326.55	0.0000	1.7434	1.0000	0.0
0.0676	391.05	323.75	0.4619	1.6943	1.0010	118.9
0.1321	379.15	322.15	0.6564	1.6475	1.0041	219.1
0.2249	367.25	320.85	0.7919	1.5797	1.0134	345.5
0.3673	356.05	319.45	0.8838	1.4738	1.0439	502.1
0.4693	350.75	317.95	0.9171	1.3955	1.0862	584.0
0.5988	346.25	316.95	0.9430	1.2930	1.1877	641.6
0.6763	344.25	316.05	0.9536	1.2302	1.2979	642.6
0.7769	342.45	315.35	0.9642	1.1480	1.5667	590.5
0.8513	341.45	314.75	0.9709	1.0882	1.9907	494.9
0.9126	340.85	314.15	0.9768	1.0421	2.7751	359.4
1.0000	339.95	313.75	1.0000	1.0000	8.4963	0.0

where

$$\Lambda_{12} = \frac{V_2^L}{V_1^L}\exp\left[-\frac{\Delta\lambda_{12}}{RT}\right] \tag{3}$$

$$\Lambda_{21} = \frac{V_1^L}{V_2^L}\exp\left[-\frac{\Delta\lambda_{21}}{RT}\right]. \tag{4}$$

Here V_1^L and V_2^L are the liquid molar volumes and $\Delta\lambda_{12}$ and $\Delta\lambda_{21}$ are Wilson model constants. The optimum Wilson parameters are obtained by minimizing the objective function defined as

$$S = \sum\left[\frac{P_{cal}}{P_{exp}} - 1\right]^2 \tag{5}$$

where P_{exp} and P_{cal} are experimental and calculated values of the total pressure. The Nelder–Mead optimization technique described by Kuester and Mize [16] was used. Vapour pressure needed in the computations are calculated from the Antoine constants derived from the compilation in the data bank of Riddick *et al.* [12].

Table 4. Antoine constants of the components.

Component	A	B	C
Diisopropyl ether	6.85188	1143.07	219.34
Dimethoxymethane	7.10401	1162.58	233.15
Benzene	6.89710	1206.53	220.91
Toluene	6.96050	1348.77	219.97
o-Xylene	7.00582	1479.82	214.31
m-Xylene	7.01295	1465.39	215.51

Table 5. Representation of the measurements by the Wilson model.

System	$\Delta\lambda_{12}/R$ (K)	$\Delta\lambda_{21}/R$ (K)	σ (K)
Diisopropyl ether (**1**) + *o*-xylene (**2**)	32.03	740.6	0.05
Diisopropyl ether (**1**) + *m*-xylene (**2**)	−91.9	846.7	0.06
Dimethoxymethane (**1**) + benzene (**2**)	297.5	65.56	0.03
Dimethoxymethane (**1**) + toluene (**2**)	−19.43	982.6	0.04

The Antoine constants are given in table 4 for ready reference. The vapour pressure of compounds (in mm Hg) are calculated using Antoine equation,

$$\log\left[\frac{P}{\text{mm Hg}}\right] = A - \left[\frac{B}{(t/^{\circ}\text{C}) + C}\right]. \tag{6}$$

The vapour pressure data of pure liquids obtained using equation (6) are in agreement with the experimental values with an average absolute deviation of 0.4%. Molar volumes of liquids are calculated from the liquid density data of the present work recorded in table 1. Critical properties and the other input data required for the estimation are collected from Reid *et al.* [17]. The values of Wilson parameters along with the standard deviation are given in table 5. Activity coefficients computed on the basis of Wilson model are used to evaluate the molar excess Gibbs free energy at 720 mm Hg for four binary systems over the entire range of composition. Calculated boiling points (T_{cal}), vapour phase mole fraction (y_1) of oxygenate, the liquid phase activity coefficients (γ_1 and γ_2) and molar excess Gibbs free energies (G^{E}) are included in tables 2 and 3, plots of excess Gibbs free energy *versus* liquid phase mole fraction are shown in figures 1 and 2. The excess Gibbs free energies for the systems were calculated using the equation,

$$\frac{G^{\text{E}}}{RT} = x_1 \ln \gamma_1 + x_2 \ln \gamma_2. \tag{7}$$

The results presented in the tables indicate that all the systems studied here show positive deviation from ideal behaviour and do not exhibit azeotrope. An observation of plots in figures 1 and 2, the excess Gibbs free energies for binary system of DIPE with *o*-xylene is higher than *m*-xylene. Positive deviation from ideal behaviour found in this work for DIPE with *o*-xylene and *m*-xylene agrees with the excess molar enthalpies reported in [18], where the curves of H^{E} *versus* x_1 have symmetrical

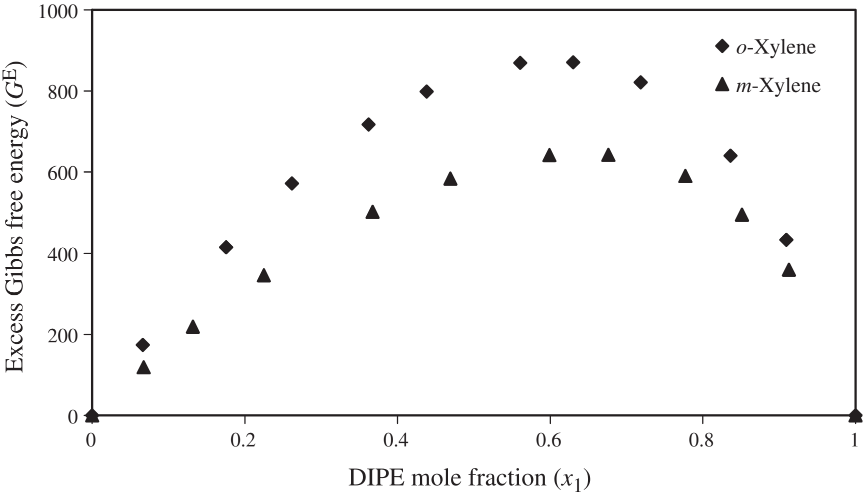

Figure 1. Excess Gibbs free energy (G^E) *vs*. DIPE mole fraction (x_1) for two binary systems.

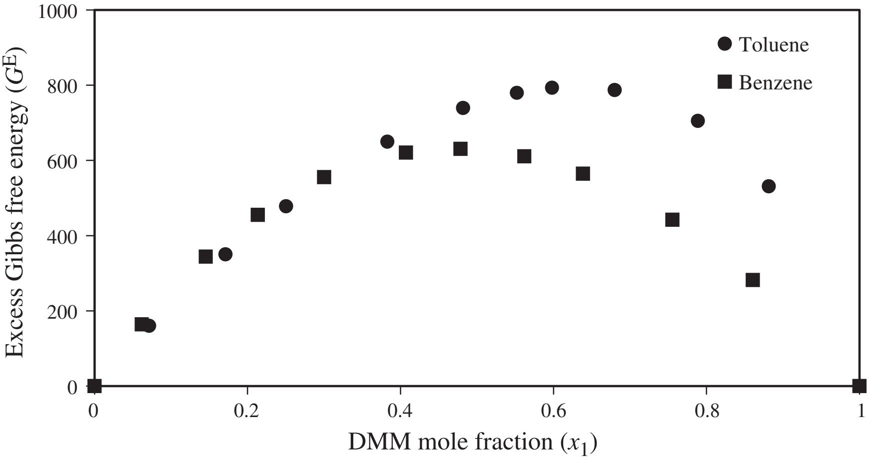

Figure 2. Excess Gibbs free energy (G^E) *vs*. DMM mole fraction (x_1) for two binary systems.

shape and exhibit moderate positive values of H^E, 49.4 J mol^{-1} for *o*-xylene and 41.0 J mol^{-1} *m*-xylene. DMM with toluene exhibit higher Gibbs free energy value than benzene. This same order found in our unpublished work for enthalpies of DMM with benzene (118.9 J mol^{-1}) and toluene (132.8 J mol^{-1}). In view of the care taken in carrying out the measurements and good representation by the Wilson model, the results presented in this article are expected to be useful for design purpose.

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