Fluid Phase Equilibria 268 (2008) 39–44

Contents lists available at ScienceDirect

Fluid Phase Equilibria

journal homepage: www.elsevier.com/locate/fluid

Isothermal vapour–liquid equilibria of binary systems of 1,2-dichloroethane with ethers

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ARTICLE INFO

Article history:
Received 18 December 2007
Received in revised form 13 March 2008
Accepted 18 March 2008
Available online 29 March 2008

Keywords:
Vapour–liquid equilibria
1,2-Dichloroethane
Methyl 1,1-dimethylethyl ether
Diethyl ether
Diisopropyl ether
The Modified UNIFAC (Do) model

ABSTRACT

The vapour pressures of the binary systems 1,2-dichloroethane + diethyl ether, +diisopropyl ether or +methyl 1,1-dimethylethyl ether and of the four pure components are measured by a static method in the temperature range from 273 to 354 K. The isoplethal *T–P* data are reported and correlated with the Antoine equation. Interpolated data are also reported. Excess molar Gibbs energies, G^E, are calculated for several constant temperatures, taking into account the vapour phase imperfection in terms of the second virial coefficients, and are fitted to the Redlich–Kister equation. The experimental VLE data are analysed in terms of the Modified UNIFAC (Do) model.

1. Introduction

At present, there is a general interest in thermodynamic properties for mixtures containing oxygenated organic compounds (usually ethers and alcohols). Resulting from recent increasing concerns about the environmental problems, ethers, especially, are increasingly being used as additives to gasoline owing to their octane number-enhancing and pollution-reducing properties. Also, ethers and chloroalkanes represent two interesting families of molecules for the purpose of testing group-contribution models. Moreover, the measurement of fluid phase equilibrium is a powerful thermodynamic tool to explore the behaviour of liquid mixtures and plays an essential role in phase equilibrium thermodynamics, which is one of the most important fundamental sciences for process development in the chemical industry. These are, probably, the reasons that contribute to the constant need for reliable experimental vapour–liquid equilibrium (VLE) data for mixtures containing oxygenated compounds such as ethers. However, a survey of the open literature revealed a scarcity of VLE data on mixtures of 1,2-dichloroalkanes with ethers.

Guided by the above and continuing our investigations on the thermodynamic behaviour of binary mixtures containing aliphatic monoethers [1,2], we report here new experimental data of total vapour pressures for 1,2-dichloroethane (1,2-DCE) with diethyl ether (DEE), diisopropyl ether (DIPE) or methyl 1,1-dimethyl ethyl ether (MTBE). The experimental data were analysed in the framework of the Modified UNIFAC (Do) [3–5] models.

2. Experimental

2.1. Materials

The chemicals used were commercial products of first grade purity, either from Carlo Erba Reagents (MTBE 99+% and DEE 99.8%) or Prolabo (1,2-DCE 99+% and DIPE 99+%). Evidence of chemical purity was provided by comparison of measured vapour pressures with the literature values [6–15]. No additional purification has been carried out. However, all the liquids used were thoroughly degassed before performing the static vapour pressure measurements.

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doi:10.1016/j.fluid.2008.03.015

2.2. Apparatus and procedure

The experimental vapour pressure, P for given constant values of the mole fraction composition x_i, was measured with an apparatus described previously by Blondel-Telouk et al. [16], as a function of the temperature T. The estimated uncertainties in P and T are, respectively: $\sigma(P) = 0.15P$ (if $P < 13.3$ Pa), $\sigma(P) = 0.05P$ (in the range $13.3 < P < 200$ Pa), $\sigma(P) = 0.005P$ (in the range $200 < P < 1000$ Pa), $\sigma(P) = 0.002P$ (in the range $1000 < P < 200 \times 10^3$ Pa), and $\sigma(T) = 0.01$ K. Mixtures were prepared by mass and degassed as described in [16]. The final composition of the liquid mixture was determined after each pressure measurement by GLC. The estimated uncertainties in the liquid mole fraction composition, x_i, is $\sigma(x_i) = 0.0002$.

3. Results and data reduction

The primary vapour pressure measurements, obtained by the experimental procedure described above, are isoplethal T–P data. For evaluation purposes, these direct experimental data, for the pure components and for the three binary mixtures, are summarized in Table 1 and in Tables 2–4, respectively. The experimental vapour pressure data were correlated with the Antoine equation, the overall mean relative deviations in pressure being between 0.03 and 0.25%. Interpolated values at several arbitrarily chosen temperatures, for the pure components and the binary mixtures at constant compositions, are reported in Tables 5 and 6 , respectively. The interpolated isothermal VLE data were then reduced using Barker's method [17] to obtain values of the activity coefficient γ_i, of component i in the liquid state. Molar excess Gibbs energies G^E, were calculated for constant temperatures, taking into account the vapour phase imperfection and the variation of the Gibbs energy of the pure liquids components with pressure, in terms of second virial coefficients and molar volumes at saturation pressure, and were fitted to the Redlich–Kister equation [18]:

$$\frac{G^E}{RT} = x_1(1 - x_1)\sum_{i=1}^{i=3} A_i(2x_1 - 1)^{i=1} \tag{1}$$

where x_1 is the mole fraction of chloroalkane in the liquid phase.

Table 1
Direct isoplethal T–P data, for the pure components

1,2-DCE		DIPE		MTBE		DEE	
T (K)	P (kPa)	T (K)	P (kPa)	T (K)	P (kPa)	T (K)	P (kPa)
284.86	5.38	284.93	10.74	274.90	11.59	255.47	10.11
284.87	5.37	284.93	10.75	274.91	11.59	255.48	10.13
294.83	8.96	294.90	17.21	284.82	18.55	255.50	10.14
294.84	8.95	294.91	17.21	294.80	28.78	265.44	17.06
304.82	14.33	304.87	26.57	294.80	28.78	265.44	17.06
304.82	14.32	304.89	26.58	294.81	28.78	265.45	17.07
314.81	22.18	314.86	39.71	304.79	43.24	274.86	26.90
314.83	22.18	314.87	39.72	304.79	43.26	274.87	26.91
324.82	33.28	324.85	57.64	314.75	62.95	284.83	41.98
324.83	33.27	324.87	57.65	314.76	62.97	284.84	42.00
334.79	48.45	334.85	81.41	314.76	62.97	294.77	62.89
334.82	48.46	334.85	81.42	324.90	89.66	294.78	62.93
344.81	67.97	344.84	112.36	324.90	89.69	304.75	91.58
344.81	67.97	344.85	112.39	334.85	124.02	304.75	91.56
344.82	67.98	354.87	151.81	344.84	167.14	304.76	91.60
344.82	67.98	354.88	151.82	344.85	167.57	314.74	129.30
354.89	94.95			354.82	221.79	314.74	129.45
354.89	94.94			354.82	221.39	314.75	129.42
354.89	94.94					324.89	179.51
354.89	94.95					324.89	179.65
						324.89	179.77

The coefficients A_i of Eq. (1) were determined by regression through minimization of the sum of deviations in the pressure, all points weighted equally. The values of these coefficients are reported in Table 7 with the standard deviations in pressure, $\sigma(P)$.

Calculated pressures P_{calc}, and vapour phase composition $y_{i,\text{calc}}$, were obtained from:

$$P_{\text{calc}} = \sum_{i=1}^{i=2} \frac{x_i \gamma_i P_i^* \exp[-(B_{ii} - V_i^*)(P - P_i^*) - P\delta_{12}(1 - y_i)^2]}{RT} \tag{2}$$

$$y_{i,\text{calc}} = \frac{x_i \gamma_i P_i^*}{P} \exp[-(B_{ii} - V_i^*)(P - P_i^*) - P\delta_{12}(1 - y_i)^2] \tag{3}$$

$$\delta_{12} = 2B_{12} - B_{11} - B_{22} \tag{4}$$

where, P_i^*, V_i^* and B_{ii} are the interpolated vapour pressure, the saturated liquid molar volume and the second molar virial coefficient, of the pure component i, and B_{ij} the cross second virial coefficient, at temperature T, respectively.

Table 2
Direct isoplethal T–P data, for 1,2-DCE (1) + DEE (2) binary mixtures, at five constant experimental chloroalkane liquid phase composition, x_1

$x_1 = 0.1681$		$x_1 = 0.3603$		$x_1 = 0.5199$		$x_1 = 0.6958$		$x_1 = 0.9148$	
T (K)	P (kPa)	T (K)	P (kPa)	T (K)	P (kPa)	T (K)	P (kPa)	T (K)	P (kPa)
255.02	8.35	255.54	6.62	255.16	5.16	255.07	3.73	255.69	1.82
255.02	8.35	255.56	6.63	265.09	8.89	265.06	6.50	255.71	1.82
255.03	8.34	255.56	6.63	265.09	8.89	265.07	6.51	265.55	3.26
264.98	14.11	265.50	11.30	274.95	14.59	265.07	6.51	274.92	5.43
264.99	14.11	265.51	11.30	274.96	14.58	275.84	11.30	284.89	8.99
274.93	22.92	275.13	18.17	284.89	23.10	275.84	11.29	294.86	14.29
274.95	22.92	275.13	18.17	284.90	23.10	286.09	18.26	304.82	21.97
284.89	35.72	285.10	28.57	294.86	35.29	286.20	18.35	314.81	32.77
284.92	35.75	285.11	28.58	294.87	35.31	295.98	27.96	324.92	47.74
294.87	53.85	295.08	43.38	294.87	35.29	296.03	28.01	334.81	67.48
294.87	53.84	295.09	43.37	304.82	52.18	305.91	41.58	344.84	93.29
304.83	78.44	305.05	63.67	304.82	52.19	305.91	41.58		
314.80	111.66	315.02	90.90	304.83	52.21	315.80	59.90		
314.81	111.71	315.02	90.94	314.81	75.06	315.81	59.86		
314.81	111.57	325.13	127.28	314.82	75.06	325.69	84.11		
324.92	155.26	325.14	127.32	314.82	75.00	325.70	84.03		
324.92	155.25	325.14	127.35	324.92	105.76	325.70	84.06		
324.93	155.10	335.07	172.92	324.92	105.77	335.71	115.96		
		335.08	172.95	324.93	105.79	335.73	115.94		
		335.09	172.98	334.88	144.47	335.73	115.81		
				344.83	193.09	345.64	155.68		
				344.85	193.37	345.65	155.80		