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Isothermal vapour–liquid equilibria for 1,2-dichloroethane + nitromethane and + nitroethane binary systems at temperatures between 333.15 and 353.15 K[☆]

Mariana Teodorescu*, Alexandru Barhala, Dana Dragoescu

"Ilie Murgulescu" Institute of Physical Chemistry, Romanian Academy, Splaiul Independentei 202, 060021 Bucharest, Romania

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ABSTRACT

Isothermal vapour–liquid equilibrium (VLE) data are reported at three temperatures, 333.15, 343.15 and 353.15 K, for binary mixtures containing 1,2-dichloroethane with nitromethane or nitroethane. Use has been made of an ebulliometer which allows sampling from both phases in equilibrium. The experimental data were correlated using the Redlich–Kister, Wilson, NRTL and UNIQUAC excess Gibbs energy models by means of the maximum likelihood method, taking into account the vapour phase imperfection in terms of the second virial coefficients. Both systems are zeotropic and show positive deviations from ideal behaviour. The experimental VLE data are analysed in terms of the Modified UNIFAC (Do) model.

1. Introduction

In this paper, the first results of a new project dealing with phase equilibria in chloroalkane + nitroalkane mixtures are presented.

Nitromethane is a highly polar liquid commonly used as a solvent in a variety of industrial applications such as in extractions, as a reaction medium, and as a cleaning solvent. As an intermediate in organic synthesis, it is widely used in the manufacture of pharmaceuticals, pesticides, explosives, fibers, and coatings. It is also utilized as a racing fuel and in miniature internal combustion engines (e.g., in radio-controlled models). The principal use of nitromethane is as stabilizer for chlorinated solvents, which are used in dry cleaning, semiconductor processing, and degreasing. It is also the most effective solvent for dissolving acrylate monomers, such as cyanoacrylates (more commonly known as "super-glue").

Nitroethane, via different condensations, converts to several compounds of commercial interest, e.g., antihypertensive and surfactants. Like some other nitrated organic compounds, nitroethane is also used as a fuel additive and a precursor to explosives. Besides, it is a useful solvent for polymers such as polystyrene and for dissolving cyanoacrylate adhesives.

The thermodynamic study of chloroalkane + nitroalkane mixtures is important for the determination of the type and magnitude of molecular interactions in these systems and for the further development of group contribution models frequently used in prediction of thermodynamic properties [1–4].

In the literature, for this family, VLE data were presented for the 1-chlorobutane + nitromethane system by Khurma et al. [5] and for the carbon tetrachloride + nitromethane system by Brown and Smith [6]. Activity coefficients at infinite dilution for carbon tetrachloride, nitromethane or nitroethane in 1,2-dichloroethane and nitromethane in chloroform or in carbon tetrachloride were obtained at three temperatures [7]. Excess enthalpy and mixing volume data were reported by Marsh [8] for the binary systems carbon tetrachloride + nitromethane and + nitroethane.

Isothermal P, x, y data are reported here for the binary systems of 1,2-dichloroethane + nitromethane and + nitroethane at temperatures of 333.15, 343.15 and 353.15 K. For these systems no VLE data are referenced in [9] and no experimental excess Gibbs energy data, G^E, was found in the literature [10].

The experimental VLE data were correlated using different models for G^E, namely the Redlich–Kister [11], Wilson [12], NRTL [13], and UNIQUAC [14] equations. Afterwards, they were compared with the predicted results obtained by means of Modified UNIFAC model (Dortmund – Do) [15].

2. Experimental

2.1. Materials

The 1,2-dichloroethane was purchased from Aldrich (99.8%, HPLC grade) and the nitromethane and nitroethane from Fluka (purum ≥97%). The liquids were dried and stored over 4A molecular

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[☆] In the memory of our dear mentor and friend, Dr. Henry V. Kehiaian (1929–2009).

* Corresponding author. Tel.: +40 213167912; fax: +40 213121147.
E-mail address: mateodorescu@chimfiz.icf.ro (M. Teodorescu).

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Table 1
Refractive indices and vapour pressures of pure compounds.

Compound/temperature (K)	$n_D^{298.15K}$		P (kPa)	
	This work	Lit.	This work	Lit.
1,2-Dichloroethane/				
298.15	1.4421	1.4421[a,b]		
333.15			45.76	45.60[c], 45.40[d]
343.15			64.62	64.82[c], 64.62[d]
353.15			90.35	90.59[c], 89.87[d]
Nitromethane/				
298.15	1.3793	1.37941[b]		
333.15			24.02	23.74[d], 23.43[e]
343.15			35.02	35.04[d], 34.46[e]
353.15			50.42	50.42[d], 49.43[e]
Nitroethane/				
298.15	1.3897	1.38960[f]		
333.15			15.07	14.69[e]
343.15			22.45	22.13[e]
353.15			32.78	32.47[e]

[a] [16].
[b] [17].
[c] [18].
[d] [19].
[e] [20].
[f] [21].

sieves and used without further purification. The purity of substances checked by gas chromatograph was better than the stated purity. The test of purity is provided by comparison of measured refractive indices, $n_D^{298.15K}$, and vapour pressures at three temperatures, with the literature values, as shown in Table 1.

2.2. Methods

The vapour pressure measurements of pure compounds and of the two binary mixtures were carried out by an ebulliometric method using a Swietoslawski ebulliometer modified according to Rogalski and Malanowski [22]. The apparatus, which enables sampling of both phases in equilibrium, is described in details elsewhere together with the procedure [23]. The procedure is the one usually employed [22,24,25].

The equilibrium temperatures in the ebulliometer were measured by means of mercury thermometers, previously calibrated at National Institute of Metrology, Bucharest, with an accuracy of ±0.05 K.

The vapour pressure was measured by means of a mercury manometer. Manometric readings were performed with a cathetometer to an accuracy of ±0.1 mm, and pressure reproducibility was better than 50 Pa. The accuracy of the pressure measurements is believed to be 0.1% of measured values. The composition of the phases in equilibrium was analysed by the refractometric method making use of calibration curves obtained by measurements of the refractive index of weighed samples (accuracy ±0.1 mg) at 298.15 K, $n_D^{298.15K}$, and data correlation, within experimental uncertainties, with Redlich–Kister polynomials of the

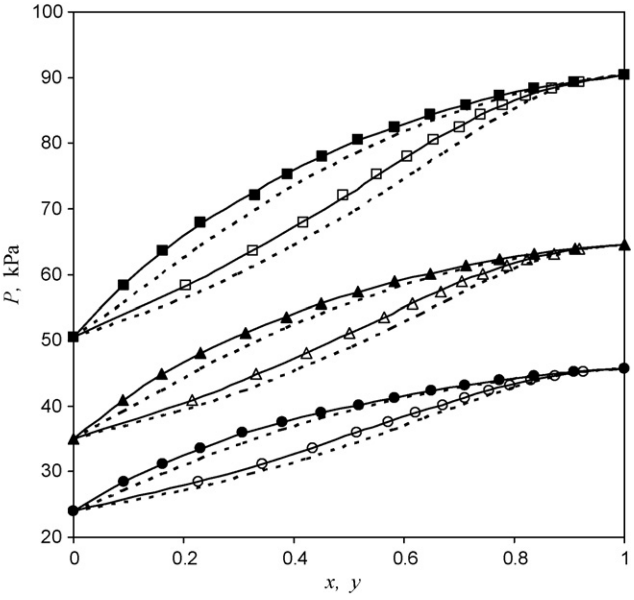

Fig. 1. Isothermal (vapour–liquid) equilibrium data for 1,2-dichloroethane + nitromethane system at 333.15 K (●, ○), 343.15 K (▲, △), and 353.15 K (■, □); solid points: liquid phase, open points: vapour phase; (—) 3rd order Redlich–Kister correlation; (–-) Modified UNIFAC (Do) prediction.

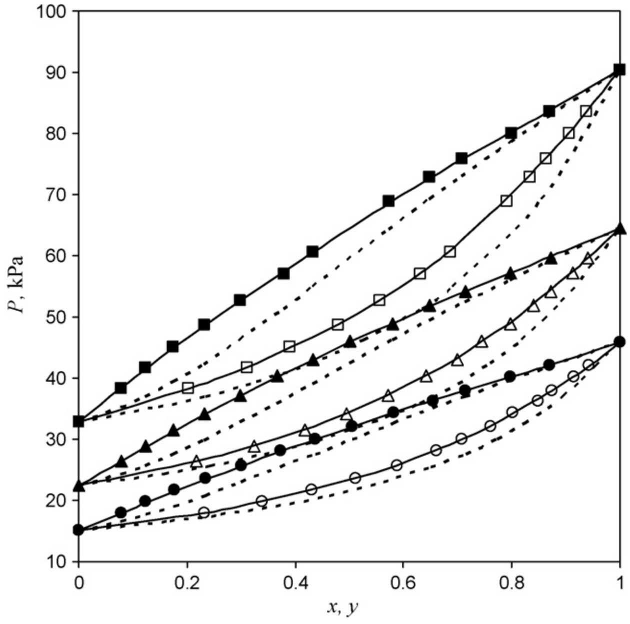

Fig. 2. Isothermal (vapour–liquid) equilibrium data for 1,2-dichloroethane +nitroethane system at 333.15 K (●, ○), 343.15 K (▲, △), and 353.15 K (■, □); solid points: liquid phase, open points: vapour phase; (—) 3rd order Redlich–Kister correlation; (–-) Modified UNIFAC (Do) prediction.