

Phase Equilibrium Data for the Binary System Dinitrogen Monoxide + Propane

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Summary. Isothermal vapor-liquid equilibrium data at 10°C for the binary system dinitrogen monoxide + propane were experimentally determined with the static analytical method. The experimental data were correlated with the UNIQUAC model and by treating the vapor phase with the *Soave-Redlich-Kwong* equation of state. Furthermore, the data were compared to predictions using the PSRK group contribution equation of state.

Keywords. Vapor-liquid equilibrium; Experimental; g^E model; Equation of state; PSRK.

Introduction

For the synthesis and design of separation processes, a reliable knowledge of the phase equilibrium behavior is needed. For the binary system dinitrogen monoxide (N₂O) + propane, no experimental vapor-liquid equilibrium (VLE) data could be found in literature. Only critical data were measured in a former work [1] for this system and also for the system N₂O + ethane. To these critical data and to VLE data for N₂O + ethane taken from literature, group interaction parameters for the PSRK (predictive *Soave-Redlich-Kwong*) group contribution equation of state (EoS) [2, 3] were fitted. Now, isothermal P - xy data were measured with the static analytic technique at 10°C in order to validate the results of this predictive method. Moreover, a correlative approach to describe the experimental data is presented herein. Therefore,

the UNIQUAC model [4] considering the real vapor phase behavior with the SRK EoS was used.

Results and Discussion

The experimental VLE data are listed in Table 1. To these data interaction parameters for the UNIQUAC model were fitted. The experimental and calculated results are shown in Fig. 1 in terms of the isothermal plots P vs. x_1y_1 , y_1 vs. x_1 , $K_i = y_i/x_i$ vs. x_1 , and $\alpha_{12} = K_1/K_2$ vs. x_1 . As can be seen in the different diagrams, regarding the vapor phase as ideal, the UNIQUAC calculation yield in an unsatisfying description of the phase equilibrium behavior (dashed line in Fig. 1), *i.e.* the description of the vapor phase compositions is wrong. When considering the real vapor phase behavior by the SRK EoS with classical *van der Waals* mixing rules where the adjustable parameter k_{ij} in the combinatorial rule is set to zero, a reliable description of the VLE is obtained (dotted line in Fig. 1). The optimized interaction parameters are given in Table 2. The pure component critical data $T_{c,i}$ and $P_{c,i}$ and the acentric factors ω_i required for the EoS and the *van der Waals* properties r_i and q_i for the UNIQUAC model were taken from the Dortmund Data Bank (DDB 2005) and are given in Table 3. For the description of the pure component vapor pressures, coefficients for the *Antoine* equation for vapor pressures

$$\log(P_i^s/\text{kPa}) = A_i - \frac{B_i}{C_i + T/\text{K}} \quad (3)$$

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Table 1. Experimental P - xy data (mole fractions) for the binary system N_2O (1) + propane (2) at 283.18 K

x_1	y_1	P/kPa
0.0000	0.0000	638.5
0.0699	0.3068	906.1
0.1550	0.4978	1208.4
0.2016	0.5649	1386.0
0.2687	0.6383	1621.0
0.3401	0.6964	1864.6
0.4751	0.7774	2312.3
0.5136	0.7972	2458.2
0.5850	0.8269	2671.2
0.5954	0.8312	2709.7
0.6890	0.8687	3003.1
0.7082	0.8767	3082.8
0.8153	0.9179	3405.0
0.8830	0.9466	3637.1
0.9502	0.9761	3864.7
0.9869	0.9934	3996.9
1.0000	1.0000	4041.3

were fitted to experimental data from numerous authors from this data compilation. The obtained parameters A_i , B_i , and C_i are also included in Table 3.

As mentioned above, group interaction parameters for the PSRK model were fitted simultaneously to critical data for the N_2O + propane and N_2O + ethane system and to VLE data for N_2O + ethane [1]. The VLE results of this predictive method are also included in Fig. 1. Figure 2 shows the predicted critical data for N_2O + propane. Again, very good agreement between experiments and calculations can be observed which is a prove for the reliability of the measured data and the predictive capability of the PSRK model. This method is able to predict the VLE behavior of systems over a large temperature range up to the supercritical region and also the critical lines of systems can be accurately described. Furthermore, it is possible to correlate critical data

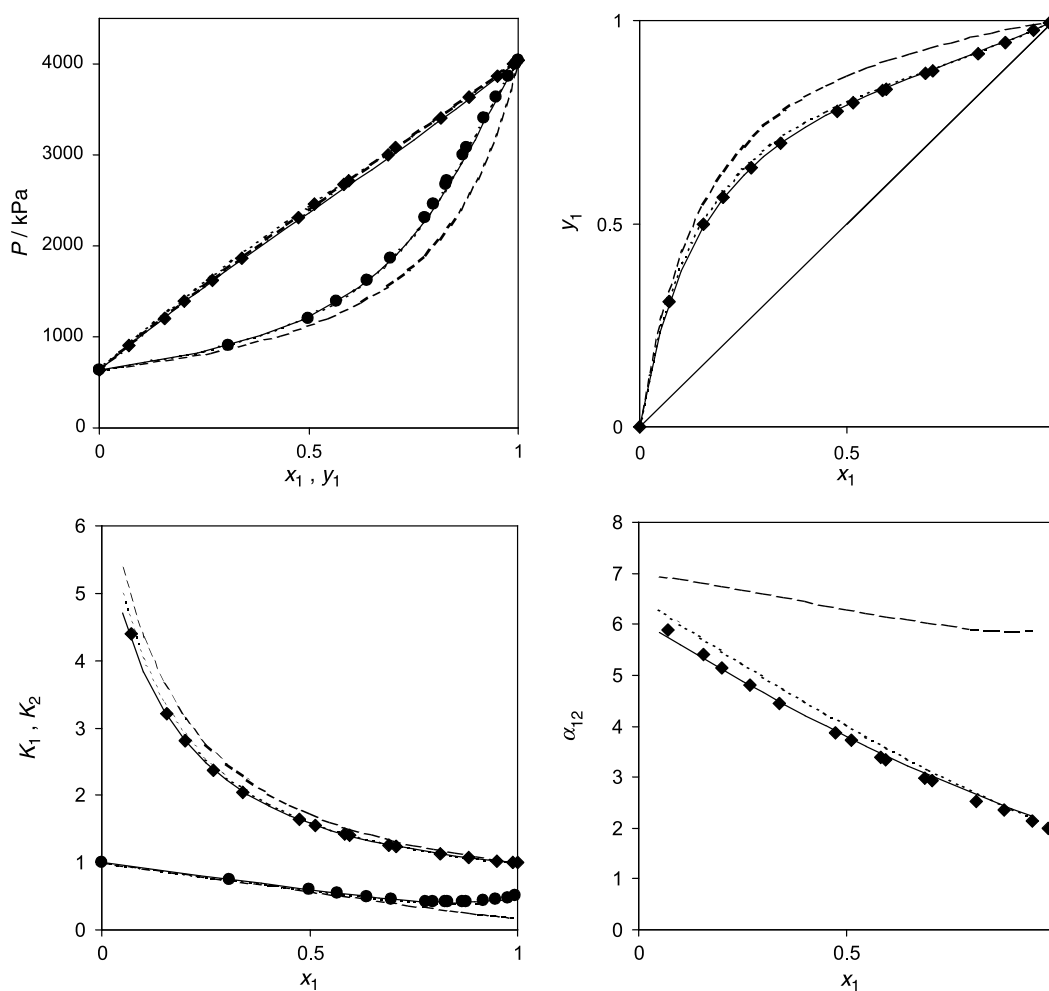
**Fig. 1.** Experimental and calculated vapor-liquid equilibrium data for the binary system N_2O (1) + propane (2) at 283.18 K: (\blacklozenge , \bullet) experimental data from this work, (---) UNIQUAC with ideal vapor phase, (\cdots) UNIQUAC + SRK EoS, (—) PSRK

Table 2. Interaction parameters for the UNIQUAC + SRK EoS (for vapor phase) model for the binary system N₂O (1) + propane (2)

Component 1	Component 2	<i>i</i>	<i>j</i>	$\Delta u_{ij}/\text{J mol}^{-1}$
N ₂ O	propane	1	2	-213.08
		2	1	2062.49
				$k_{ij}=0$

Table 3. Pure component properties: Antoine coefficients A_i , B_i , and C_i , van der Waals properties r_i and q_i , critical data $T_{c,i}$ and $P_{c,i}$, and acentric factor ω_i

	N ₂ O	Propane
A_i	6.38076	6.22361
B_i/K	738.08	942.43
C_i/K	-16.958	-7.450
r_i	0.9800	2.4766
q_i	0.888	2.236
$T_{c,i}/\text{K}$	309.60	369.95
$P_{c,i}/\text{MPa}$	7.245	4.246
ω_i	0.1733	0.1520

of binary mixtures which can be measured quite fast and to use this set of PSRK interaction parameters for the prediction of the VLE behavior (as long as the temperatures are in a similar range) as it was shown for further examples before [7]. In order to cover the whole temperature range it is useful to combine VLE and critical data in the parameter fitting procedure, as it was done for the N₂O + alkane group combination.

Conclusions

Experimental VLE data measured with the static analytic technique are presented and compared to the results of UNIQUAC correlations and predictions with the PSRK group contribution EoS. While the VLE behavior at moderate pressures can usually be described by g^E models like UNIQUAC + ideal vapor phase, for higher system pressures as for the investigated system N₂O + propane it is necessary to consider the real vapor phase behavior. This was done using the SRK EoS and the classical van der Waals mixing rule. With this model a reliable correlation of the experimental data was achieved. Using the PSRK method almost identical prediction results were obtained which prove the reliability of experiments and calculations.

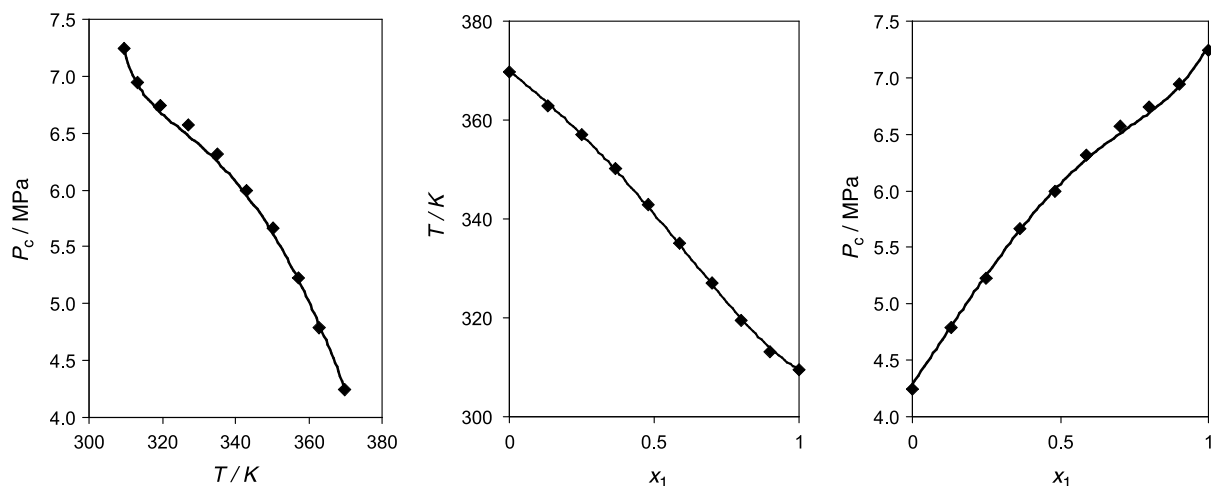
Experimental

Chemicals

The chemicals (liquefied gases) were purchased from commercial sources, and the purity was checked by gas chromatography to be >99.8 mol%. Since they were, as delivered, free from volatile components such as air, they were used without further purification.

Apparatus and Procedure

For the measurements of the complete VLE data (isothermal P - xy data) a magnetically stirred equilibrium cell made of Hastelloy C-276 was used. The cell and its applicability for the measurement of phase equilibria was first presented by Horstmann *et al.* [5] and is schematically shown in Fig. 3. This setup can be applied for the experimental determination

**Fig. 2.** Experimental and calculated critical points for the binary system N₂O (1) + propane (2): (◆) experimental data from former work [1], (—) PSRK

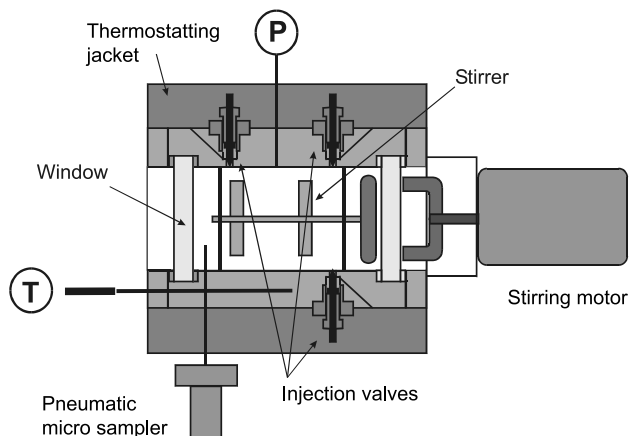


Fig. 3. Schematic diagram of the equilibrium cell with sampling device

of phase equilibrium data such as V(L)LE or gas solubility data at temperatures of about 270 to 470 K and pressured up to 10 MPa. The temperature regulation of the cell is performed with a metal jacket heated electrically or with an external thermostat enabling the temperature to be constant within ± 0.05 K. The pressure inside the cell is monitored with a calibrated pressure sensor (Model PDCR 4010, Druck, range 0–7 MPa), and the temperature is measured with a Pt100 resistance thermometer (Model 1502, Hart Scientific) inside the metal body of the cell. The estimated accuracy for the pressure measurement is $(\pm 0.0005 \times \text{Pressure [Pa]} + 100 \text{ Pa})$. After equilibration and phase settling, samples can be taken from both phases and analyzed by gas chromatography. Therefore, small amounts of the substances are directly injected

into the carrier gas stream using a pneumatically driven micro-sampler (ROLSI: rapid on-line sampler injector, *Guilbot et al.* [6]). The complete compact cell can be turned so that the tip of the sampling capillary is immersed in the desired phase. For this purpose the cell is equipped with glass or sapphire windows which are sealed with *PTFE*. Because of the very small sample size, the equilibrium inside the cell is not disturbed. To avoid condensation and adsorption of high boiling components, the micro-sampler and the lines for the gas stream of the gas chromatograph are superheated.

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