



# Vapour pressures and isobaric (vapour + liquid) equilibrium data for the binary system of (*RS*-4-vinyl-1-cyclohexene + *ZE*-3-pentenenitrile) at (50.0 and 100.0) kPa



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## ABSTRACT

In this work, great efforts have been made to achieve the large-scale industrial separation of *RS*-4-vinyl-1-cyclohexene and *ZE*-3-pentenenitrile. Initially, the vapour pressures of *ZE*-3-pentenenitrile were determined. The experimental values were correlated by an Antoine-type equation, and the predicted results of vapour pressures showed that the average relative deviation from experimental values was 0.254% for *ZE*-3-pentenenitrile. Then the isobaric (vapour + liquid) equilibria data of *RS*-4-vinyl-1-cyclohexene and *ZE*-3-pentenenitrile were determined at (50.0 and 100.0) kPa. These experimental values were found to be thermodynamically consistent, by means of the point-to-point test and the direct test methods. Two liquid phase activity coefficient models (Wilson and NRTL) were used to correlate the (vapour + liquid) equilibria data of the binary system, and the model parameters were obtained. All models represent the experimental values quite well. The activity coefficients and the reduced excess molar Gibbs energy were calculated by Margules equation, which were found to be in satisfactory agreement with the experimental values.

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## 1. Introduction

*ZE*-3-pentenenitrile (3PN) is an important intermediate in the production of commercially versatile adiponitrile (ADN), as the few examples of large-scale industrial application of alkene hydrocyanation [1,2]. *RS*-4-vinyl-1-cyclohexene (4VCH) is routinely obtained as the major non-hydrocyanation side product [3,4]. It is highly necessary to find a good solution for the separation of this two bulk products. Distillation exhibits its superiority compared with other separation methods, especially in achieving economies of large-scale industrial operation. The prerequisite for the design of distillation processes is a reliable knowledge of the vapour pressures of the pure compounds and (vapour + liquid) equilibrium (VLE). Although the vapour pressures of *RS*-4-vinyl-1-cyclohexene were reported in the literature [5], the vapour pressures of *ZE*-3-pentenenitrile and isobaric VLE for the binary system of (*RS*-4-vinyl-1-cyclohexene + *ZE*-3-pentenenitrile) have not been reported currently.

In this work, the vapour pressures of the pure components and isobaric VLE of the binary system at (50.0 and 100.0) kPa were

measured and correlated using the adequate modelling equations. The relevant parameters were given. This could provide the basic data of the system for distillation process.

## 2. Experimental

### 2.1. Chemicals

The chemicals *RS*-4-vinyl-1-cyclohexene and *ZE*-3-pentenenitrile were all obtained commercially and then purified by rectification with about 100 theoretical plates in our laboratory before use. The specifications of the used chemicals are listed in table 1.

### 2.2. Apparatus and procedures

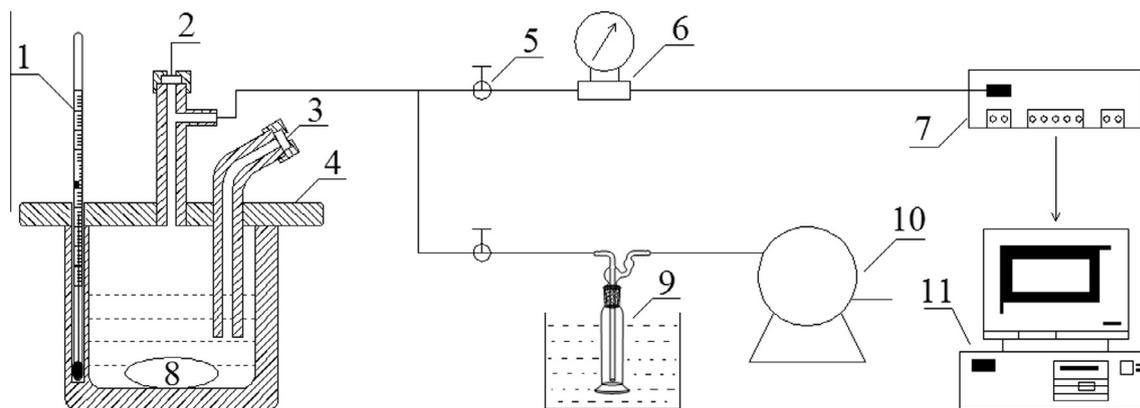
The apparatus is designed for the measurements of the vapour pressure of the pure compounds and the isobaric VLE of the binary system. A schematic representation is shown in figure 1. This device is equipped with a stainless steel (vapour + liquid) balancing still, a pressure transmitter, a data acquisition system, an operation desk and a 2XZ-4 vacuum pump. The still possesses a series of characteristics and advantages over others. For example, the still only requires a small quantity of sample about 30 mL, with short

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**TABLE 1**  
Provenance and mass fraction purity of chemical samples.

Component	Source	Initial mass fraction purity	Purification method	Final mass fraction purity	Analysis method
RS-4-vinyl-1-cyclohexene (100-40-3)	Chongqing Unisplendour Chemical Co., Ltd.	0.959	Rectification	0.996	GC
ZE-3-pentenenitrile (4635-87-4)	Chongqing Unisplendour Chemical Co., Ltd.	0.940	Rectification	0.977	GC



**FIGURE 1.** VLE experimental device. 1, mercury-in-glass thermometer; 2, septum in the condensate outlet; 3, septum in the liquid outlet; 4, stainless steel (vapour + liquid) balancing still; 5, regulating valve; 6, pressure transmitter; 7, data acquisition system; 8, magnetic stirrer; 9, cold trap; 10, vacuum pump; 11, operation desk.

thermodynamic equilibrium time. Temperature control for the still includes two parts: one is constant temperature magnetic stirrer (Shanghai Sile Instrument Co., Ltd, China) for the coarse adjustment of temperature, the other part is resistance wire winding around the still for fine adjustment of temperature, which can ensure a homogeneous steady heating. The inlet and outlet are sealed by septa (Shanghai Techcomp Instrument Ltd, China) having the ability to take a sample or inject a sample with syringes continuously, which is similar to the injection port of gas chromatography.

In the measurements of vapour pressures, the pure component was injected into the vessel from the inlet with a syringe and evacuated to a proper degree of pressure. Subsequently, the sample was heated and stirred well with a magnetic stirrer to prevent superheating. After thermodynamic equilibrium was reached, the temperature of the pure component and the pressure of the apparatus were measured. Mercury-in-glass thermometer, with a standard uncertainty of 0.01 K, was applied to record the temperatures. The pressure was acquired by the pressure transmitter (Beijing collhigh sensing technology co., Ltd, China), with a relative standard uncertainty of 0.01, and data acquisition system in the operation desk.

In the measurements of isobaric VLE, a mixing sample of a desired proportion was prepared and injected into the vessel from the inlet with a syringe. The following experiments were performed under a dried inert air atmosphere at a constant pressure of (50 or 100) kPa. Under constant pressure, equilibrium conditions were assumed when constant temperature was observed and kept for 15 min or longer. About 1.5 mL of the vapour and liquid samples were taken from the liquid outlet and the condensate outlet with syringes at almost the same time for GC analysis, and the temperature was recorded simultaneously.

### 2.3. Analytical methods

The equilibrium compositions of the liquid and vapour phases were determined by using a GC7900 gas chromatograph with a

flame ionisation detector (FID), a TM-1701 capillary column (column length 30 m, diameter 0.32 mm), and a D-7900P chromatographic workstation (Shanghai Techcomp Instrument Ltd, China). An external standard *n*-propanol was used for peak-area quantification. The carrier gas was high purity nitrogen at a constant flow rate of 50 mL · min<sup>-1</sup>. The hydrogen was produced by a SPGH-300 hydrogen generator with a flow rate of 20 mL · min<sup>-1</sup>, and the flow rate of air is 150 mL · min<sup>-1</sup>. Column, injector and detector temperatures were (90, 200 and 200) °C, respectively. At least three measurements were performed for each composition, and the average values are given in following tables.

## 3. Results and discussion

### 3.1. Pure component vapour pressures

The pure component vapour pressures of ZE-3-pentenenitrile were determined, and the pertinent results are shown in table 2. The measured vapour pressures are correlated using the Antoine equation:

$$\ln(P_i^s/\text{kPa}) = A - B/\{(T/\text{K}) + C\} \quad (1)$$

where  $P_i^s$ ,  $T$  are the vapour pressure and absolute temperature of the pure components, respectively. The parameters  $A$ ,  $B$  and  $C$  are fitted by a non-linear optimisation method to minimise the average relative deviation in pressure (ARDP) and are reported in table 3. The calculated values are in good agreement to the experimental values, given a correlation of the experimental vapour pressures with an ARDP = 0.254% for ZE-3-pentenenitrile.

### 3.2. Binary systems

Experimental VLE values of the binary system {RS-4-vinyl-1-cyclohexene (1) + ZE-3-pentenenitrile (2)} were measured at (50.0 and 100.0) kPa. The results are shown in table 4, where  $x_i$  and  $y_i$  are the mole fractions of component  $i$  in the liquid phase and vapour phase, and  $\gamma_i$  is the activity coefficient of component

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