Experimental Determination of the Critical Locus of the Acetone + Chloroform Binary System

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Abstract—In this paper, vapour-liquid critical locus for the binary system acetone + chloroform was determined experimentally over the whole range of composition. The critical property measurements were carried out using a dynamic-synthetic apparatus, employed in the dynamic mode. The critical points are visually determined by observing the critical opalescence and the simultaneous disappearance and reappearance of the meniscus in the middle of a high-pressure view cell which withstands operations up to 673K and 20MPa. The experimental critical points measured in this work were compared to those available in literature.

Keywords—Experimental measurement, critical point, critical locus, negative azeotrope.

I. INTRODUCTION

THE acetone + chloroform system is well-known to exhibit a negative azeotrope. It is used as an important solvent medium in many chemical processes [1-2] and attracted a rather large number of experimental and theoretical investigations. Many spectra analyses [2]-[4] highlighted that the negative deviations from Raoult's low and the negative heat of mixing [5]-[13] could be attributed to the formation of a complex between acetone and chloroform. As an example, Jalilian and Alibabei [4] studied the structure of the acetone + chloroform azeotropic system using infrared spectroscopy and H NMR technique and concluded that there were two different hydrogen bonds between these unlike molecules: one between hydrogen on chloroform and oxygen of acetone and another one between hydrogen of methyl group of acetone and chloride on chloroform.

Moreover, many works on this system focused on vapour-liquid equilibrium measurements at low temperatures and pressures [6], [11], [14]-[26]. All of these studies confirmed the existence of the pressure minimum azeotrope. As a general case, in binary mixtures exhibiting a negative azeotrope, the azeotropic composition becomes richer in the less volatile compound when the temperature is increased. In the case where the azeotrope becomes critical, the critical locus often exhibits a maximum in critical temperature. For the studied system, Röch and Schröder [14] worked at temperatures

ranging from 15 to 55°C and found that the composition of the azeotrope shifts towards higher chloroform content as the temperature is increased. Campbell and Musbally [27] came to the same conclusion from their study of this mixture at 100, 150, 160, 170 and 180 °C. Kamath et al. [28] used a force field technique to predict the pressure and composition of the azeotrope at 35, 76.85, 126.85 and 176.85°C and also came to the same conclusion. Kuenen and Robson [29], who measured critical points for the acetone + chloroform mixture and the vaporisation curves of each compound, reported that the minimum pressure azeotrope disappeared before becoming critical. Although many vapour-liquid equilibrium measurements were performed on the acetone + chloroform binary system, only few took place at high temperature and pressure [27], [29].

In this paper, the critical properties (critical temperatures and critical pressures) of the acetone + chloroform system were measured along the whole composition range with the aim of understanding the phase behaviour of this system at high temperatures and pressures. We indeed wanted to check whether the azeotrope became critical. An apparatus capable of determining critical properties of pure components and mixtures was used in this work. It can be operated using both the dynamic and the static methods. The measurements on the acetone + chloroform system were carried out using the dynamic method. The critical properties can be determined by visually observing the critical opalescence phenomenon in the view cell. The experimental results in this work were compared to those available in the literature.

II. EXPERIMENTAL PROCEDURE

A. Materials

TABLE I
PURITY AND SUPPLIER OF COMPOUNDS USED IN THIS STUDY

Compound	Purity	Supplier
acetone	$\geq 99.9\%$	Sigma-Aldrich
chloroform	$\geq 99.8\%$	Sigma-Aldrich

All compounds used were purchased from commercial sources. Their purity and their suppliers are listed in Table 1. Acetone was used without any further purification. Chloroform was used after its small quantity of ethanol (about 0.5-0.8%) – added for stabilization – was removed with 5A molecular sieves. Such molecular sieves were activated by heating at 300°C for 3 hours and then by cooling in a vacuum desiccator. A large quantity of these molecular sieves was

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added in chloroform, left overnight and finally filtered. The resulting chloroform was degassed using a vacuum pump and stored in a round bottom flask wrapped in aluminium paper in order to avoid a reaction with oxygen when exposed to the air and light. Fresh treatments of chloroform were realized every 3 days. A gas chromatographic analysis indicated that chloroform had a purity of at least 99.9 %.
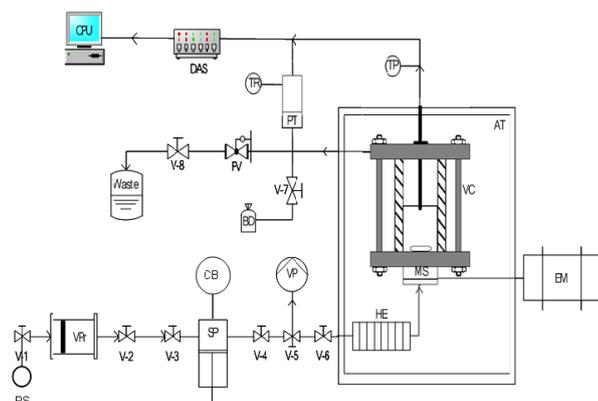
B. Apparatus and Procedure

Fig. 1 Schematic diagram of the apparatus. PS: Pressurized source, VPr: Volumetric press, SP: syringe pump; CB: cryostat bath; VP: vacuum pump; HE: heat exchanger; EM: electric motor; MS: magnetic stirrer; VC: view cell; AT: air thermostat bath (oven); TP: platinum resistance temperature probe; PT: pressure transducer; TR: temperature regulator; BD: bursting disc; FV: flow regulation valve; DAS: data acquisition system; CPU: central processor unit; V: valve

A schematic diagram of the apparatus used in this work is presented in Fig. 1. It has been developed by the ARMINES Company hosted by the Ecole Nationale Supérieure des Mines de Paris for the measurement of the critical properties of pure substances and multi-component mixtures with known overall composition. This apparatus can work using two different modes: dynamic or static. Due to short residence time, the dynamic method enables to determine the critical point of substances likely to thermally decompose but needs a large amount of matter. On the other hand, the static method requires small amounts of substances but is limited due to possible thermal decomposition of substances. The temperature and pressure upper limits of application are 673K and 20MPa for the dynamic method and 493K and 20MPa for the static method. The temperatures upper limits are different owing to the use of a magnetic stirrer, which withstands conditions up to 493K, in the static mode. In this work, the measurements were carried out using the dynamic method in which circulation of fluid ensures an efficient stirring. The state of the art of critical point measurements can be found in the book edited by Weir and de Loos [30] (in particular chapter 16 by Teja and Mendez-Santiago – entitled Critical Parameters – gives all the necessary details). It is thus not necessary to recall it in this paper. A critical point can be determined by visually observing the critical opalescence and

the simultaneous disappearance and reappearance of the meniscus i.e. of the liquid-vapour interface from the middle of the view cell. Fig. 2 illustrates the transition of a fluid from subcritical state to the critical state on temperature increase. The apparatus was calibrated and validated and the critical point measurements for pure compounds and binary mixtures were performed [31]-[32]. The experimental setup used in this work is the same as that clearly described in our previous study [31]. Chloroform and mixtures containing high composition of chloroform develop a yellowish colour on prolonged heating explaining why in this study, only the dynamic method was employed. The used flowrate was increased with concentration of chloroform and varied between 3 to 5ml/min. The uncertainties obtained in the critical temperature and critical pressure for pure compounds and mixtures at different mole fractions were $\leq 0.11°C$ and $\leq 0.009MPa$, respectively. Likewise, a mean value uncertainty in the mole fraction, $u(x_i) = \pm0.00004$ was obtained.

Fig. 2 The transition of a fluid from the subcritical state to the critical state on the temperature increase. From left to right: classical liquid–vapour mixture (the two phases are perfectly separated by a thin meniscus); cloudy subcritical state (the meniscus is not thin any more, it is coloured in orange which characterizes the critical opalescence); a thick and cloudy subcritical state (the meniscus becomes thicker and thicker); disappearance of the liquid–vapour interface (the meniscus occupies the entire view cell which is orange: we are at the critical point)

III. RESULTS AND DISCUSSION

In this work, the vapour-liquid critical points for the acetone (1) + chloroform (2) binary system were determined experimentally throughout the entire range of composition. The measurements were carried out using the dynamic-synthetic apparatus which was employed in the dynamic method. The experimental critical values with different mole fractions and their uncertainties for the system investigated were presented in Table 2. The comparison between the experimental critical data in this work and the literature data was shown graphically in the Fig. 3a, 3b and 3c which correspond to pressure – temperature (P-T), temperature – composition (T-x_1) and pressure – composition (P-x_1) diagrams, respectively. As can be seen in Fig. 3a, the acetone (1) + chloroform (2) binary mixture, displays a monotonous continuous vapour-liquid critical locus which connects the critical points of the pure components. Such an uninterrupted critical locus indicates that this binary mixture belongs to type I fluid phase behaviour according to the classification of Van

Konynenburg and Scott [33]. Furthermore, the critical locus intersects the vaporisation curve of chloroform thus highlighting the existence of a critical azeotrope. The existence of a critical azeotrope found in this work opposes to the very old investigation by Kuenen and Robson [29] who reported that the azeotrope did not exist up to the critical point. In comparison to the work by Kuenen and Robson, the critical temperatures in this work are lower while the critical pressures are higher. These differences may come from an insufficiently accurate experimental setup used in Kuenen and Robson's experiment in which – as reported by the authors – a chemical reaction takes place between chloroform and mercury at high temperature.

available literature data.

TABLE II
EXPERIMENTAL CRITICAL TEMPERATURES (T_C) AND PRESSURES (P_C) FOR THE SYSTEM ACETONE (1) + CHLOROFORM (2) AT DIFFERENT MOLE FRACTIONS (X_1) WITH THEIRE STANDARD UNCERTAINTIES

X_1	T_C/ K	u (T_C)/ K	P_C/ MPa	u (P_C)/ MPa
1.0000	508.05	0.06	4.693	0.003
0.9215	510.68	0.03	4.760	0.003
0.8486	513.52	0.03	4.825	0.001
0.7852	515.78	0.07	4.854	0.005
0.7001	518.63	0.07	4.926	0.005
0.6195	521.04	0.07	4.999	0.004
0.6009	521.86	0.07	5.007	0.008
0.5455	523.15	0.04	5.035	0.009
0.5053	524.86	0.04	5.084	0.002
0.4834	525.56	0.04	5.082	0.003
0.4174	527.52	0.05	5.154	0.003
0.3895	527.64	0.10	5.148	0.003
0.3082	529.98	0.11	5.213	0.005
0.3050	530.31	0.04	5.205	0.003
0.2015	531.80	0.05	5.262	0.001
0.2006	532.19	0.03	5.251	0.002
0.1597	532.96	0.04	5.295	0.004
0.1086	533.90	0.06	5.332	0.006
0.0998	534.54	0.03	5.357	0.007
0.0608	535.26	0.03	5.398	0.007
0.0000	536.12	0.05	5.451	0.005

The Fig. 3b illustrates a very strong correlation between the critical temperatures in this work and those collected by Campbell and Musbally [27]. The azeotropic compositions at high temperature [27] were also plotted in this Figure. Unfortunately, only few experimental values are available and the highest temperature investigated is at 180 °C. Therefore, the existence or inexistence of the critical azeotrope in the acetone + chloroform system can not be confirmed by these
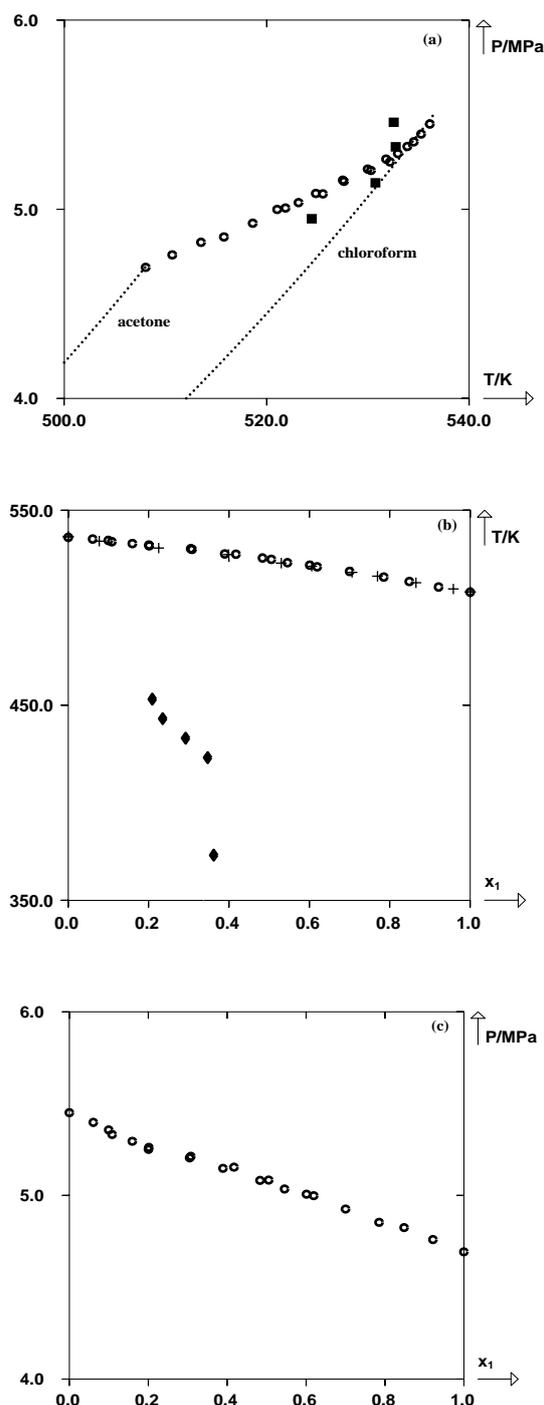
Fig. 3 Experimental critical points and critical locus in the (a): (P-T), (b): (T-x_1) and (c): (P-x_1) projections for the binary system acetone (1) + chloroform (2). Critical values (○): this work, (■): Kuenen and Robson, (+): Campbell and Musbally and azeotrope compositions (♦): Campbell and Musbally.

IV. CONCLUSION

The critical points of the acetone + chloroform binary system were determined experimentally throughout the entire range of composition. The measurements were carried out using a synthetic-dynamic apparatus, in the dynamic method. The experimental critical values obtained in this work were compared to those available in the literature. Large differences were found when compared to the very old literature data collected by Kuenen and Robson. However a strong agreement was obtained with the data collected by Campell and Musbally. The acetone + chloroform system is characterized by the presence of a negative azeotrope at low temperatures and pressures. In this work, it was shown for the first time that the negative azeotrope became critical owing to an intersection between the critical locus and the chloroform's vaporisation curve.

NOTATION

P_C : critical pressure

T_C : critical temperature

x_i: mole fraction of component i

$u(P_C)$: pressure uncertainty

$u(T_C)$: temperature uncertainty

$u(x_i)$: composition uncertainty

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