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Please cite this article as: Gonçalo V.S.M.Carrera, Zoran P.Visak, Rafal M.Lukasik, Manuel Nunes da Ponte, CO2x202f;+x202f;Methanolx202f;+x202f;Glycerol: Multiphase behaviour, The Journal of Supercritical Fluids https://doi.org/10.1016/j.supflu.2017.12.032

CO₂ + Methanol + Glycerol: Multiphase behaviour

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Graphical Abstract

Graphical representation of the multiphase behaviour of the system CO_2 + Methanol + Glycerol with stepwise addition of CO_2 to a 4 cm³ liquid mixture of methanol and glycerol at molar ratio of 30 and 313 K.
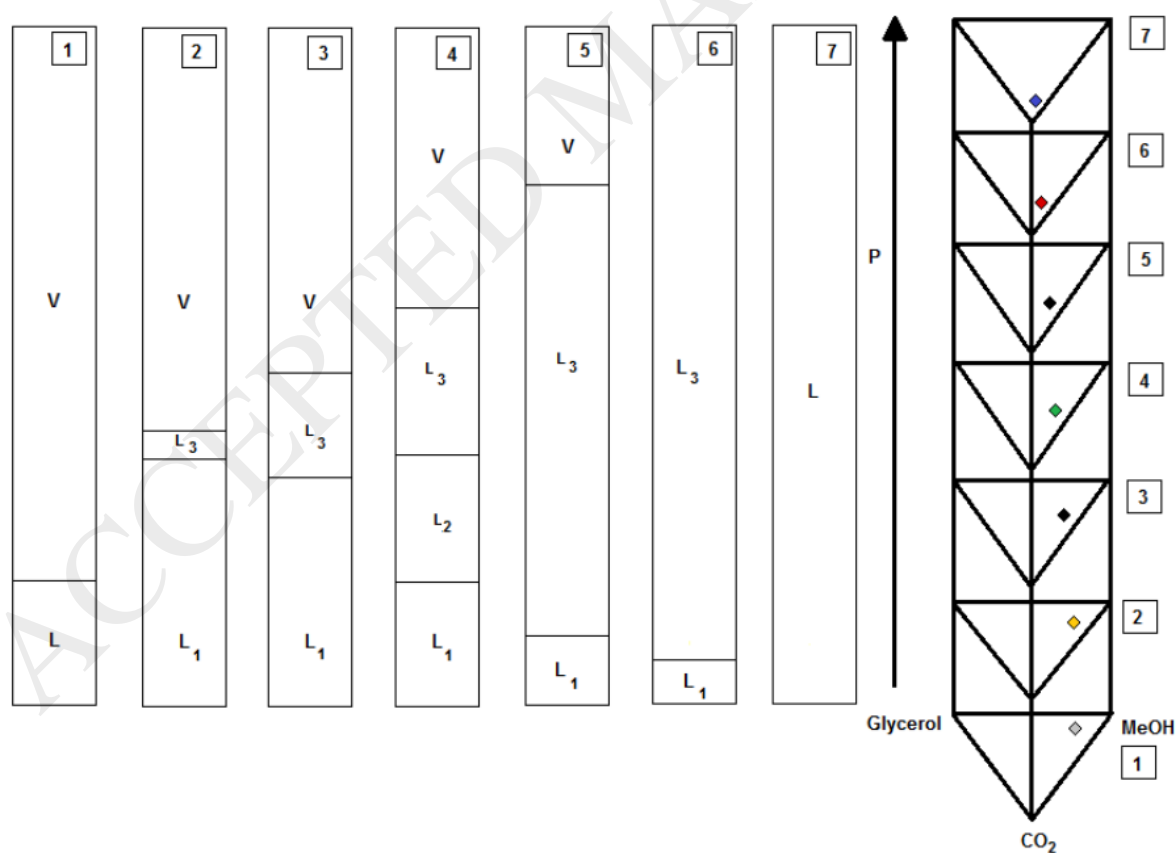
Highlights

- The phase behaviour of the system CO_2 + methanol + glycerol was checked.
- Multiphase phenomena were detected with the decrease in the MeOH/glycerol ratio.
- VLLLE equilibrium was spotted.

Abstract

The phase behaviour of the system CO_2 + methanol + glycerol has been studied at low concentrations of this tri-alcohol. The synthetic method was implemented in a visual sapphire cell. New phase diagrams were obtained at temperatures of 313.15 and 333.15 K. Different methanol/glycerol molar ratios of 113, 50 and 30 were considered and its influence on phase behaviour accounted for. Pressures were varied from 6.03 to 11.44 MPa. A specific experiment is reported, starting from an initial volume of 4 mL of liquid mixture methanol + glycerol (methanol/glycerol molar ratio 30), where, with a stepwise addition of CO_2, diverse fluid phase phenomena were detected, such as VLE, Critical Point, VLLE, VLLLE, LLE and LE.

1. Introduction

The reaction of CO_2 and glycerol to obtain glycerol carbonate has been intensively studied, nevertheless with scarce results, due to several adverse factors, including a very low mutual solubility of the reactants and a small equilibrium constant of the reaction. [1-2] Attempts to carry out the reaction with both reactants dissolved in methanol have uncovered the potential impact of the complex phase behaviour of the methanol + CO_2 + glycerol system on the reaction yields. [3]

Pinto et al. [4] studied the fluid phase equilibria of those mixtures. Complex fluid phase phenomena, such as three-phase vapour-liquid-liquid (VLLE) equilibrium and liquid-liquid (LLE) immiscibility at higher pressures, were reported. Diverse studies were carried out in this context for mixtures of CO_2 + water + a low chain alcohol, ethane or ethane + water + 1-propanol, and CHF_3 + water + 1-propanol [5-7]. In those studies multiphase behaviour has been detected, including four phase equilibria (VLLLE). In a case study relevant for the present work [6], the domains of existence, in the pressure-temperature space, of these equilibria were carefully measured and a complex picture emerged.

The results of Pinto et al. referred to above could be qualitatively interpreted on the basis of this picture, if we hypothesise that the replacement of water by glycerol does not bring any essential modifications to the phase behaviour. In fact, glycerol is a highly polar molecule, it is completely miscible with methanol, such as water, and the solubilities of carbon dioxide in glycerol and in water are of the same order of magnitude. [2]

Results of phase behaviour of CO_2+methanol+glycerol from this laboratory have already been published, for a methanol to glycerol molar ratio of 113, at 423 K. [3] More detailed measurements are however necessary, especially for carbon dioxide-rich compositions, close to the critical line of the binary system methanol + carbon dioxide. The work hereby presented extends the experimental conditions to dilute solutions of glycerol in methanol, permitting an understanding of the phase behaviour of this system at low glycerol/methanol molar ratios. The present work extends the temperatures of the system to 313 and 333 K, and considers the methanol/glycerol molar ratios of 113, 50 and 30.

2. Experimental Section

2.1 Materials

Methanol (> 99.9%, GC) and glycerol (> 99.5%, GC) were purchased from Sigma-Aldrich, while CO_2 N48 (99.9998% purity) was supplied by Air Liquide.

2.2 Methods

2.2.1 Experimental

A previously described apparatus [8, 9] was used to examine fluid phase equilibria. It consists of a sapphire tube-shaped cell that permits visualisation of fluid phase phenomena along an experiment. The sapphire cell has an internal volume of 34.6 cm^3 and it is kept inside an air bath with controlled temperature. The synthetic method [10] was used in a typical experiment. A measured mass of liquid mixture methanol + glycerol (molar ratio tested as variable) is introduced in the cell and CO_2 is added stepwise. The diverse fluid phase phenomena are detected visually along the experiment, until a single

phase is observed. The quantity of CO_2 introduced in the cell, at each specific state, consists of three parts: I) the initial CO_2 admitted to the cell that occupies the vapour phase; II) the initial part dissolved in the liquid phase; III) the amounts of CO_2 incrementally added from a manually-driven screw-injector, at 273 K, connected to the bottom of the cell. The volume per turn of this screw injector was previously calibrated.

The quantities of CO_2 added in parts I) and III) were calculated with densities given by an equation of state. [11] The CO_2 + methanol phase diagram at the working temperature of the cell, in combination with the known quantity of the liquid mixture introduced initially in the cell, was used in order to estimate part II).

The estimated uncertainties are 0.01 mole fraction for composition ± 0.01 MPa for the pressure and ± 0.01 K for the temperature. A regular mixture was obtained during a proper mixing by a vertically aligned magnetic bar rotating disorderly with consequent mitigation of vortexes. The mixing was promoted by stepwise increments of CO_2 entering from the bottom of the cell. The time of equilibration was about 30 min for each specific measurement.

3. Results and Discussion

Results were obtained at the temperatures 313 K and 333 K, pressures from 6.03 to 11.44 MPa), and methanol to glycerol molar ratios of 113, 50 and 30. The volume of liquid (methanol+glycerol) initially fed to the sapphire cell was also varied, in different experiments, in order to explore different regions of total carbon dioxide compositions. The phase equilibrium results are given in Tables 1, 2 and 3. The global molar fraction of each component, CO_2, methanol and glycerol, pressure and type of phase behaviour is shown in each table. Table 1 characterizes straightforward phase behaviour with two different type phase transitions detected - bubble point and dew point.

Differently, Table 2, at lower methanol to glycerol molar ratio (50), shows more complex phase behaviour, with transitions between vapour-liquid (VLE) and vapour-liquid-liquid equilibrium (VLLE) spotted besides the conventional cloud points.

Cloud Points and VLLE Phenomena molar ratio MeOH/Glycerol 50 - 313.15 K					
n	x_{CO2}	x_{MeOH}	$x_{Glycerol}$	p MPa	
1	0.77121	0.22430	0.00449	8.09	Bubble Point
2	0.83168	0.16502	0.00330	8.07	VLE/VLLE transition
3	0.83606	0.16072	0.00321	8.09	VLLE
4	0.84064	0.15623	0.00312	8.16	Bubble Point
5	0.86617	0.13121	0.00262	8.18	Bubble Point
6	0.90238	0.09571	0.00191	8.29	Bubble Point
7	0.92416	0.07435	0.00149	8.32	Bubble point
8	0.93775	0.06103	0.00122	8.27	Bubble point
9	0.94518	0.05375	0.00107	8.23	Dew Point

Table 2: Composition vs pressure and type of detected fluid phase equilibrium, for CO_2 + Methanol + Glycerol, molar ratio Methanol/Glycerol = 50, 313.15 K.

Table 3 gives the results of a single experiment with multiphase equilibrium phenomena detected, following a step-by-step addition of CO_2 to a 4 cm^3 mixture of methanol and glycerol, and consequent increase of pressure. The diverse equilibria include VLE, critical point (transition VLE to VLLE), VLLE, four fluid phase VLLLE, LLE and LE. The volume of the high pressure cell is 34.6 mL. and, measuring the dimension of each phase (Table 3), an estimated volume can be obtained.

The phase behaviour indicated in Table 3 resembles in multiple aspects the phase behaviour of the system CO_2 + isopropanol + water described by Maurer and collaborators. [6] In fact our system, CO_2 + methanol + glycerol, presents, similarly, a low chain alcohol (methanol vs isopropanol) and a highly polar molecule (glycerol vs water). Both systems present CO_2 as fluid phase modeller. [12] Initially, in our experiment, at moderate pressures of CO_2, VLE equilibrium is observable (Table 3, n = 1, Figure 1 - 1) and, with the progressive increment of CO_2, the liquid phase expands. Vapour-liquid equilibrium is conserved until a pressure of 8.16 MPa (Table 3 - n = 2, Figure 1 - 2, Figure 2 - A) is attained, and a critical point emerges. A pale orange colour in the liquid phase indicates a phase split, with another incipient liquid phase L3 forming between the bottom liquid phase L1 and the vapour phase V, starting of VLLE equilibrium.

In fact, Maurer and collaborators [6] reported similar split at 313.15 K with a liquid CO_2-rich phase emerging between the bottom isopropanol-rich phase and the vapour phase. With further increment of CO_2 in our system the initially incipient CO_2-rich L_3 liquid phase expands and the bottom liquid phase contracts (Table 3 - n = 3, Figure 1 - 3). With additional increments of CO_2, at pressures near the critical point of the binary system CO_2 + methanol [13], the VLLE equilibrium originates four-phase VLLLE equilibrium (Table 3 - n = 4, Figures 1 - 4, Figure 2 - B). Considering the Gibbs phase rule, [14] for a specific temperature, the four phases only exist for a single pressure in a ternary system. A four phase VLLLE equilibrium was similarly detected for the system CO_2 + isopropanol + water [6] as a result of the convergence of two three-phase VLLE regions represented in a composition vs pressure triangular prism phase diagram (for a specific temperature of 313.15 K). Afterwards, with increment of CO_2 in the system, the VLLLE equilibrium dissipates.
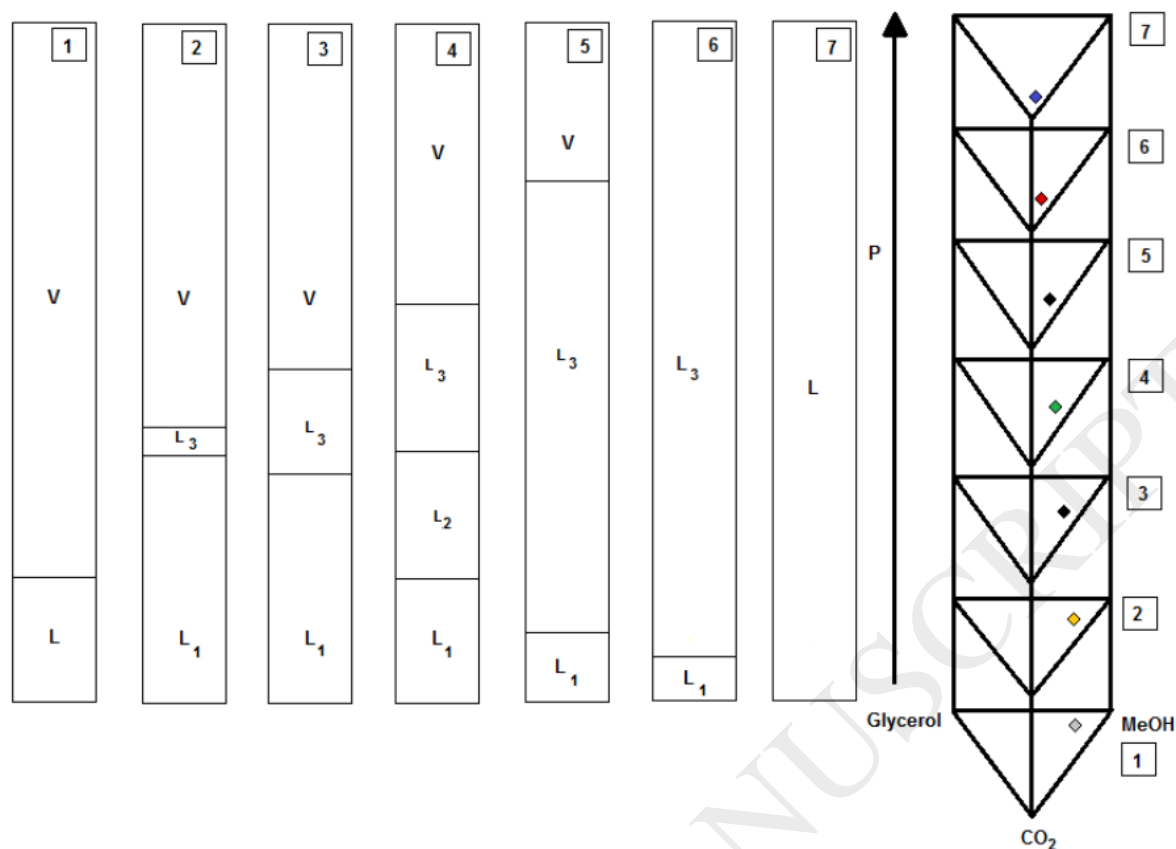
Figure 1: Schematic representation of the phase equilibrium experiment, system CO_2 + methanol + glycerol at 313.15 K, initial 4mL. liquid mixture methanol + glycerol (molar ratio methanol/glycerol = 30) and stepwise addition of CO_2 (1-7). Parallelism in a composition vs pressure triangular phase diagram.

Again, VLLE forms with a progressive decrease of the volume of the bottom liquid phase and simultaneous expansion of the CO_2-rich intermediate-liquid phase (Table 3 - n = 5, Figure 1 - 5). With further increase of the quantity of CO_2 in the system, at even higher pressures, the VLLE equilibrium is converted into LLE equilibrium, with the vapour phase being replaced by a CO_2-rich liquid phase above a progressive smaller alcohol-rich liquid phase (Table 3 – n = 6, Figure 1 - 6), similarly to Wendland et al system. [6] This transition occurs at 8.23 MPa. All these steps (2 - 6) were detected in a narrow interval of pressures (8.16-8.23 MPa). Finally in the last step (Table 3 - n = 8, Figure 1 - 7), and after increments in the quantity of CO_2, the

bottom liquid phase is diminished progressively until being replaced completely by the up CO_2-rich phase and a single liquid phase is obtained at 9.46 MPa. It is important to highlight that, from the LLE equilibrium to single liquid phase (LE), small increments on the quantity of CO_2 lead to considerable increase of pressure, due to lower compressibility of liquids. Finally, and similarly to the ternary CO_2 + isopropanol + water system, [6] there is an area of complete miscibility in the triangular prism phase diagram, near the CO_2 + methanol binary diagram, at pressures above its critical point.
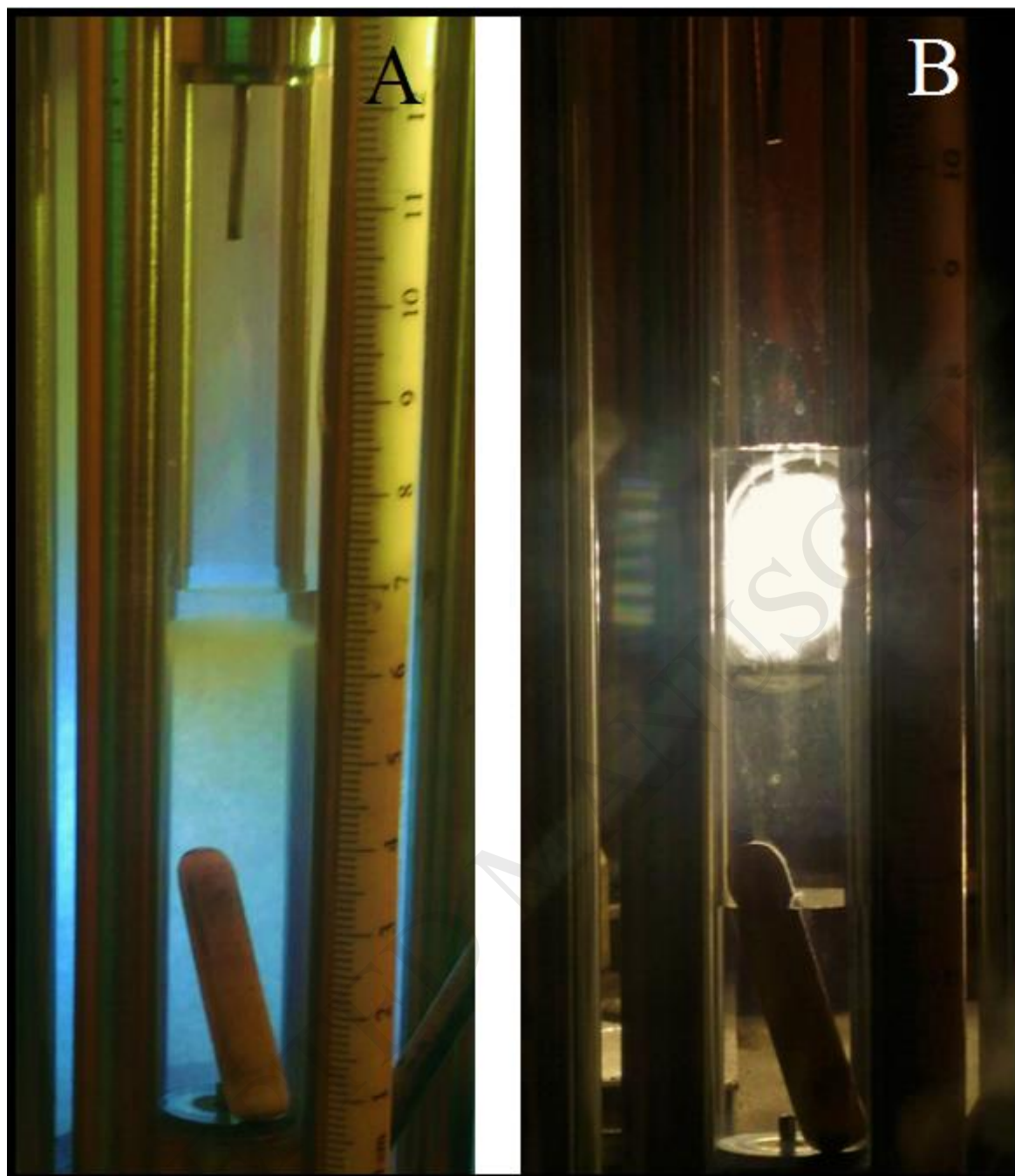
Figure 2: Experiment - molar ratio Methanol/Glycerol 30 – 313.15 K - initial volume of liquid mixture 4 mL. A - Transition VLE/VLLE, 8.16 MPa. B - VLLLE, 8.19 MPa.

One variable tested systematically in this work was the methanol/glycerol molar ratio, specifically the proportions 113 and 50 (Figure 3). These phase diagrams were compared with previously reported data (Pinto et al [4]) for methanol/glycerol molar ratio 30. The CO_2 + methanol binary system was

additionally considered. [13] The complete series of diagrams were obtained at 313.15 K (Figure 3) at low concentration of glycerol. However, small absolute increments on the quantities of glycerol in the system lead, progressively to an increase of complexity of the system. Similarly to the system CO_2 + methanol, with the highest dilution of glycerol (ratio methanol/glycerol 113) only transitions from VLE to single phases were observed. Differently, at methanol/glycerol molar ratio 50, VLLE equilibrium was also detected, with a new L_3 liquid phase (presumably CO_2 rich [6]) forming between the bottom liquid L_1 and vapour V. This VLLE equilibrium was detected in a narrow range of pressures and x_{CO2}. At higher concentration of glycerol (molar ratio methanol/glycerol 30 [4]) the region of VLLE is broader (Figure 3), and transition to LLE equilibrium is additionally spotted. In fact, as mentioned earlier, we could detect VLLLE equilibrium at this methanol to glycerol molar ratio. Probably the highly specific conditions necessary to detect this phenomenon were not fulfilled in Pinto et al work. [4] This increment of complexity on fluid phase behaviour with the decrease in low chain alcohol/polar molecule molar ratio resembles, in part, the system carbon dioxide + isopropanol + water. [6] As schematically indicated in that work, at 313.15 K, and at pressures near the critical point of the binary system CO_2 + isopropanol, even with low increments of the proportion of water (polar) in the system, the phase behaviour is more complex (VLLE or even VLLLE). Similarly, in our system, with the increment of the concentration of glycerol (polar - expressed in methanol/glycerol molar ratio), the phase behaviour becomes more complex at pressures near the critical point of the system CO_2 + methanol (Tables 2 and 3, Figure 3).

The *a priori* qualitative/quantitative prediction of the phase behaviour is an important aspect when considering multicomponent systems. This increment of complexity, usually, is not compatible with resources and time available to set a complete experiment. The insight of binary systems usually is a good starting point in order to consider an increment of the number of components. [17] The binary interaction parameters and single component constants are combined in an algorithm in order to obtain the singularities of the phase diagram. It's important to highlight that most of these models

consider just binary interactions between like and unlike components, which is a valid simplification for diverse systems. However in other cases, there is an extended network of interactions, as in hydrogen bond-forming alcohol systems. [18-20] Our system, methanol + carbon dioxide + glycerol, is an example of a ternary system with complex phase behaviour, as shown in the results of Table 3 and Figures 1 and 2. In those experiments, a mixture of alcohols, methanol and glycerol (30:1 molar), forming an extensive cooperative hydrogen bond-based network, [18] is introduced into the high pressure cell at 313.15K. During the step-by-step increment in the quantity of carbon dioxide in the system, a significant decrease in the hydrogen bond-based interactions should happen, [21] resulting in the formation of additional phases.

According to the well-established classification of binary mixture phase behaviour, [22, 23] CO_2 + methanol presents type I phase behaviour, [24] and CO_2 + glycerol is a type III system, with both components presenting low mutual solubility. [25] The systematic classification of ternaries is a difficult task, nevertheless some steps forward have been made in that direction. [26, 27] Considering these diverse aspects, and in order to understand the increment of complexity of the system methanol + CO_2 + glycerol with the decrease in the methanol/glycerol molar ratio (Figure 3), it is important to highlight the stepwise movement from a CO_2 + methanol equilibria towards a CO_2 + glycerol like behaviour.

Table 4 represents the phase behaviour of the system under consideration at a higher temperature of 333 K (methanol to glycerol molar ratio 113). Similarly to 313 K (identical molar fraction methanol to glycerol), bubble and dew point transitions were detected. Differently a critical point was spotted. VLLE was not detected.

4. Conclusion

This work comprises a phase equilibrium study of the system CO_2 + methanol + glycerol. The temperature, pressure, methanol/glycerol molar ratio and overall composition were varied. It was possible to observe an incremental complexity on the phase behaviour with the decrease of the methanol/glycerol molar ratio at a constant temperature of 313.15 K. At a low methanol/glycerol molar ratio of 30, diverse fluid phase phenomena, such as VLE, Critical Point, VLLE, VLLLE, LLE and LE, were detected.

This work can be interpreted in the context of multiphase behaviour of CO_2 + low chain alcohol + water described by other authors.

Acknowledgments

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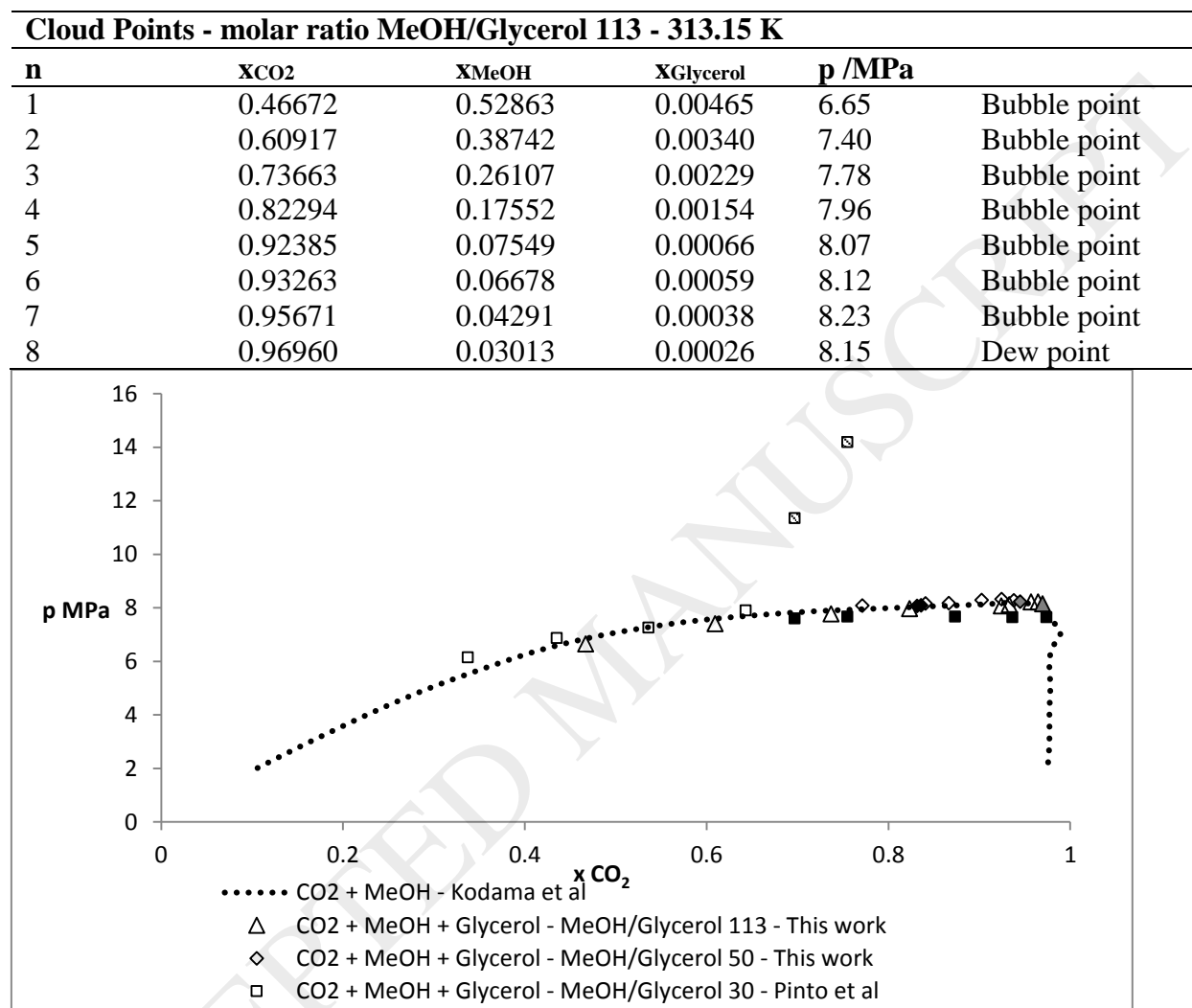
Cloud Points - molar ratio MeOH/Glycerol 113 - 313.15 K

n	x_{CO2}	x_{MeOH}	$x_{Glycerol}$	p /MPa	
1	0.46672	0.52863	0.00465	6.65	Bubble point
2	0.60917	0.38742	0.00340	7.40	Bubble point
3	0.73663	0.26107	0.00229	7.78	Bubble point
4	0.82294	0.17552	0.00154	7.96	Bubble point
5	0.92385	0.07549	0.00066	8.07	Bubble point
6	0.93263	0.06678	0.00059	8.12	Bubble point
7	0.95671	0.04291	0.00038	8.23	Bubble point
8	0.96960	0.03013	0.00026	8.15	Dew point

Figure 3: Effect of the presence of glycerol in the system CO_2 + methanol and influence of the methanol/glycerol molar ratio in the phase behaviour at 313.15 K. White symbols - bubble points. Grey symbols – dew points. Black symbols - VLLE. Diagonal lines - LLE.

Table 1: System CO_2 + MeOH + Glycerol, molar ratio MeOH/Glycerol = 113. 313.15 K. Composition versus pressure and corresponding cloud points.

Table 3: Experiment - System CO_2 + MeOH + Glycerol, molar ratio MeOH/Glycerol = 30, 313.15 K - initial volume of liquid mixture MeOH + Glycerol (4 cm^3). The composition, pressure, corresponding fluid phase phenomena and extension of each phase in a 34.6 cm^3 volume/12.5 cm length in a cylindrical sapphire cell, are the considered factors.

Experiment - molar ratio MeOH/Glycerol 30 – 313.15 K - initial volume liquid mixture 4 mL				
n	x_{CO2}	x_{MeOH}	$x_{Glycerol}$	p MPa	Phenomena
1	0.58929	0.39746	0.01325	6.03	VLE
2	0.82616	0.16823	0.00561	8.16	
					Critical Point - Transition VLE/VLLE - 34.6 ml/0 - 12.5 cm |0 - 6.0 cm L1|6.0 - 6.6 cm L2|6.6 - 12.5 cm V|
3	0.82856	0.16591	0.00553	8.16	VLLE |0 - 3.8 cm L1|3.8 - 7.0 cm L2|7.0-12.5 cm V|
4	0.83141	0.16315	0.00544	8.19	VLLLE |0 - 2.5 cm L1|2.5 - 5.0 cm L2|5.0 - 7.4 cm L3|7.4 - 12.5 cm V|
5	0.85374	0.14154	0.00472	8.20	VLLE |0 - 1.0 cm L1|1.0 - 11.8 cm L2|11.8 - 12.5 cm V|
6	0.85586	0.13949	0.00465	8.23	
					Transition VLLE/LLE |0 - 0.8 cm L1|0.8 - 12.5 cm L2|
7	0.85913	0.13633	0.00454	8.40	LLE |0 - 0.3 cm L1|0.3 - 12.5 cm L2|
8	0.86847	0.12728	0.00424	9.46	Transition LLE/LE

Table 4: Composition, pressure and corresponding cloud points, molar ratio methanol to glycerol 113 and temperature 333.15 K.

Cloud Points - molar ratio MeOH/Glycerol 113 - 333.15 K				
n	x_{CO2}	x_{MeOH}	$x_{Glycerol}$	p /MPa	Phenomena

1	0.63212	0.36465	0.00323	11.04	Bubble point
2	0.72494	0.27265	0.00241	11.27	Bubble point
3	0.79359	0.2046	0.00181	11.44	Critical point
4	0.83459	0.16396	0.00145	11.44	Dew Point
5	0.86564	0.13318	0.00118	11.42	Dew Point
6	0.9242	0.07514	0.00066	11.34	Dew Point
7	0.94092	0.05856	0.00052	11.15	Dew Point
8	0.9703	0.02944	0.00026	10.73	Dew Point
9	0.97286	0.0269	0.00024	10.62	Dew Point