

CO₂ + Methanol + Glycerol: Determination of the Compositions in VLLLE from a Synthetic Method-Based Experiment/Theoretical Procedure

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ABSTRACT

The experimental synthetic-based method is a straightforward procedure to obtain a complete resolution of the phase behaviour of VLE of binary mixtures; however, it has limited applicability for multicomponent mixtures/multiphase phenomena. The analytical method is an alternative that offers a reasonable solution for complex configurations, however, the investment of time and resources is high. A straightforward alternative presented in this work consists on the application of the synthetic method allied to a theoretical procedure in order to obtain the composition of the existent phases in equilibrium in complex system's configurations. The case study is a CO₂ + methanol + glycerol mixture that at concrete conditions of global composition, pressure and temperature leads to VLLLE. The composition of each phase in equilibrium was determined using the Peng-Robinson EOS with Mathias-Klotz-Prausnitz mixing rule allied to a combination algorithm to find and check the suitable arrangement of derived compositions that respect the thermodynamic criteria of equilibria, balance of masses and order of densities. A single solution was obtained and discussed along the manuscript.

INTRODUCTION

The system CO₂ + methanol + glycerol have been studied in diverse contexts. Carbon dioxide and glycerol are massively produced from combustion and biodiesel preparation, respectively. The possibility to combine these chemicals and obtain valuable products is a challenge. One application consists on the preparation of 1,2-glycerol carbonate from glycerol and CO₂. [1-5] The reduced reactivity of carbon dioxide, the low mutual solubility of this chemical and glycerol and consequent requirement of noxious solvents, such as methanol, and other non-sustainable system's conditions, for significant yields, precluded, so far, the implementation of this concept in real life applications. A different concept consists on the application of high pressure technology on the refination of crude glycerol

from biodiesel production, [6] however the costs associated to the use of high pressure equipment and the relative low commercial value of glycerol hampered its implementation.

Nevertheless, even considering the lack of applications in daily life routine, the study of the system $\text{CO}_2 + \text{methanol} + \text{glycerol}$ deserves a close check in the context of multiphase behaviour detected in Pinto et al studies, [6] and verified in our recent work. [7] We reported multiphase phenomena in one concrete experiment based on the stepwise increment of CO_2 into one 30:1 molar ratio methanol:glycerol mixture, where its included VLE, Critical Point, VLLE, VLLLE, LLE and LE, detected in a sapphire window based-cell [8,9] with the implementation of the synthetic method. [10] In fact, and in order to understand the phase behaviour of our system is important to highlight the work of Maurer and collaborators that, studied the multiphase behaviour of the systems $\text{CO}_2 + \text{water} + \text{low chain alcohols}$ (propanol or isopropanol). [11, 12] VLE, transitions to single phase (liquid or vapour), critical points, VLLE, LLE and VLLLE have been spotted. Considering these incidences we can establish a parallelism, considering that both polar, glycerol and water have a similar role on phase behaviour of the considered systems. The same approach for methanol and propanol's isomers.

The determination of the compositions in complex systems, where multiphase phenomena is detected, is a challenge. The analytical method, based on chromatographic evaluation consumes time and resources for adequate measures and straightforward/alternative methodologies are necessary. The experimental synthetic method is one of these approaches; however, the information in the context of multicomponent mixtures/multiphase behaviour is limited. The alternative presented on this proceeding consists on the use of the experimental synthetic-method allied to a theoretical procedure for a consistent estimation of the compositions in equilibrium. The case study is a VLLLE of the system $\text{CO}_2 + \text{methanol} + \text{glycerol}$. Other theoretical procedures determined with relative success the correct number of phases/types/associated compositions by typical minimization of Gibbs free energy of the system. [13-15] Our methodology is a new approach that combines experimental/theoretical procedures for a straightforward solution.

MATERIALS AND METHODS

The global composition of the VLLLE system, the case study of this work was obtained with the experimental synthetic method, described in our previous study. [7]

The total number of moles of CO_2 (n_{CO_2}), methanol (n_{MeOH}) and glycerol (n_{Gly}) existent in VLLLE, determined experimentally, have been considered to obtain 63000 combinations of sub-compositions. The n_{CO_2} (1), n_{MeOH} (2) and n_{Gly} (3) in this equilibrium, determined experimentally by the synthetic method, are 0.525335634, 0.093046313 and 0.003101544, respectively. An elaboration of 100 subgroups of n_{CO_2} was carried out: 25 evenly spread

subgroups from 0 to 0.003101544, similarly, 30 subgroups from 0.003101544 to 0.093046313, and finally 45 subgroups (0.093046313-0.525335634). A similar procedure was followed for n_{MeOH} (30 subgroups): 15 for the interval 0-0.003101544 and 15 from 0.003101544 to 0.093046313 moles. Finally, n_{Gly} was evenly spread in 21 subgroups, from 0 to 0.003101544 moles. All the possibilities of combinations between sub-compositions of CO_2 , methanol and glycerol account the number of 63000. This procedure assures an almost complete representation of compositions along a triangular composition phase diagram. The Peng-Robinson equation of state (Eq. 1) in order to the molar volume (V_m - Eq. 2) with Mathias-Klotz-Prausnitz mixing rule (Eqs. 4, 5, 6, 7, 8) was tested to validate the upcoming described method. A temperature of 313.15 K, pressure 8.19 MPa (conditions of VLLLE), the binary interaction parameters, [1] critical properties and acentric factors, considering the three components (Table 1) have been inserted into eq. 2 and a volume of cell was determined - 34.2 cm^3 , which is similar to the experimental volume - 34.6 cm^3 . The V_m (and respective volume V) of all the 63000 compositions have been determined with Eq. 2 (in Excell). The Delta (Eq. 3) applied to all the combinations, indicates negative values in each case. This implies that only one real solution is possible for V_m (Eq. 2). Additionally, the length of each phase of VLLLE in the cylindrical cell was measured during the experiment, which prompted us to estimate, roughly, the volume of each phase. A selection of 3070 compositions, based on estimations of the volumes of the phases in VLLLE, was carried out (range of volumes from 6 to 7.1 cm^3 and 14.3-15 cm^3). The fugacities have been determined with the program Mathematica, [16] based on Eqs. 9-11 and using n_{CO_2} , n_{MeOH} , n_{Gly} and the respective volume of each selected composition. An algorithm was written and executed, considering that chemical potential, and therefore fugacity, have uniform value in the entire system. [17] The most appropriate combination of four compositions that respect highest coherence of balance of components, order of densities, more resemblant fugacities, highest similarity of summed volume (considering the selected four phases) and the estimated total volume, was found.

Peng-Robinson equation of state

$$(1) \quad P = \frac{RT}{V_m - b} - \frac{a(T)}{V_m^2 - 2bV_m - b^2}$$

Molar Volume

$$(2) \quad V_m = -\frac{p}{3o} -$$

$$\frac{1}{3o} \sqrt[3]{\frac{1}{2} [2p^3 - 9opq + 27o^2r + \sqrt{(2p^3 - 9opq + 27o^2r)^2 - 4(p^2 - 3oq)^3}]} -$$

$$\frac{1}{3o} \sqrt[3]{\frac{1}{2} [2p^3 - 9opq + 27o^2r - \sqrt{(2p^3 - 9opq + 27o^2r)^2 - 4(p^2 - 3oq)^3}]}$$

$$o = P; p = bP - RT; q = 3b^2P + 2bRT - a; r = b^3P + RTb^2 - ab$$

Delta

$$(3) \quad \Delta = 18opqr - 4p^3r + p^2q^2 - 4oq^3 - 27o^2r^2$$

$$(4) \quad a_i(T) = 0.45724 \frac{R^2 T_c^2}{P_c} [1 + (0.37464 + 1.54226w - 0.266992w^2) \times (1 - \sqrt{T_r})^2]$$

$$(5) b_i = 0.0778 \frac{RT_c}{P_c}$$

Mathias-Klotz-Prausnitz mixing rule

$$(6) a = \sum_{i=1}^N \sum_{j=1}^N x_i x_j \sqrt{a_i a_j} (1 - k_{ij}) + \sum_{i=1}^N x_i \left[\sum_{j=1}^N x_j (\sqrt{a_i a_j} \lambda_{ij})^{1/3} \right]^3$$

$$(7) b_{ij} = \frac{b_i + b_j}{2} (1 - l_{ij})$$

$$(8) b = \sum_{i=1}^N \sum_{j=1}^N x_i x_j b_{ij}$$

Residual Helmholtz Free Energy

$$(9) \frac{(A-A^{IG})}{RT} = -n_T \ln(1 - b\rho) - \frac{an_T^2}{\sqrt{8bRTn_T}} \left[(\ln(1 + (1 + \sqrt{2})b\rho) - \ln(1 + (1 - \sqrt{2})b\rho)) \right]$$

ρ = density, n_T = total number of moles.

Logarithm of fugacity coefficient

$$(10) \ln \varphi_i = \left(\frac{\partial}{\partial n_i} \frac{(A-A^{IG})}{RT} \right)_{T,V,n_j} - \ln Z$$

Z = compressibility factor

Fugacity

$$(11) f_i = x_i \varphi_i P$$

Thermodynamic conditions for multiple phases in equilibrium

$$(12) T^\alpha = T^\beta = \dots = T^\omega; P^\alpha = P^\beta = \dots = P^\omega; f_1^\alpha = f_1^\beta = \dots = f_1^\omega; f_2^\alpha = f_2^\beta = \dots = f_2^\omega \dots f_n^\alpha = f_n^\beta = \dots = f_n^\omega$$

Table 1: Binary interaction parameters, critical properties and acentric factors, considering: 1 - CO₂, 2 - methanol and 3 - glycerol.

k11	k12	k13	λ11	λ12	λ13	111	112	113
0	0.074598	0.007005	0	-0.02462	-0.00992	0	-0.07644	-0.037019
k21	k22	k23	λ21	λ22	λ23	121	122	123
k12	0	-0.026996	-λ12	0	0.025116	112	0	0.067209
k31	k32	k33	λ31	λ32	λ33	131	132	133
k13	k23	0	-λ13	-λ23	0	113	123	0
Tc1	Pc1	w1	Tc2	Pc2	w2	Tc3	Pc3	w3
304.1	7.38	0.225	512.6	8.09	0.556	726	6.68	0.513

RESULTS

Table 2 consists on the estimated compositions in glycerol of the four phases in equilibrium of VLLLE, criteria of stability $g(y)$ as well as the determined fugacities of each component and respective ARD's:

Table 2: Glycerol composition, fugacities of the three components in equilibrium, respective ARD - average relative deviation and criteria of stability $g(y)$.

Phase	$x_{Gly} \times 10^{-3}$	$f_{Gly} \times 10^{-6}$	ARD f_{Gly} (%)	f_{CO_2}	ARD f_{CO_2} (%)	$f_{MeOH} \times 10^{-2}$	ARD f_{MeOH} (%)	$g(y)$
V	2.5	4.8	0.50	5.05	0.31	3.5	2.49	0.000584
L3	4.3	5.1	5.46	5.03	0.13	3.6	0.53	3.05×10^{-5}
L2	6.2	4.8	0.07	5.03	0.27	3.6	1.58	9.34×10^{-5}
L1	9.5	4.6	5.03	5.04	0.08	3.6	0.38	8.77×10^{-7}

The results indicate that the top less dense phase presents the highest value in the molar fraction of CO_2 , lowest value in methanol and glycerol. The opposite profile is observed for the bottom more dense phase. The intermediate phases present a gradation of the composition profiles comprehended in the extreme phases. This is a logical result that, allied to the high resemblance of fugacities of each component in all the phases, is a step further in the confidence on the estimation method. Glycerol, a high polar tri-alcohol presents a significant higher value of molar fraction in the bottom denser phase than in the other phases (lowest molar fraction in CO_2 and highest in methanol) – Table 2 and Figure 1. A gradation of the composition of glycerol among the other phases is obtained, with the extreme upper vapor phase presenting the lowest molar fraction in glycerol, the less-dense/polar medium – Table 2 and Figure 1. The absolute molar fraction in glycerol is very low in all the phases; this is also a logical result because the volume of each phase is considerably high (above 6 cm^3 for each liquid phase and above 14 cm^3 for the vapour phase), and the initial quantity of glycerol introduced in the cell is very low. The method used is valid to estimate the composition of multiple phases in equilibrium with the *a priori* knowledge of the global composition considering the results obtained and the justification of the determination steps.

The four-phases respect the thermodynamic criteria of equilibria, however and in order to have a measure of stability of VLLLE is important to highlight the formula/criteria of stability (the Gibbs tangent plane criterion) of each phase's composition respective to the global feed applied by Michelsen et al in his developed algorithm [13] to an equation of state:

$$(13) \quad g(y) = \sum_i y_i (\ln(y_i) + \ln \phi_i - (\ln(z_i) + \ln \phi(z)_i)) \geq 0$$

Where y_i is the composition of the compound i in a specific phase in equilibrium. The value of z_i is the respective global feed. ϕ represents the fugacity coefficient. The values of g are positive in all the four phases (Table 2) which corresponds to simultaneous stability of the four phases in equilibrium.

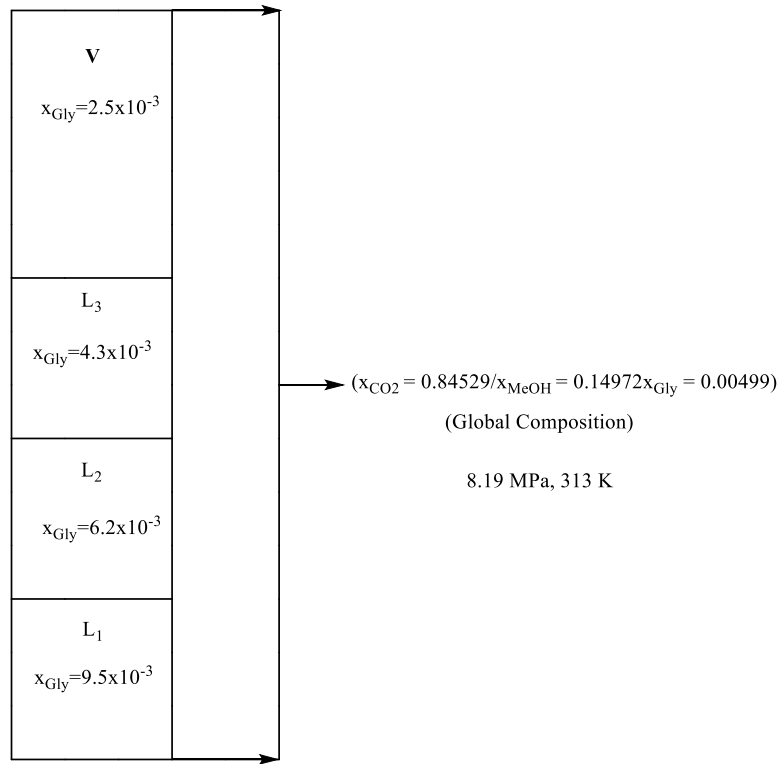


Figure 1: Schematic representation of the glycerol composition in the VLLLE corresponding to concrete values of global composition, pressure and temperature.

CONCLUSION

A new theoretical-based procedure was developed. The method complements the experimental synthetic method in finding the correct compositions of multi-component/multiphase systems. The case study tested in this work respects the thermodynamic criteria of equilibria, stability of the phases, balance of masses, order of the densities of the phases in equilibria and total volume of the high pressure cell. This work is a step forward on the search for effective systems of determination of compositions in complex/multiphase systems.

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