Fluid phase equilibria of the reacting mixture in the dimethyl carbonate synthesis from supercritical CO_2

S. Camy [a], J.-S. Pic [b], E. Badens [b], J.-S. Condoret [a,*]

[a] *Laboratoire de Génie Chimique, UMR CNRS 5503, ENSIACET, 118 Route de Narbonne, 31077 Toulouse, Cedex 4, France*
[b] *Laboratoire d'Etudes et d'Applications de Procédés Séparatifs, Université d'Aix-Marseille III, Case 512, Avenue Escadrille Normandie Niemen, 13397 Marseille, Cedex 20, France*

Abstract

In order to investigate the dimethyl carbonate synthesis from methanol and supercritical CO_2, the thermodynamic behaviour of the reacting mixture, i.e. the quaternary methanol–CO_2–DMC–water mixture, has to be known. The SRK equation of state with MHV2 mixing rules has been chosen to predict fluid phase equilibria in the reactor. The first part of this work is dedicated to the determination of binary interaction parameters, needed in the use of this model. These parameters are deduced from the fitting of experimental data concerning binary or ternary sub-systems existing in the quaternary mixture. Literature data was used for most of the binary sub-systems, but for the DMC–CO_2 and DMC–water mixtures, specific experiments were carried out. The agreement between experimental and predicted fluid phase equilibria was found to be satisfactory. With a view to studying of the operating conditions for the reaction, the thermodynamic model was used to predict fluid phase equilibria in the reactor, by considering several hypothetical feed ratios and conversions. This work shows that CO_2 has to be used in large excess in order to be sure of running the reaction in a homogeneous fluid medium.

1. Introduction

The dimethyl carbonate molecule (DMC), in addition to its application as a reacting agent for polycarbonates synthesis and as a methylation or a carbonation agent [1], is also today regarded as a promising oxigenative agent for fuel [2]. Because of all these emerging applications, the industrial production of DMC should now benefit from a real boost. However, present industrial processes exhibit important safety or environmental limitations, phosgene or carbon monoxide being used in the most common processes. As a consequence, for a few years, investigations for new ways to synthesize DMC have been in progress. Among

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* Corresponding author
E-mail address: jeanstephane.condoret@ensiacet.fr (J.-S. Condoret).

Nomenclature

a	mixture parameter in the SRK equation of state (m^6 bar^{-1} mol^{-1})
A_{ij}	binary interaction parameter in UNIQUAC model (cal mol^{-1})
b	mixture parameter in the SRK equation of state (m^3 mol^{-1})
g	excess Gibbs energy (J mol^{-1})
N	number of components
p	UNIQUAC parameter
P	pressure (Pa)
q	van der Waals area in UNIQUAC formulation
q_1, q_2	constants in the MHV2 mixing rules
r	van der Waals volume in UNIQUAC formulation
R	universal gas constant (J mol^{-1} K^{-1} except in Eq. (11) where it is cal mol^{-1} K^{-1})
T	temperature (K)
$u_{ji}-u_{ii}$	binary interaction parameter in UNIQUAC model (cal mol^{-1})
v	molar volume (m^3 mol^{-1})
x	liquid mole fraction
y	vapour mole fraction

Subscripts

c	critical
0	zero pressure
i,j	component

Superscripts

E	excess

Greek letters

ϕ	UNIQUAC parameter
θ	UNIQUAC parameter
τ	UNIQUAC parameter
ω	acentric factor

these new processes, the use of carbon dioxide for direct carbonation of methanol seems particularly interesting, especially from an environmental point of view. Nevertheless, the poor reactivity of the CO_2 molecule is here the major difficulty, the main problem being to find an efficient catalyst, as well as optimal operating conditions. First investigations [3–7], using gaseous CO_2 and liquid methanol have clearly indicated biphasic mass transfer limitations and their possible alleviation when operating under pressure. From this observation has emerged the idea of using carbon dioxide in its supercritical state ($SCCO_2$), where it would behave both as a solvent and a reactant in a monophasic mixture. Such a concept is perfectly in line with the present trends of supercritical science, where the value of chemical reactions in these media is regularly encouraged [8,9].

Studies upon the direct carbonation of methanol with CO_2 have shown a severe limitation because the water produced by the reaction causes the decomposition of the organotin catalyst as well as the reverse hydrolysis of DMC [4–6]. As a consequence, first thoughts were that the continuous elimination of water from the reactor, as the reaction proceeds, could avoid the detrimental effect of water. In order to continuously eliminate water from the reactor, one of the simplest solutions consists in operating the reaction in a continuous or a semi-continuous process config-

uration and then investigating the possibility of a post-reaction fractionation, in order to separate water and DMC from the reacting mixture and to reintroduce CO_2 and methanol into the reactor.

First of all, the study of such an integrated reaction-separation scheme obviously necessitates the knowledge of the thermodynamic behavior of the reacting mixture, i.e. the quaternary mixture methanol–CO_2–water–DMC. This knowledge is essential to characterize the possible phases coexisting in the reactor and to define the optimum reaction conditions, as well as to design an efficient post-reaction fractionation.

However, measurements of multi-component phase equilibria are very time and money consuming, and thermodynamic models have proved to be of great help in predicting thermodynamic behavior of mixtures. However, these models need specific mixture parameters, obtained by fitting a limited set of experimental equilibrium data. The data used to determine mixture parameters can be equilibrium data from the binary or ternary subsystems constituting the quaternary methanol–CO_2–water–DMC mixture. In our case, some binary or ternary data can be found in the existing literature. For DMC–water and DMC–CO_2 mixtures, no experimental work is available.

As a preliminary step in the novel DMC synthesis process study, this work presents the determination of the binary interaction parameters necessary for the use of a suitable thermodynamic model representing phase equilibria existing in the quaternary mixture. This determination is achieved from experiments concerning the DMC–water and DMC–CO_2 mixtures, and from experimental data from literature concerning the other binary parameters. As a first application, this work will predict the phase behaviour of the reacting mixture, considering several possible operating conditions in the reactor.

2. Materials and methods

2.1. High-pressure experimental apparatus

The high-pressure apparatus was used in order to study the phase equilibrium for the DMC–CO_2

mixture. This set-up is based on the so called synthetic method [10]. In this simple experimental method, the phase transitions, resulting from pressure variations, are studied by direct visualisation and no sampling is necessary. The main elements of the set-up are represented schematically in Fig. 1 and details about these elements are described elsewhere by Crampon et al. [11], who validated the experimental apparatus and the procedure by measuring solubility of fatty acid esters in supercritical CO_2. It mainly consists in a high-pressure view cell (Top Industries S.A., France), a magnetic stirrer, a thermostatic bath, a camera, a TV monitor and temperature and pressure gauges. The temperature is measured within an accuracy of ± 0.2 K and the pressure measurement is accurate to ± 0.02 MPa. The uncertainty in mole fraction values mainly concerns the CO_2 and has been estimated to be better than 0.003 [11].

The set-up employed here allows experimental data to be obtained in a over a wide range of pressure and temperature, except for low pressure zones.

2.2. Low-pressure apparatus

The low-pressure set-up, a vapour-liquid equilibrium apparatus (FISCHER, Type 0601), shown in Fig. 2, was used to study water–DMC liquid–vapour equilibrium. Equilibrium is reached here in a glass cell with circulation of both the vapour and the liquid phases. The mixture to be studied is
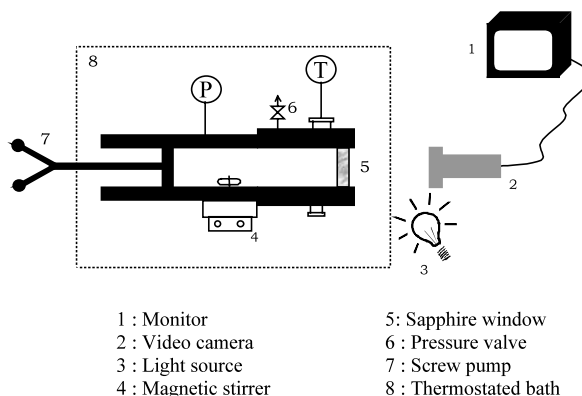

1 : Monitor	5: Sapphire window
2 : Video camera	6: Pressure valve
3 : Light source	7: Screw pump
4 : Magnetic stirrer	8: Thermostated bath

Fig. 1. High-pressure experimental set-up.

1 : Heating device   5 : Magnetic stirrer
2 : Liquid introduction   6 : Temperature control
3 : Liquid sampling   7 : Pressure regulation
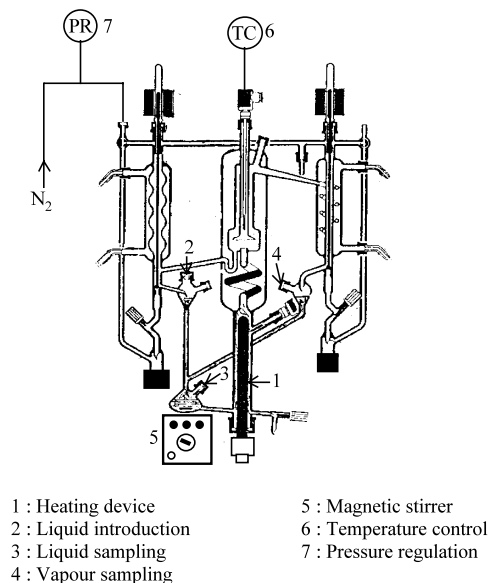4 : Vapour sampling

Fig. 2. Low pressure experimental set-up.

heated by means of an electrical resistance (1) and vapour and liquid phases are mixed and separated using a Cottrell pump. The vapour is condensed and samples can be collected in a receiver (4) to be analyzed. The condensed vapour is then re-mixed with the liquid phase (whose samples are withdrawn in collector (2)) in flask (3), before reintroduction in the cell. The Cottrell pump and the vapour chamber are thermostated. The temperature of the cell is controlled by means of a thermocouple placed in the Cottrell pump and the pressure is regulated with an inert gas (N_2). After filling the equilibrium cell with the mixture to be studied, the mixture is heated to its boiling point. When vaporization starts, the Cottrell pump receives a stream of bubbles and liquid and the circulation starts. Equilibrium is reached when the liquid and vapour flowrates and the temperature are constant. The temperature is measured to an accuracy of ± 0.01 K and the pressure accuracy is about ± 0.0001 bar.

Analyses of samples are done using a gas chromatograph (Chrompack CP-9003) with a packed column (Porapack-Q, 1.50 m, 1/8 inch i.d.) and a thermal conductivity detector (TCD). Analyses are repeated at least three times and are reproducible to about ± 0.005 mole fraction.

Because the DMC-water binary system is an heteroazeotropic mixture, the suitability of the experimental set-up for studying the behavior of such systems was checked. The butan-1-*ol*-water mixture was chosen for this verification and comparison between our experimental results and literature data collected in Dechema was done. A very good agreement was found between the previously published experimental data and experimental results obtained with the apparatus described before.

2.3. Materials

CO_2 (99.9% purity) was supplied by l'Air Liquide. The butan-1-ol used is from Prolabo (Normapur) and has a minimum purity of 99.5%. Dimethyl carbonate, from Aldrich, has a stated purity of 99%, impurities not being water.

3. Phase equilibria modelling

In this work, phase equilibria are calculated using the cubic equation of state proposed by Redlich and Kwong [12], modified by Soave [13] and named SRK equation:

$$P = \frac{RT}{v - b} - \frac{a(T)}{v(v + b)} \tag{1}$$

where equation parameters $a(T)$, b and α are defined as:

$$a(T) = a_c \cdot F(T) \tag{2}$$

$$a_c = 0.42748 \frac{R^2 T_c^2}{P_c} \tag{3}$$

$$b = 0.08664 \frac{RT_c}{P_c} \tag{4}$$

$$F(T) = \left\{ 1 + [0.48 + 1.574\omega - 0.176\omega^2] \right.$$
$$\left. \times \left[1 - \left(\frac{T}{T_c} \right)^{0.5} \right] \right\}^2 \tag{5}$$

with ω being the acentric factor.

To account for interaction taking place between components in the mixture, the mixing rules developed by Huron and Vidal [14] and modified

by Michelsen [15] are used, for calculating the parameter a. This parameter is obtained by resolving the following equation, which involves the calculation of excess Gibbs energy at zero pressure:

$$g_0^E = R \cdot T \sum_{i=1}^{N} x_i \cdot \ln\left(\frac{b_{ii}}{b}\right) + \left(\frac{a}{bRT} - \sum_{i=1}^{N} x_i \cdot \frac{a_{ii}}{b_{ii}RT}\right) \cdot$$

$$q_1 + \left(\left(\frac{a}{bRT}\right)^2 - \sum_{i=1}^{N} x_i \cdot \left(\frac{a_{ii}}{b_{ii}RT}\right)^2\right) \cdot q_2 \quad (6)$$

while b parameter is calculated using a classical mixing rule:

$$b = \sum_{i=1}^{N} b_{ii} \cdot x_i \quad (7)$$

To use Eq. (6), the excess Gibbs energy at zero pressure has to be firstly calculated. In our work, it is obtained using the UNIQUAC activity coefficient model [16,17]:

$$\frac{g^E}{R \cdot T} = \sum_{i=1}^{N} x_i \cdot \ln\frac{\phi_i}{x_i} + \frac{p}{2} \cdot \sum_{i=1}^{N} x_i \cdot q_i \cdot \ln\frac{\theta_i}{\phi_i}$$

$$- \sum_{i=1}^{N} x_i \cdot q_i \cdot \ln\left(\sum_{j=1}^{N} \theta_j \cdot \tau_{ji}\right) \quad (8)$$

with

$$\phi_i = \frac{r_i \cdot x_i}{\sum_{j=1}^{N} r_j \cdot x_j} \quad (9)$$

$$\theta_i = \frac{q_i \cdot x_i}{\sum_{i=1}^{N} q_j \cdot x_j} \quad (10)$$

$$\tau_{ji} = \exp - \left(\frac{u_{ji} - u_{ii}}{R \cdot T}\right) \quad (11)$$

and $\tau_{ii} = \tau_{jj} = 1$; $p = 10$; $u_{ji} - u_{ii} = A_{ji}$ is the binary interaction coefficient; r_i is the component i van der Waals volume; and q_i is component i van der Waals area.

The use of this model requires the knowledge of pure component parameters T_c, P_c and ω referring to the equation of state and r_i and q_i referring to the activity coefficient model. For each compo-nent, these parameters can be found in the DIPPR^{TM} data base (Design Institute for Physical Properties data).

Moreover, this model implies knowledge of binary interaction parameters A_{ij} and A_{ji}, for each sub-binary system existing in the mixture, values that are obtained by fitting experimental data for each system.

The fitting is realised thanks to the commercial software ProReg^{TM} (PROSIM S.A., France), the binary interaction parameters being obtained by minimisation of an objective function, depending on the type of the fitted equilibrium data. Gen-erally, this criterion corresponds to the relative difference between calculated and experimental bubble pressure or composition.

4. Fitting model parameters

4.1. Experimental data from literature

As stated before, experiments are necessary to determine phase equilibria existing in the DMC–water and DMC–CO_2 systems, but, concerning other binary systems, experimental data can be found in the literature. Tables 1 and 2 summarises references where data have been found.

The CO_2–methanol and methanol–DMC inter-action parameters were obtained from experimen-tal P-x,y phase equilibria data. For the methanol–water system, both P-x,y and T-x,y experimental data were used. Finally, the CO_2–water interac-tion parameters were obtained from P-x data only.

In Figs. 3–8, the experimental data used for the fitting are compared with phase equilibria pre-dicted using MHV2 model with the calculated interaction parameters listed in Table 3. In Fig. 5 are presented P-y experimental [27] and predicted phase equilibria for the CO_2-water systems. Be-cause the ProReg^{TM} software does not allow a fitting from P-y experimental data, these data were not taken into account for the calculation. Predicted equilibrium presented in Fig. 5 were obtained using binary interaction parameters cal-culated from P-x experimental data (Fig. 4).

Table 1
Pure components parameters (from DIPPR^{TM})

Component i	T_c (K)	P_c (bar)	ω	R	q
CO_2	304.2	73.83	0.223621	1.29862	1.292
CH_3OH	512.6	80.97	0.563991	1.43110	1.4320
DMC	548.0	45.00	0.384621	3.04812	2.816
H_2O	647.1	220.55	0.344861	0.92000	1.4000

Table 2
Literature references for experimental data

Binary system	References	Isothermal conditions (K)	Isobaric conditions
CO_2-methanol	Ohgaki and Katamaya [18]	298.15–313.15	–
	Robinson et al. [19]	323.15	–
CO_2–water	Houghton et al. [20]	298.15–373.15	–
	Wiebe and Gaddy [21,22]	323.15–373.15	–
Methanol–water	Bredig and Bayer [23]	312.9–322.91	1 bar
	Butler et al. [24]	298.15	–
	Broul et al. [25]	333.15	–
Methanol–DMC	Comelli and Francesconi [26]	313.15	–

As can be observed from Figs. 3–8, the agreement between experimental and calculated phase equilibria is quite satisfactory, but, for each system, some discrepancies occur. For the CO_2–methanol system, the greatest discrepancies exist for the CO_2 concentrated liquid-phase, but calculated points of the vapour phase match-up correctly with the measurements. From Figs. 4 and 5, we can see, for the CO_2–water system, that predictions are in good agreement with experimental data, considering the scale of the figure and the wide range of temperature used for the fitting. Concerning the methanol–water system, we can note in Figs. 6 and 7 a small deviation between experimental and predicted results, mainly at high temperature and in the zone of high methanol concentrations. However, results shown in Fig. 7 for this system are quite satisfactory. This can also be observed for the DMC–methanol system equilibrium represented in Fig. 8, where some discrepancies occur to the left of the azeotropic point. On the whole, predictions are in accordance with experimental results.

To validate these results, we used the SRK-MHV2 model, with fitted parameters obtained from binary experimental data, to predict ternary CO_2–methanol–water phase equilibria at 313.15 K for three different pressures around the critical point of CO_2 [28]. Experimental and predicted results are shown in Figs. 9–11. As can be seen from these figures, the model predictions match the measurements very well, the greatest discre-
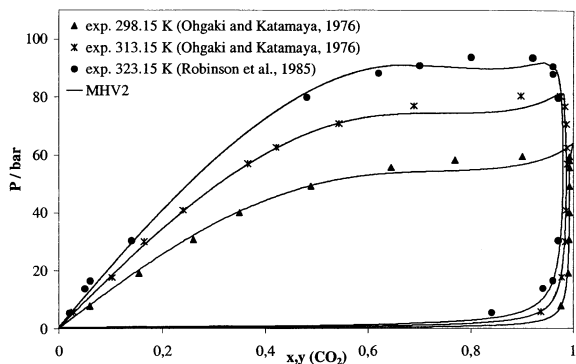

Fig. 3. Experimental and calculated P-x,y phase equilibrium for the CO_2–methanol system at three different temperatures.
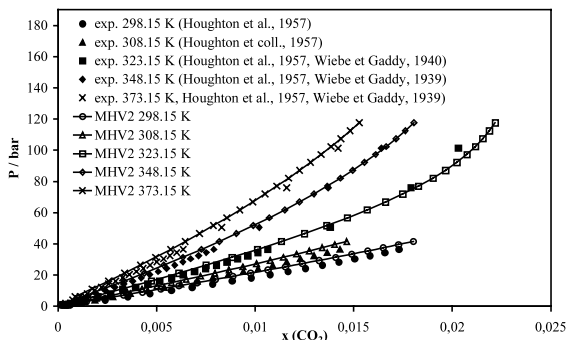
Fig. 4. Experimental and calculated *P-x* phase equilibrium for the CO_2–water system at five different temperatures.
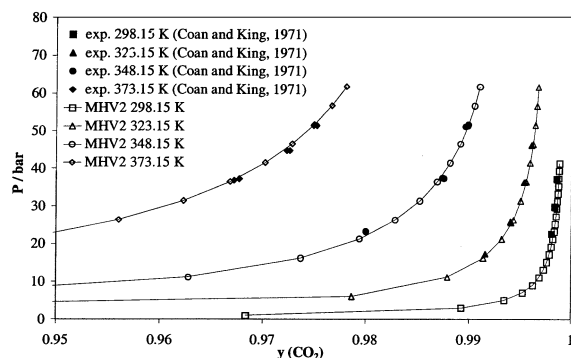

Fig. 5. Experimental and calculated *P-y* phase equilibrium for the CO_2–water system at four different temperatures.
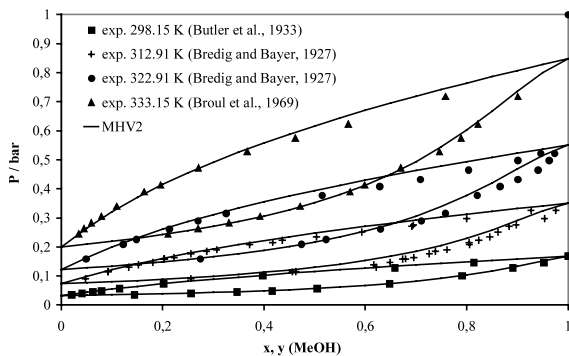

Fig. 6. Experimental and calculated *P-x,y* phase equilibrium for the methanol–water system at four different temperatures.

pancies concerning the prediction of vapour phase compositions, where experimental results are always less accurate, due to the very low methanol and water concentrations in this phase.

Results obtained in this part of the study show that the SRK-MHV2 model is able to correctly predict high and low pressure phase equilibria of the different binary sub-systems existing in the quaternary CO_2–methanol–water–DMC mixture. In addition, the ability of the model, using interaction parameters fitted from binary experimental data only, to predict phase equilibria existing in the ternary mixture CO_2–methanol–
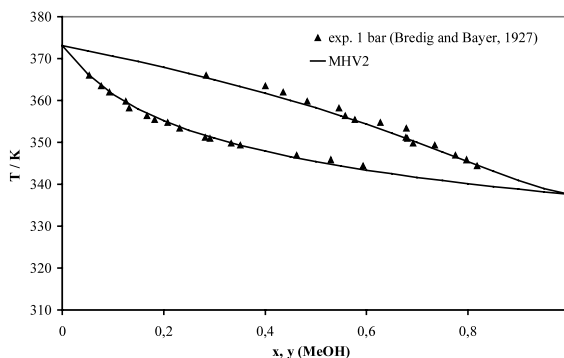

Fig. 7. Experimental and calculated *T-x,y* phase equilibrium for the methanol–water system at 1 bar.
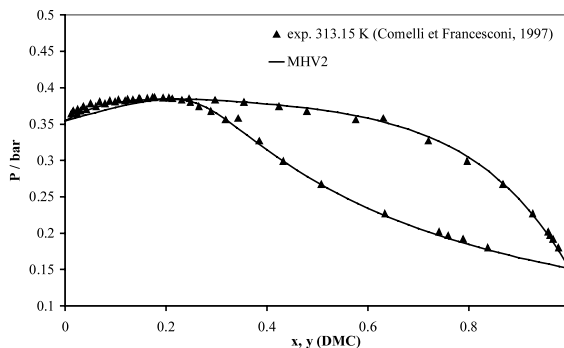

Fig. 8. Experimental and calculated *P-x,y* phase equilibrium for the DMC–methanol system at 313.15 K.

Table 3
Binary interaction parameters for binary experimental data extracted from the literature

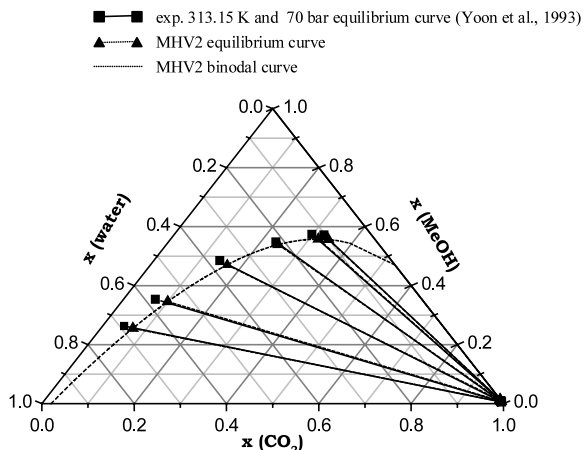| i	j	A_{ij} (cal mol^{-1})	A_{ji} (cal mol^{-1})
CO_2	Methanol	502.12	131.709
CO_2	Water	1546.5	994.997
Methanol	Water	781.604	−435.901
Methanol	DMC	636.888	36.6887

Fig. 9. Experimental and calculated phase equilibrium for the CO_2–methanol–water system at 313.15 K and 70 bar.
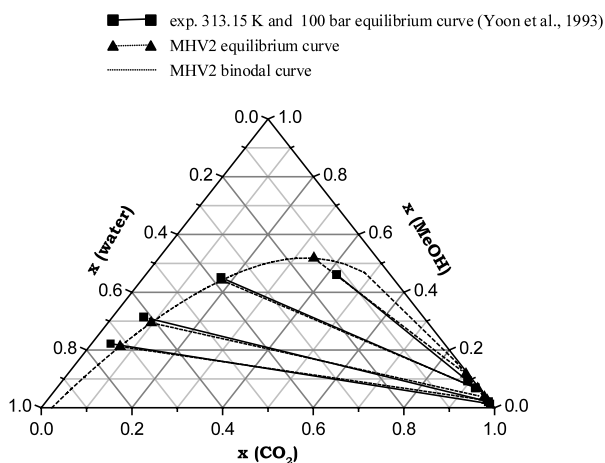
Fig. 10. Experimental and calculated phase equilibrium for the CO_2–methanol–water system at 313.15 K and 100 bar.

water was also checked. The aim of the next part of this study is to apply the same fitting method in order to deduce binary interaction parameters corresponding to the DMC–CO_2 and DMC–water binary sub-systems, whose experimental data were not available in the literature, and which were obtained experimentally in this work.

4.2. Experimental data determined in this work

The DMC–CO_2 equilibrium transition pressures were isothermally measured, using the appa-

ratus presented in Fig. 1, at 322.65, 348.15 and 373.55 K, and results are presented in Table 4. Thus, experiments were performed over a wide range of temperature and pressure, but it should be noted that the experimental set-up does not allow measurements at low pressures, so the dew curves could not be obtained. Experimental and calculated results are shown on Fig. 12. Because of the wide range of temperature investigated, binary interaction parameters were found to be temperature dependent. The binary interaction parameter values are recorded for each temperature in Table 5. This table shows the form of the linear equations resulting from the linear fitting of the interaction parameters values with respect to the temperature. In this case, these parameters are divided into two terms, in the form:

$$A_{ij} = A_{ij}^0 + A_{ij}^T \cdot T \tag{12}$$

As can be seen from Fig. 12, the agreement between experimental and calculated phase equilibria is relatively good. However, it must be pointed out that experimental points are difficult to obtain near the critical point of the mixture and, in this zone, a non-negligible scattering can be observed.

Experimental equilibrium data obtained for the DMC–water mixture, by means of the apparatus presented in Fig. 2, are gathered in Table 6. In Table 7 are recorded the values of binary interaction parameters, obtained by fitting these results.
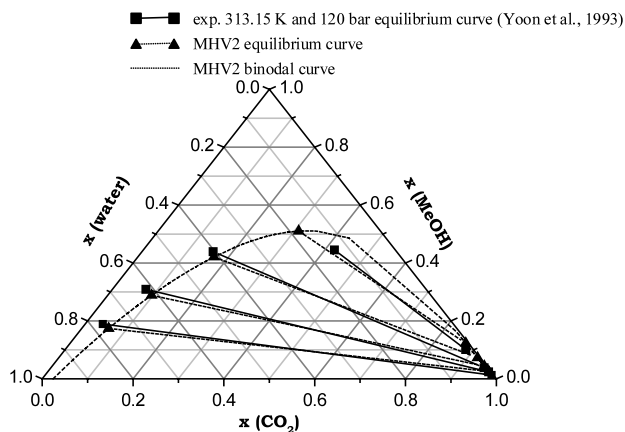
Fig. 11. Experimental and calculated phase equilibrium for the CO_2–methanol–water system at 313.15 K and 120 bar.

Table 4
Experimental data for the system DMC–CO_2 at 322.65, 348.15 and 373.55 K

T = 322.65 K		T = 348.15 K		T = 373.55 K	
DMC mole fraction	P (bar)	DMC mole fraction	P (bar)	DMC mole fraction	P (bar)
0.038	88.1	0.050	105.4	0.050	122.3
0.043	89.7	0.050	110.2	0.065	106.6
0.050	88.4	0.056	108.3	0.072	125.2
0.068	89.3	0.059	110.3	0.076	124.4
0.078	89.9	0.076	110.5	0.228	127.5
0.079	87.2	0.228	107.1	0.271	126.2
0.166	81.0	0.228	106.9	0.461	76.8
0.228	77.6	0.271	102.7	0.569	62.6
0.254	73.8	0.569	50.6	0.569	61.0
0.271	74.6	0.569	49.9	0.576	62.5
0.271	73.9	0.730	27.3	0.675	45.7
0.318	69.5			0.730	33.6
0.327	68.8			0.801	33.0
0.381	59.3				
0.555	47.1				
0.559	42.7				
0.569	44.3				
0.569	43.7				
0.700	29.0				
0.730	21.9				
0.805	13.3				
0.830	24.1				

These parameters were used to predict phase equilibrium drawn in Fig. 13. This figure shows that the DMC–water mixture is an hetero-azeotropic mixture.

First of all, two comments have to be made concerning this particular hetero-azeotropic system. On the one hand, liquid-vapour equilibrium is quite easy to study because of the relatively large zone of liquid–liquid immiscibility, up to about 0.85 DMC mole fraction. Conversely, the vapour phase composition cannot be easily determined for low molar fraction of DMC because analysis of the vapour phase is realised after condensation, so the resulting mixture splits into two liquid phases, preventing a correct sampling. However, the study of the bubble curve is sufficient to extract binary interaction coefficients from liquid-vapour equilibria, and, from experiments realised with the butan-1-ol-water mixture, it appears that our experimental set-up allows an accurate determination of bubble temperature and liquid phase composition.

Good agreement between experimental and calculated points of the liquid phase is seen. The predicted azeotropic point can be compared to the experimental point given in Azeotropic Data [29] and we find a discrepancy of about 5% between the two values of composition but the azeotropic temperature is correctly calculated.
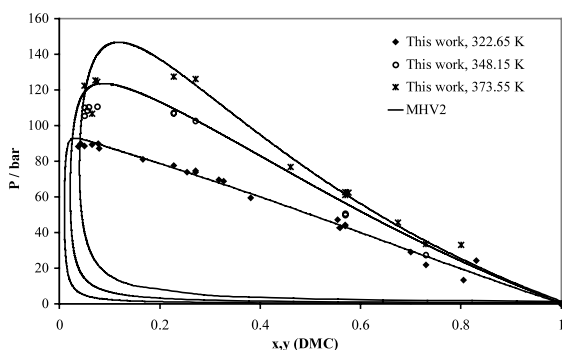

Fig. 12. Experimental and calculated phase equilibrium for the DMC–CO_2 system at 322.65, 348.15 and 373.55 K.

Table 5
Binary interaction coefficients for the DMC–CO$_2$ mixture

T (K)	$A_{DMC\text{-}CO_2}$ (cal mol^{-1})	$A_{CO_2\text{-}DMC}$ (cal mol^{-1})
322.65	503.850	−245.268
348.15	212.329	−131.800
373.55	−103.173	−2.98487
	$A_{DMC\text{-}CO_2} = 4355.8 - 11.925.T$ (cal.mol^{-1})	
	$A_{CO_2\text{-}DMC} = -1783.6 + 4.7598.T$ (cal.mol^{-1})	

Table 6
Experimental data for the DMC–water system at 1.01325 bar.

DMC mole fraction	T (K)
0.0031	370.13
0.0031	369.95
0.0032	367.82
0.0032	369.25
0.0095	362.11
0.0103	361.84
0.0117	361.23
0.0147	359.32
0.0181	357.55
0.0251	355.25
0.0257	355.35
0.0259	354.55
0.0288	354.55
0.0307	353.30
0.0320	353.14
0.0337	352.85
0.0346	352.70
0.6876	351.33
0.7205	351.38
0.7637	351.70
0.8924	354.01
0.9104	354.89
0.9483	356.15
0.9546	356.71
0.9578	356.87
0.9628	357.57
1	362.85

Table 7
Binary interaction parameters for the DMC–water system

$A_{DMC\text{-}water}$ (cal mol^{-1})	$A_{water\text{-}DMC}$ (cal mol^{-1})
851.326	160.648

5. Application: study of operating conditions

As an interesting application, the number of phases existing in the reactor as a function of pressure and temperature can be investigated. For this, a hypothetical perfectly mixed continuous reactor, fed with a methanol/CO$_2$ mixture was considered, where the DMC synthesis reaction (Eq. (1a)) takes place with an arbitrarily chosen conversion value (i.e. the mixture in the reactor corresponds to concentrations readily obtained from the value of the conversion). This conversion was given the values of 0.6 and 1.0 with respect to methanol, this last value giving information of what would happen in the reactor in the most favourable case. Indeed, for the moment, no information is available concerning the kinetics of this reaction.

$$2CH_3OH + CO_2 \rightarrow (CH_3O)CO + H_2O \qquad (1a)$$
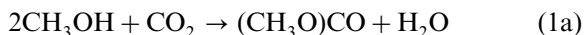
Several feed compositions are used, ranging from a stoechiometric mixture (66.7 mol% methanol) to an excess of CO$_2$ and the thermodynamic equilibrium existing in the reactor was investigated, using the SRK-MHV2 thermodynamic model using the parameters determined in this work. For each feed mixture, the temperature range investigated was 283.15–423.15K and the pressure range from 10 to 400 bar. Composition of the feed mixture, conversion and composition of the resulting reacting mixture are shown in Table 8.

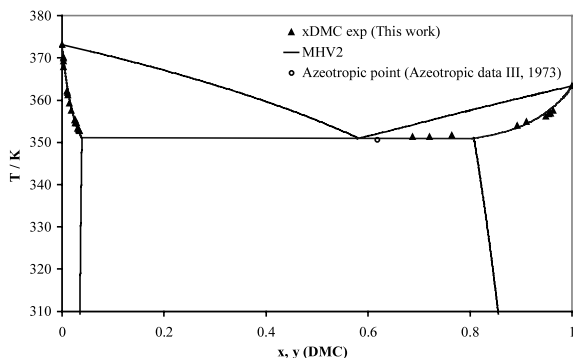Fig. 14 presents, for each of the five mixtures studied, the zones of coexistence of monophasic

Fig. 13. Experimental and calculated phase equilibrium for the DMC–water system at 1.01325 bar.

Table 8
Reacting mixture compositions

Mixture	Conversion	Feed mixture composition		Reacting mixture composition			
		x_{MeOH}	x_{CO_2}	x_{MeOH}	x_{CO_2}	x_{water}	x_{DMC}
1	0.6	0.667	0.333	0.333	0.167	0.250	0.250
2	0.6	0.500	0.500	0.236	0.412	0.176	0.176
3	0.6	0.167	0.833	0.070	0.824	0.053	0.053
4	0.6	0.091	0.909	0.037	0.907	0.028	0.028
5	1.0	0.091	0.909	0.000	0.904	0.048	0.048

and diphasic states. In each diagram, qualitative information about the 'state' of the mixure is marked for each zone. The letter 'L' refers to a liquid phase, whose density is high (around 800–900 kg m^{-3}). Conversely, the vapour state, marked with the letter 'V', refers to a low density phase (<100 kg m^{-3}). Finally, the letter 'F' designates a 'fluid' state whose density lies between that of a liquid and a gas. Because the critical line of this quaternary mixture was not calculated here, these denominations remain qualitative.

Several remarks can be made from observation of Fig. 14. First of all, consider the first diagram, marked (a) and referring to a methanol rich feed mixture (Mixture 1), i.e. a stoichiometric mixture. In this diagram, there is a large diphasic zone, where a first liquid phase, mainly composed of water and methanol, is in equilibrium with a second liquid phase containing a large proportion of CO_2 and DMC. This equilibrium zone exists for low temperatures, at a pressure greater than about 80 bars. A second diphasic zone exists for low pressure, consisting in the equilibrium between a liquid phase and a CO_2 rich vapour phase. The monophasic zone is a liquid and, for high temperature and low pressure, a restricted vapour phase zone. Mixture 2 (refer to (b) on Fig. 14), corresponds to an equimolar feed mixture of methanol and CO_2 (2-fold the stoichiometric quantities). For this mixture, zones similar to the case of mixture 1 can be observed, the liquid zone being relatively smaller and the vapour zone being larger. For a mixture containing a larger quantity of CO_2, as in mixture 3 (10-fold the stoichiometric quantities) (Fig. 14 (c)), the phase diagram undergoes perceptible modifications: first of all, the thin

part of the liquid zone observed for the previous mixtures is very restricted and, conversely, a large zone of monophasic mixture is now present. In this zone, depending on temperature or pressure, the mixture is liquid (low temperature), vapour (low pressure and high temperature), or 'fluid'. The diphasic mixture encountered for low temperatures is liquid-liquid type, with a DMC-CO_2 rich liquid and a water rich liquid, as described before. This diphasic mixture transforms to liquid-'fluid' type, when temperature and pressure are increased. With an excess of CO_2, as in the case of mixture 4 (20-fold the stoichiometric quantities) (Fig. 14d), the same tendencies can be observed. The diphasic zone is further reduced and no liquid–liquid equilibrium is now observed. The last diagram (e) refers to the same feed mixture (excess of CO_2) but with a conversion equal to 1.0, that is to say that, in this case, because all methanol has been consumed, the mixture present in the reactor is a ternary CO_2–DMC–water mixture. The distribution of phases is not very different from that obtained when methanol is still present, the diphasic zone being slightly larger. This can be explained by the fact that, in mixture 4, methanol has acted as a co-solvent for the partially miscible DMC-water mixture.

From these observations, several conclusions can be put forward. The different studies realised on the DMC synthesis have shown that, for the moment, the most interesting results are obtained using an organotin catalyst, like dibutyltin dimethoxide ($Bu_2Sn(OBu)_2$), this latter being active at about 423.15 K [5–7]. Moreover, as mentioned before, to avoid mass transfer limitations which had been observed with gaseous CO_2, the reaction

(a)Mixture 1 : methanol rich feed. Conversion : 0.6

(b)Mixture 2 : equimolar feed. Conversion : 0.6

(c)Mixture 3 : CO$_2$ excess feed. Conversion : 0.6

(d)Mixture 4 : CO$_2$ large excess feed. Conversion : 0.6

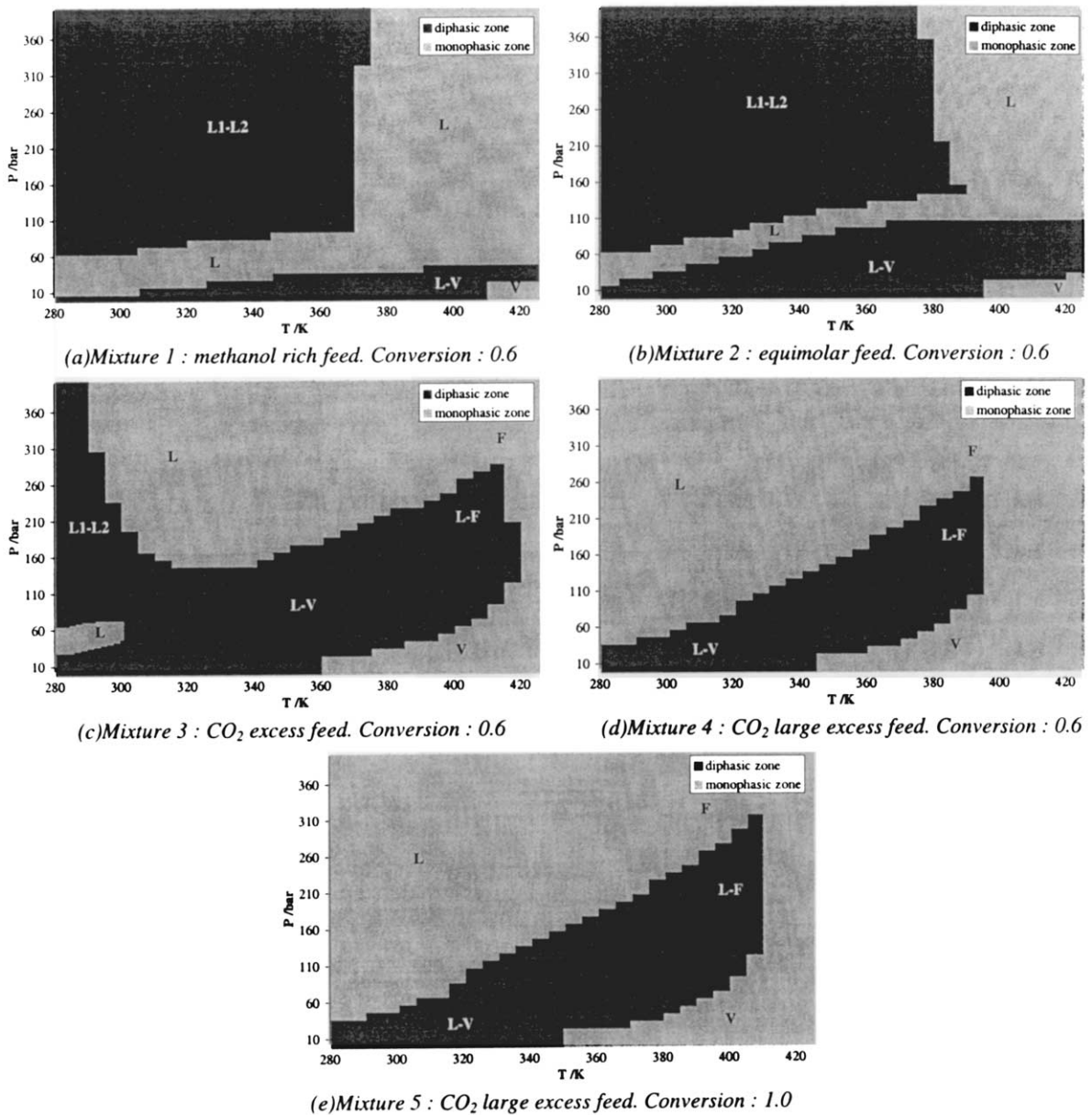(e)Mixture 5 : CO$_2$ large excess feed. Conversion : 1.0

Fig. 14. Coexisting zones of monophasic and diphasic mixtures for five different reacting mixtures.

has to be operated in a monophasic reacting mixture, and preferably in a 'fluid' state or vapour state. By comparison with the vapour state, the 'fluid' state is more interesting because (i) the volume of the reactor will be smaller; (ii) the effect of pressure has been proved to be positive on the kinetics of the reaction; and (iii) the separation of reaction products can be made easier by using the tuneable solvent power of supercritical fluids. From Fig. 14, it can be concluded that, to be sure of running the reaction in an homogeneous fluid media, it seems more worthwhile to work with a large excess of CO$_2$. For example, it can be seen with mixtures 3–5 that, at 423.15 K and

whatever the pressure, the reacting mixture is found to be in a vapour or a fluid state. Moreover, for these mixtures, a drop of pressure and temperature after the reactor would allow a return to a diphasic state, with a view to obtaining an efficient mixture fractionation.

6. Conclusion

Binary interaction coefficients, necessary to predict phase equilibria occurring in the quaternary CO_2–methanol–water–DMC mixture, have been determined in this work. A part of them were obtained from literature data, but for others, experiments were necessary.

Binary interaction coefficients calculated from literature data using the SRK-MHV2 thermodynamic model (i.e. for the CO_2–methanol, CO_2–water, methanol–water and DMC–methanol systems), were obtained and gave a satisfactory correlation. Moreover, the model was used with fitted parameters obtained from binary data, in order to predict ternary phase equilibrium, and results match closely the experimental results.

Concerning DMC–CO_2 and DMC–water mixtures for which experiments were carried out, agreement between experimental and predicted phase equilibria is less satisfactory. However, these results remain usable.

From another point of view, this work has shown the ability of the SRK-MHV2 model to predict phase equilibria of systems under high or low pressure, containing polar or apolar components. Moreover, results obtained here can be used for calculations of phase equilibria occurring in the quaternary system, and, more generally, the study of a process for the synthesis of DMC using CO_2 and methanol could be carried out. As a first application, this model has been used in order to predict phase equilibria in the reactor. Several hypothetical reacting mixtures have been studied, and results show the value of working with CO_2 in large excess, as a solvent for the reaction, in order to be sure of running the reaction in an homogeneous fluid system.

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