

Bubble Point Determination for CO₂ + Ethanol + Alkanolamines (Monoethanolamine, Diethanolamine, or Triethanolamine) at High Pressures

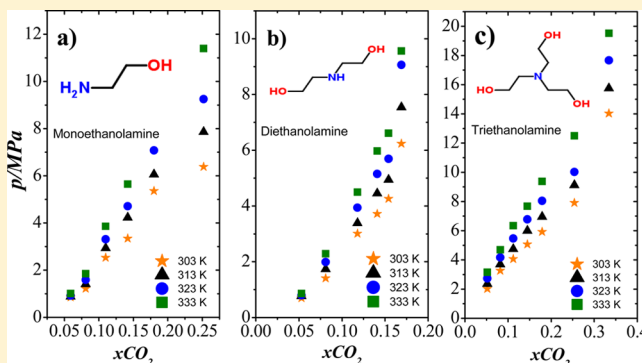
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ABSTRACT: Experimental data from the phase transition of the ternary systems {CO₂(1) + [0.25 monoethanolamine(2) + 0.75 ethanol(3)]}, {CO₂(1) + [0.25 diethanolamine(2) + 0.75 ethanol(3)]} and {CO₂(1) + [0.25 triethanolamine(2) + 0.75 ethanol(3)]} is reported. A variable volume cell was employed using the static synthetic method in a temperature range of (313–343) K, pressures up to 14 MPa and CO₂ mole fractions between 0.05 and 0.35. For $x_{\text{CO}_2} > 0.35$ phase transition data could not be measured for pressures up to 35 MPa. Vapor–liquid transitions (VLE) of bubble point (BP) are determined for the three ternary systems studied. The determination of measures of the phase equilibrium of systems involving CO₂ and alkanolamines are of great importance in the development of absorption processes. A great feature of alkanolamines is the possibility of capturing carbon dioxide (CO₂) and promoting separation of this gas from other gas streams.



1. INTRODUCTION

The concern with emission reduction or even removal of acid gases CO₂, H₂S, and COS from the burning of fossil fuels is increasing nowadays because of the importance of reducing the concentrations of these pollutants in atmosphere. In pursuit of this goal, alkanolamines such as monoethanolamine (MEA), diethanolamine (DEA), and triethanolamine (TEA) have been widely used in chemical absorbents such as acid gases.^{1–3} Thus, studies on the solubility of gases in alkanolamines become of great importance for a better understanding of the molecular systems and interactions between them.^{1,4,5}

Some authors have focused on the study of kinetic and transport properties of the CO₂ absorption in aqueous mixtures of alkanolamines.^{6,7} Other studies report physicochemical properties, i.e., surface tension, density, amount of excess isentropic compressibility, and speed of sound for systems containing alcohols and amines.^{2,3,8} However, phase behavior experimental information on ternary systems involving alkanolamines, alcohols, and CO₂ is demanding further contributions. Solubility data of these types of systems are useful not only for absorption of gases, but also for studies of various types of chemical reactions such as reactions production of ionic liquids.⁹ The determination of measures of phase equilibrium of systems involving CO₂ and alkanolamines are of great importance in the development of absorption processes. A great

feature of alkanolamines is the possibility of capturing carbon dioxide (CO₂) and promoting separation of this gas from other gas streams. This last feature inserts them between the technologies to reduce emissions of CO₂ or its contents in gas streams. The addition of ethanol to the system {CO₂+alkanolamine} facilitates the solubility of carbon dioxide (CO₂) in alkanolamine dioxide. In adsorption processes (for sequestration of gases) at high pressure reactions or the presence of ethanol reduces the pressures required to solubilize the system. In this context, knowledge of phase behavior of systems {ethanolamine + ethanol}, {diethanolamine + ethanol}, and {triethanolamine + ethanol} in supercritical CO₂ arises as a fundamental step to be investigated before any development or optimization processes of chemical reactions or absorption. Thus, the aim of this work is the experimental investigation of the phase behavior by bubble point determination of ternary systems involving ethanolamine, diethanolamine, triethanolamine and ethanol in pressurized carbon dioxide in the temperature range (313–343) K.

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2. EXPERIMENTAL SECTION

2.1. Materials. Sigma-Aldrich (São Paulo/SP/Brazil) provided acetone, Química Moderna (Barueri/SP/Brazil) supplied monoethanolamine (99 wt %), diethanolamine (99 wt %), and triethanolamine; VETEC (São Paulo/SP/Brazil) supplied ethanol (99.5 wt %); White Martins S.A (Osasco/SP/Brazil) delivered carbon dioxide (99.5 wt % in the liquid phase). The pure component properties of these substances are presented in Table 1.

Table 1. Critical Properties and Molar Mass of the Studied Compounds^a

compound	T_c /K	p_c /MPa	M_w /g·g·mol ⁻¹
CO ₂	304.21	7.38	44.01
monoethanolamine	678.2	7.12	61.08
diethanolamine	736.6	4.27	105.14
triethanolamine	772.1	2.74	149.19
ethanol	514.0	6.14	46.07

^a[DIPPR],²² T_c , critical temperature; p_c , critical pressure; M_w , molar mass.

2.2. Phase Equilibrium Apparatus and Experimental Procedure.

The apparatus and the experimental procedure used in this work were described in detail in previous papers published by our group work.^{9–14} Measurements of phase transition were evaluated from the static synthetic method using a variable-volume cell provided with a sapphire window. The experimental setup consists of a variable-volume view cell with two sapphire windows for visual observation, an absolute pressure transducer (Smar, model LD 301), with an accuracy of ± 0.01 MPa, for pressure data acquisition, and a syringe pump (ISCO, model 260D). The equilibrium cell contains a movable piston that permits the pressure control inside the cell. The cell is equipped with an aluminum jacket for temperature control and PID controller (DIGI MEC mark, SHM 112 model). The temperature controller was connected to a thermocouple (T type, accuracy 1.0 K), which was in direct contact with the fluid mixture inside the equilibrium cell. The desired temperature was successfully controlled with an error range near to 0.5 K. An amount of solution was weighed on a high accuracy scale balance (Marte, model AM220, uncertainty: 0.0001 g) and loaded into the cell. The insertion of a known quantity of CO₂ was carried out with the aid of syringe pump, introducing uncertainties associated with the overall concentration of the mixture no greater than 0.002 according to the calculation methodology of Rodrigues-Reartes.¹⁵ These uncertainties, added to each experimental uncertainties the observed patterns in Tables 2, 3, and 4, do not change significantly their values. Then the cell content was kept at continuous agitation with a magnetic stirrer and a Teflon-coated stirring bar. Based on three repetitions of each experimental point, the standard deviations in pressure were estimated to be equal to in the range 0.01–0.08 MPa.

3. RESULTS AND DISCUSSION

Data transition phase liquid–vapor system {CO₂+acetone} (see Figure 1) were obtained to verify the reliability of the methodology and experimental apparatus. The data showed substantial agreement with data reported in the literature.^{16–18} The phase transition date presented good consistency with

Table 2. Experimental VLE Data for Temperature (T), Pressure (p) with Standard Uncertainty $u(p)$, and Mole Fraction x for the Ternary System {CO₂(1) + [0.25 Monoethanolamine(2) + 0.75 Ethanol(3)]}

T^a /K	x_1	x_2	p /MPa	$u(p)$ /MPa	transition ^b
313	0.059	0.235	0.85	0.05	VLE (BP)
313	0.081	0.230	1.22	0.03	VLE (BP)
313	0.110	0.222	2.53	0.03	VLE (BP)
313	0.142	0.214	3.34	0.02	VLE (BP)
313	0.180	0.205	5.36	0.01	VLE (BP)
313	0.252	0.187	6.38	0.02	VLE (BP)
323	0.059	0.235	0.88	0.01	VLE (BP)
323	0.081	0.230	1.41	0.02	VLE (BP)
323	0.110	0.222	2.94	0.02	VLE (BP)
323	0.142	0.214	4.23	0.01	VLE (BP)
323	0.180	0.205	6.06	0.02	VLE (BP)
323	0.252	0.187	7.86	0.02	VLE (BP)
333	0.059	0.235	0.92	0.02	VLE (BP)
333	0.081	0.230	1.59	0.02	VLE (BP)
333	0.110	0.222	3.31	0.04	VLE (BP)
333	0.142	0.214	4.71	0.02	VLE (BP)
333	0.180	0.205	7.08	0.03	VLE (BP)
333	0.252	0.187	9.25	0.01	VLE (BP)
343	0.059	0.235	1.01	0.02	VLE (BP)
343	0.081	0.230	1.85	0.01	VLE (BP)
343	0.110	0.222	3.86	0.02	VLE (BP)
343	0.142	0.214	5.65	0.01	VLE (BP)
343	0.180	0.205	8.07	0.04	VLE (BP)
343	0.252	0.187	11.40	0.04	VLE (BP)

^a $u(T) = 0.5$ K, $u(x) = 0.002$. ^bBP, bubble points.

Table 3. Experimental VLE Data for Temperature (T), Pressure (p) with Standard Uncertainty $u(p)$, and Mole Fraction x for the Ternary System {CO₂(1) + [0.25 Diethanolamine(2) + 0.75 Ethanol(3)]}

T^a /K	x_1	x_2	p /MPa	$u(p)$ /MPa	transition ^b
313	0.053	0.237	0.70	0.01	VLE (BP)
313	0.081	0.230	1.41	0.02	VLE (BP)
313	0.118	0.221	3.01	0.02	VLE (BP)
313	0.141	0.215	3.72	0.03	VLE (BP)
313	0.154	0.211	4.26	0.03	VLE (BP)
313	0.169	0.208	6.24	0.01	VLE (BP)
323	0.053	0.237	0.77	0.01	VLE (BP)
323	0.081	0.230	1.74	0.01	VLE (BP)
323	0.118	0.221	3.39	0.01	VLE (BP)
323	0.141	0.215	4.45	0.01	VLE (BP)
323	0.154	0.211	4.94	0.01	VLE (BP)
323	0.169	0.208	7.54	0.01	VLE (BP)
333	0.053	0.237	0.80	0.01	VLE (BP)
333	0.081	0.230	1.99	0.01	VLE (BP)
333	0.118	0.221	3.94	0.02	VLE (BP)
333	0.141	0.215	5.15	0.02	VLE (BP)
333	0.154	0.211	5.69	0.01	VLE (BP)
333	0.169	0.208	9.06	0.01	VLE (BP)
343	0.053	0.237	0.86	0.01	VLE (BP)
343	0.081	0.230	2.29	0.01	VLE (BP)
343	0.118	0.221	4.50	0.02	VLE (BP)
343	0.141	0.215	5.97	0.01	VLE (BP)
343	0.154	0.211	6.61	0.02	VLE (BP)
343	0.169	0.208	9.56	0.01	VLE (BP)

^a $u(T) = 0.5$ K, $u(x) = 0.002$. ^bBP, bubble points.

Table 4. Experimental VLE Data for Temperature (T), Pressure (p) with Standard Uncertainty $u(p)$, and Mole Fraction x for the Ternary System $\{\text{CO}_2(1) + [0.25 \text{ Triethanolamine}(2) + 0.75 \text{ Ethanol}(3)]\}$

T^a/K	x_1	x_2	p/MPa	$u(p)/\text{MPa}$	transition ^b
313	0.052	0.237	2.02	0.03	VLE (BP)
313	0.082	0.229	3.27	0.01	VLE (BP)
313	0.112	0.222	4.07	0.03	VLE (BP)
313	0.145	0.213	5.07	0.01	VLE (BP)
313	0.179	0.205	5.92	0.01	VLE (BP)
313	0.254	0.186	7.91	0.03	VLE (BP)
313	0.334	0.166	14.03	0.03	VLE (BP)
323	0.052	0.237	2.37	0.03	VLE (BP)
323	0.082	0.229	3.70	0.01	VLE (BP)
323	0.112	0.222	4.74	0.03	VLE (BP)
323	0.145	0.213	6.00	0.01	VLE (BP)
323	0.179	0.205	6.96	0.01	VLE (BP)
323	0.254	0.186	9.12	0.02	VLE (BP)
323	0.334	0.166	15.76	0.02	VLE (BP)
333	0.052	0.237	2.73	0.03	VLE (BP)
333	0.082	0.229	4.17	0.01	VLE (BP)
333	0.112	0.222	5.47	0.01	VLE (BP)
333	0.145	0.213	6.78	0.01	VLE (BP)
333	0.179	0.205	8.04	0.02	VLE (BP)
333	0.254	0.186	10.02	0.01	VLE (BP)
333	0.334	0.166	17.67	0.01	VLE (BP)
343	0.052	0.237	3.16	0.01	VLE (BP)
343	0.082	0.229	4.69	0.01	VLE (BP)
343	0.112	0.222	6.35	0.01	VLE (BP)
343	0.145	0.213	7.68	0.02	VLE (BP)
343	0.179	0.205	9.38	0.03	VLE (BP)
343	0.254	0.186	12.50	0.01	VLE (BP)
343	0.334	0.166	19.52	0.02	VLE (BP)

^a $u(T) = 0.5 \text{ K}$, $u(x) = 0.002$. ^bBP, bubble points.

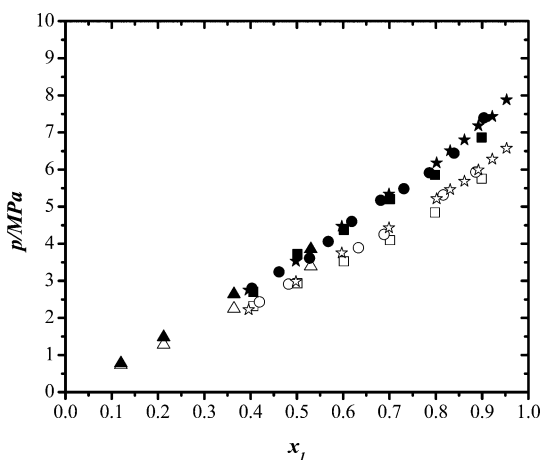


Figure 1. Experimental pressure–composition diagram for the system $\{\text{CO}_2(1) + \text{acetone}(2)\}$ under VLE conditions at 303 K (VLE-BP) (\square , this work; \circ , Chiehming et al.;¹⁶ Δ , Stievano et al.;¹⁷ \star , Chiu et al.¹⁸) and 313 K (\blacksquare , this work; \bullet , Chiehming et al.;¹⁶ \blacktriangle , Stievano et al.;¹⁷ \blackstar , Chiu et al.¹⁸).

those reported in the literature, with a maximum deviation of 0.3 MPa, especially in compositions above 0.6 mol CO_2 .

From preliminary experiments involving alkanolamines and carbon dioxide, carried out in a temperature range of (313 to 343) K, pressures up to 35 MPa and $0.1 < x\text{CO}_2 < 0.9$, it was

observed a significant immiscibility effect between the compounds. However, according to studies reported in the literature,^{19–21} it was found that the addition of an alcohol can significantly improve the miscibility of the compounds with differences in polarity. From this information, it was inserted to the mixtures an amount of ethanol in a molar ratio of alkanolamine/ethanol (1:3) [0.25 alkanolamine + 0.75 ethanol], as a cosolvent. However, for $x\text{CO}_2 > 0.35$ systems continued to show considerable immiscibility, even at pressures up to 35 MPa.

Tables 2 to 4 report experimental data in terms of mole fraction of CO_2 (x_1) and mole fraction of monoethanolamine or diethanolamine or triethanolamine (x_2), bubble point pressure (p) values, and standard uncertainties $u(p)$ of replicated pressure measurements.

The data collection phase transition was initiated from the system $\{\text{CO}_2(1) + \text{monoethanolamine}(2) + \text{ethanol}(3)\}$, see Table 2. According to Figure 2a, it was found that the pressure

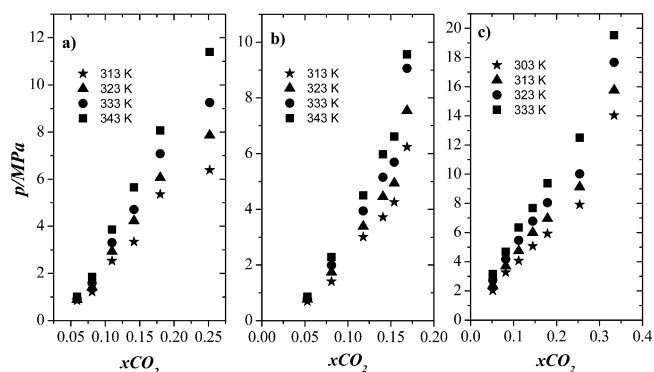


Figure 2. Pressure–composition diagrams for the system: (a) $\{\text{CO}_2(1) + [0.25 \text{ monoethanolamine}(2) + 0.75 \text{ ethanol}(3)]\}$, (b) $\{\text{CO}_2(1) + [0.25 \text{ diethanolamine}(2) + 0.75 \text{ ethanol}(3)]\}$, and (c) $\{\text{CO}_2(1) + [0.25 \text{ triethanolamine}(2) + 0.75 \text{ ethanol}(3)]\}$ at $T = 313 \text{ K}$ (\blacksquare , VLE); 323 K (\bullet , VLE); 333 K (\blacktriangle , VLE); 343 K (\blackstar , VLE).

transition to $x\text{CO}_2 = 0.05$, for all temperatures are remarkably close, while virtually no variations were detected. Throughout Figure 2a, it can be seen that the isotherms are more distanced from one another, demonstrating the effect of CO_2 . For high concentrations of CO_2 , high pressures are required for the solubilization of the system. However, for $x\text{CO}_2 > 0.25$, it was not possible to measure data phase transition due to the limit of operation pressure of the apparatus, 35 MPa.

Data for $\{\text{CO}_2(1) + \text{diethanolamine}(2) + \text{ethanol}(3)\}$ is reported in Table 3, showing phase transition pressure very close to the system containing ethanolamine, see Figure 2b. However, for $x\text{CO}_2 > 0.2$, it was not possible to measure data from phase transition, possibly due to the complexity of the diethanolamine molecule in relation to the ethanolamine, possibly viscosity.

The system $\{\text{CO}_2(1) + \text{triethanolamine}(2) + \text{ethanol}(3)\}$ is illustrated in Figure 2c and as the CO_2 concentration increases the isotherms result more separated from each other when compared to the previous systems with monoethanolamine and diethanolamine. The phase transition pressure of this system are also higher than the first two systems (see Table 4), as expected.

To check the differences and similarities between the systems, a comparison was made in the isotherms of (303 and 343) K (see Figure 3). Figure 3 highlights the discussions

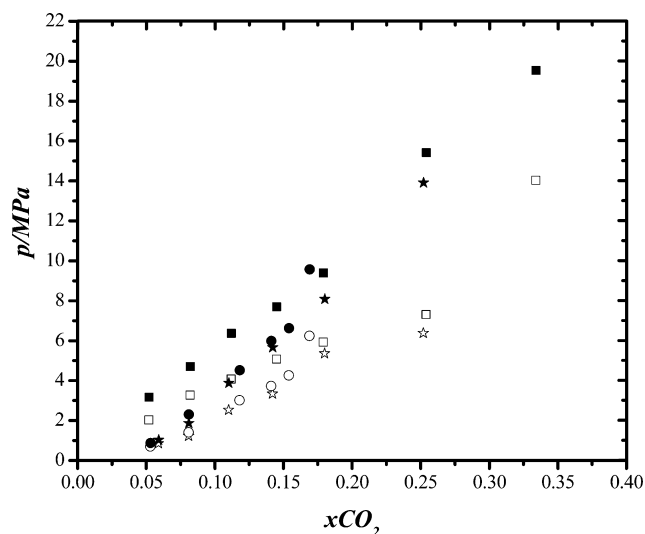


Figure 3. Pressure–composition diagram comparison between systems $\{\text{CO}_2(1) + [0.25 \text{ monoethanolamine}(2) + 0.75 \text{ ethanol}(3)]\}$ at $T = 313 \text{ K}$ (■, VLE); 343 K (□, VLE) and $\{\text{CO}_2(1) + [0.25 \text{ diethanolamine}(2) + 0.75 \text{ ethanol}(3)]\}$ at $T = 313 \text{ K}$ (●, VLE); 343 K (○, VLE) and $\{\text{CO}_2(1) + [0.25 \text{ triethanolamine}(2) + 0.75 \text{ ethanol}(3)]\}$ at $T = 313 \text{ K}$ (★, VLE); 343 K (☆, VLE).

held previously about significant immiscibility of these compounds to $x\text{CO}_2 > 0.4$ at pressures below to 35 MPa. Note that the molecular structure differences of the studied alkanolamines demonstrated to be significant factors to respect to the interaction with CO_2 . Thus, it is clear that increasing the molecular structure of the alkanolamines homologous series increases the immiscibility of the system. The difference between the data obtained can be explained by the interaction between the molecules of CO_2 and alkanolamine. That is, the larger the molecule, the greater its asymmetry, thereby increasing the pressure required to solubilize the system. However, because of the inherent complexity of the system, the thermodynamic modeling of the experimental data using the Peng–Robinson equation for the ternary systems was not carried out because of the complex behavior of the ternary alkanolamines-containing systems considered here.

4. CONCLUSION

This study investigated the solubility of systems $\{\text{CO}_2(1) + \text{ethanolamine}(2) + \text{ethanol}(3)\}$, $\{\text{CO}_2(1) + \text{diethanolamine}(2) + \text{ethanol}(3)\}$, and $\{\text{CO}_2(1) + \text{triethanolamine}(2) + \text{ethanol}(3)\}$ at temperatures of (313–343) K and pressures up to 35 MPa. It has been found that the addition of ethanol allowed the attainment of transition pressure determination of these systems. However, even with addition of ethanol, it was not possible to obtain data from phase transition for molar fractions $x\text{CO}_2 > 0.35$. Therefore, experimental and modeling work of the solubility of these systems for pressures greater than 35 MPa and higher proportions of ethanol is still necessary. However, the data obtained in this work become highly relevant in determining regions of optimal processes of chemical reactions and gas absorption.

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Notes

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