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High pressures phase equilibria of (carbon dioxide + 1-undecanol) system and their potential role in carbon capture and storage

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ABSTRACT

The influence of a large molecular alcohol on thermodynamic phase behaviour is investigated for its potential use in CCS. New isothermal (vapour + liquid) equilibria and (vapour + liquid + liquid) equilibria data for the (carbon dioxide + 1-undecanol) system are reported at several temperatures (303.15, 313.15, 323.15, and 333.15) K and pressures up to 15 MPa, together with the pressure–temperature data of the three phases (liquid + liquid + vapour) equilibrium curve up to the upper critical endpoint. A static-analytical method with phases sampling was used. The experimental results of this study are compared with literature data when available, and discussed. The new data and all available literature data for the (carbon dioxide + 1-undecanol) binary system are modelled with three cubic equations of state, namely the General Equation of State, Peng–Robinson, and Soave–Redlich–Kwong with classical van der Waals mixing rules. The aforementioned EoS were used to model the phase behaviour of the (carbon dioxide + 1-undecanol) binary system (critical curves, the three phases equilibrium curve, isothermal VLE, and (vapour + liquid + liquid) equilibria, using a semi-predictive approach. The calculations results are compared to the new data reported in this work and to all available literature data. The results show a satisfactory agreement between the models and the experimental values.

1. Introduction

In the last decade the hottest topic is carbon dioxide mitigation as a possible way to reduce the impact of global warming and climate change on future generations. One of the most important means to reduce the carbon dioxide emissions is the carbon capture and storage (CCS) [1]. Various aspects of CCS (CO_2 capture, separation, transport, storage, leakage, monitoring, and life cycle) are reviewed and discussed in numerous papers [2]. Among others, researchers are investigating the ability of different substance to dissolve carbon dioxide [3] or the influence of large molecules on thermodynamic behaviours of gas hydrates, knowing their potential use in CCS [4]. In addition, Hendriks et al. [5] stated that "there is an acute need for high-quality experimental data for both thermodynamic and transport properties, including the phase and chemical equilibrium". Therefore, in this work we made the first step and we investigate the high pressures phase behaviour of the (carbon dioxide + 1-undecanol) system. This particular alcohol was chosen as it has been investigated less. Thus, Scheidgen [6] measured the critical curve between T = (312.28 and 392.85) K and pressures up to 99.48 MPa, Pöhler [7] measured several isotherms, but at pressures higher than 10 MPa, Lam et al. [8] have reported the upper critical endpoint (UCEP) of the (vapour + liquid + liquid) three phase equilibrium curve (LLV) and the (solid + vapour + liquid + liquid) (SLLV) quadruple point (Q-point), and Artal et al. [9] have measured the pressures, compositions, and densities of the vapour phase at T = 323.15 K. Another reason for selecting this system is that the (carbon dioxide + 1-undecanol) is type III phase behaviour, according to the classification of van Konynenburg and Scott [10] or Privat and Jaubert [11].

(Vapour + liquid) equilibria (VLE) and (vapour + liquid + liquid) equilibria (VLLE) data for the (carbon dioxide + 1-undecanol) system were measured at T = (303.15, 313.15, 323.15, and 333.15) K and at pressures up to 15 MPa, as well as the pressure–temperature data up to the upper critical endpoint (UCEP) for the three phases equilibrium curve.

The second goal of this work was to represent the complex phase behaviour of this system with a simple model, using semi-predictive procedures. The equations of state (EoSs) models are

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TABLE 1
Provenance and mass fraction purity of the materials used.

Compound	Chemical formula	Source	Purification method	Minimum mass fraction purity
Carbon dioxide	CO_2	Linde Gaz Romania	None	>0.999
1-Undecanol	$C_{11}H_{24}O$	Sigma–Aldrich	None	⩾0.990

TABLE 2
Critical values (T_c, P_c, V_c), acentric factor (ω), and GEOS parameters (α_c, m) for pure compounds.

Compounds	T_c/K	P_c/MPa	V_c/cm^3 · mol^{-1}	ω	α_c	m
Carbon dioxide	304.21	7.383	93.90	0.2236	7.0517	0.3146
1-Undecanol	703.60	2.147	715.0	0.6247	8.8368	0.7953

TABLE 3
The critical compressibility factor (Z_c), and GEOS parameters (B, Ω_a, Ω_b, Ω_c, Ω_d).

EoS	GEOS		PR	SRK
Substance	CO_2	1-Undecanol	CO_2, 1-undecanol	CO_2, 1-undecanol
B	0.1785	0.1864	0.2296	0.2467
Z_c	0.2741	0.2624	0.3074	0.3333
Ω_a	0.5545	0.5386	0.4572	0.4275
Ω_b	0.0956	0.0760	0.0778	0.0866
Ω_c	−0.0483	−0.0421	−0.0121	−0.0187
Ω_d	−0.1367	−0.1444	−0.0778	−0.0434

the most common approach for the correlation and prediction of phase equilibria and properties of the mixtures. In particular, the cubic EoSs remain the preferred tool, as they are capable of describing even complex systems like petroleum fluids, as recently it was shown [12].

The cubic General Equation of State (GEOS) [13,14], Peng–Robinson (PR) [15], and Soave–Redlich–Kwong (SRK) [16] EoSs coupled with classical van der Waals (two parameters conventional mixing rules, 2PCMR) were used in this study to model the (carbon dioxide + 1-undecanol) system. These EoSs have the capability to represent the complex phase behaviour (critical curves, equilibrium LLV line, isothermal VLE and VLLE, isobars) of the (carbon dioxide + 1-undecanol) system, using a semi-predictive approach. The calculations results are compared to the new values reported in this work, and to all available literature data.

2. Experimental

2.1. Materials

Carbon dioxide (mass fraction purity >0.999) was provided by Linde Gaz Romania, and 1-undecanol (mass fraction purity >0.990) was a Sigma–Aldrich product, as presented in table 1. The chemicals were used without further purification, except for drying and degassing of 1-undecanol. The purity of the alcohol was also checked and confirmed by gas chromatograph analysis.

2.2. Apparatus and procedure

A detailed description of the experimental apparatus used for phase equilibrium measurements was presented in earlier papers [17,18]. The apparatus used in this work is based on the static-analytical method with liquid(s) and vapour phases sampling. The main component is the high pressures visual cell with constant volume, built by SEPAREX Supercritical Fluid Technology, project 4261 type SC350 [19]. The visual cell consists of a sapphire tube, closed by two metallic lids, which provides a complete view of the full cell volume. The cell is placed on a thermostation, has a protection jacket, and is equipped with appropriate instrumentation, such as pressure gauge and thermocouple for the accurate measurements of pressure and temperature. The temperature of the cell is controlled by a circulatory thermostat (Lauda E 110) connected to the heating jacket. The setup was completed with a syringe pump Teledyne ISCO model 500D.

The working procedure is the same as described previously [17,18]. The entire internal loop of the apparatus, including the equilibrium cell, is rinsed several times with carbon dioxide, followed by emptying with a vacuum pump. Then the cell is charged with liquid (in this case 1-undecanol), and it is slightly pressurized with carbon dioxide to the desired pressure, using the syringe pump. The next operation is to heat cell to the experimental temperature and keep it constant. The mixture in the cell is stirred for several hours, to facilitate the approach to an equilibrium state.

TABLE 4
Mole fraction of component 1 in the liquid 1 phase, $x_{1,L1}$, mole fraction of component 1 in the liquid 2 phase, $x_{1,L2}$, and mole fraction of component 1 in the vapour phase, y_1 at T = 303.15 K and at various pressures, p, for the binary system {carbon dioxide (1) + 1-undecanol (2)}.[a]

p/MPa	$x_{1,L1}$	$u_c(x_{1,L1})/x_{1,L1}$	$x_{1,L2}$	$u_c(x_{1,L2})/x_{1,L2}$	y_1	$u_c(y_1)/y_1$
			T/K = 303.15 ± 0.1			
1.622	0.2847	0.010			0.9918	0.014
1.746	0.2993	0.010			0.9923	0.014
1.854	0.3036	0.010			0.9927	0.014
2.661	0.3517	0.010			0.9941	0.014
2.834	0.3599	0.010			0.9949	0.015
2.961	0.3659	0.010			0.9948	0.015
3.910	0.4147	0.011			0.9946	0.015
4.068	0.4245	0.011			0.9947	0.015
4.764	0.4619	0.011			0.9946	0.015
4.874	0.4672	0.011			0.9946	0.015
5.601	0.5026	0.011			0.9943	0.014
5.711	0.5045	0.011			0.9945	0.015
6.997	0.5369	0.011			0.9935	0.014
7.003	0.5371	0.011			0.9941	0.014
7.068	0.5394	0.011			0.9939	0.014
7.185	0.5416	0.011	0.9900	0.014	0.9940	0.014
7.955	0.5614	0.011	0.9919	0.014		
8.220	0.5669	0.011	0.9927	0.014		
8.825	0.5704	0.011	0.9925	0.014		
9.011	0.5708	0.011	0.9924	0.014		
9.334	0.5716	0.011	0.9918	0.014		
9.826	0.5727	0.011	0.9916	0.014		
10.097	0.5746	0.011	0.9912	0.014		
10.127	0.5752	0.011	0.9917	0.014		
10.405	0.5766	0.011	0.9914	0.014		
10.468	0.5771	0.011	0.9913	0.014		
10.744	0.5788	0.011	0.9918	0.014		
11.771	0.5804	0.011	0.9911	0.014		
12.191	0.5826	0.011	0.9914	0.014		
13.480	0.5848	0.011	0.9913	0.014		
14.957	0.5868	0.011	0.9911	0.014		

[a] $u(T)$ = 0.1 K, $u(p)$ = 0.01 MPa, $u_c(x_{1,L1})/x_{1,L1}$ = 0.0106, $u_c(x_{1,L2})/x_{1,L2} = u_c(y_1)/y_1$ = 0.0145.