Solubility of Tridodecylamine in Supercritical Carbon Dioxide

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Using a continuous flow apparatus, the solubility of tridodecylamine (TDA) in supercritical CO_2 ($scCO_2$), have been measured at temperatures of 308, 318, and 328 K in the pressure range of (8-40) MPa and a flow rate of 150 ± 10 mL min^{-1}. At 308 and 318 K the solubility increases with pressure up to 15 MPa where it reaches a plateau. At 328 K the solubility increases with pressure up to 35 MPa and then a plateau is observed. The solubility data were correlated using Bartle equation and Mendez-Santiago and Teja model. Mendez-Santiago and Teja model correlated the solubility data better than the Bartle equation. TDA may be considered as a highly soluble compound in $scCO_2$.

Keywords: Solubility; Tridodecylamine; Supercritical Carbon Dioxide; Bartle equation, Mendez-Santiago and Teja model.

Introduction

In recent years, many supercritical fluids (SCFs) have been used as useful solvents in many applications, such as in polymer [1, 2], food [3], and pharmaceutical processing [4], performing chemical reactions and separations [5, 6]. Among different SCFs, $scCO_2$ has been widely used, because it is nonflammable, nontoxic, inexpensive, environmentally safe, and it has low critical temperature and pressure. Recently, $scCO_2$ modified by suitable chelating agents has been used to develop new techniques for the extraction of transition metal ions from various solid and liquid matrices [7, 8].

The solubility data of solids and liquids in SCFs are very important in developing any supercritical extraction process. Solubility of numerous solutes in a number of SCFs are now available in the literature [9, 10] and several methods have been developed in order to correlate and extrapolate solubility data at various pressures and temperatures. Some of these correlation methods are highly empirical, while others are based on fundamental equation of states [11, 12].

Reactivity of CO_2 is generally low, but it does reacts with primary and secondary amines at low temperatures and pressures to form carbamates. The chemistry between CO_2 and amines is simply acid–base equilibrium [13, 14]. On the other hand, aliphatic tertiary amines dissolved in an organic solvent are powerful extractants for carboxylic acids and can be used in reactive extraction processes for recovery of solutes like phenol, aniline, and some carboxylic acids[15]. For example, tridodecylamine (TDA) was used as the extractant for the recovery of shikimic and quinic acids [16].

Tertiary amines with long hydrocarbon chains, such as trioctylamine (TOA) and TDA, have been used in the extraction of metals such as platinum and ruthenium [17]. A variety of organic chelating agents, such as crownethers, dithiocarbamates, β-diketones, and tributylphosphates have been used for the extraction of metal ions from various solvents by using supercritical solvents [18, 19, 20].

The motivation for this work stems in our interest in the chemical separation of dicarboxylic acids and precious metals using $scCO_2$. Since tertiary amines are not reacted with $scCO_2$, its solubility can be measured to evaluate its applicability for the reactive chemical separation using $scCO_2$. To the best of our knowledge, the solubility of TDA in $scCO_2$ has not been previously reported. Therefore, the solubility of TDA was measured at different pressures and temperatures to evaluate the applicability of TDA for chemical separation of dicarboxylic acids and precious metals using $scCO_2$. The research is in progress in our laboratory to use tertiary amines for the extraction of carboxylic acids and metals from aqueous media using ion-pair formation and $scCO_2$ as a green solvent.

Experimental

Materials

TDA with purity > 95% was purchased from Merck Co. The purity of CO_2 was more than 99.95 mass% and were purchased from Zam Zam Co. (Isfahan, Iran). All of the chemical reagents were used without any further purification.

Apparatus and procedure

The solubility measurements were carried out using a continuous flow apparatus as shown in Fig. 1. Detailed description of the apparatus and experimental procedure was reported elsewhere [21].

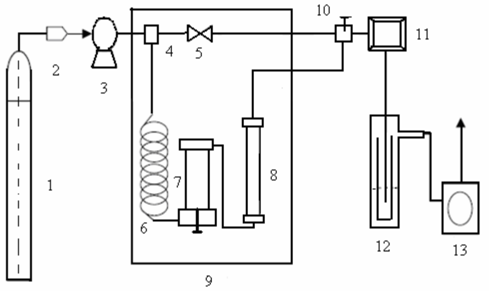

Fig. 1. Schematic of the experimental apparatus used for measurement of the solubility in the supercritical fluid. (1) CO_2 cylinder, (2) chiller, (3) HPLC pump; (4) three-way connector, (5) needle valve (6) preheating coil; (7) a three-port equilibrium vessel, (8) a two–port equilibrium cell (9) oven, (10) three-way needle valve, (11) back pressure regulator, (12) collection tube, (13) wet gas meter.

In each experiment 2.0 ± 0.1 mL of TDA was placed in equilibrium cell, which was filled with Pyrex wool. At the beginning of each experiment, the system was kept at the desired temperature and pressure for 45 min (i.e. static condition) to reach equilibrium. After that, at a constant and low flow rate, to assure that all experiments carried out at equilibrium and saturation condition, the saturated $scCO_2$ was depressurized via a BPR. Using the constant flow rate mode of the piston pump, constant pressure (±0.1 MPa) was maintained by BPR. The volume of CO_2 was determined using a wet gas meter. To ensure that saturation and equilibrium condition has been reached, the solubility of TDA was measured at 318 K and 22 MPa at various flow rates of $scCO_2$ from 80 to 610 mL/min. Since constant solubilities (i.e. 0.1150 ± 0.0028 g_{TDA}/L_{CO2}) were observed, it was concluded that the saturation and equilibrium condition has been reached. Therefore, the flow rate of 150 ± 10 mL/min was selected for the other measurements.

For binary solubility measurements, the dissolved solutes after exiting from the BPR were trapped and collected in a vial filled with Pyrex wool. Finally, the trapped solute weighed with an analytical balance (±0.1 mg). Based on measured solute mass and solvent volume, the solubility in terms g/L and mole fraction were obtained. Having the time of sample collection, and the volume of CO_2 passed through the wet gas meter, the expanded gas flow rate was calculated.. Each reported datum is an average of at least three and maximum four replicate experiments. The percent relative standard deviations of the measurements (%RSD) were generally less than 13 %.

Results and discussion

The solubility data of TDA in $scCO_2$ at different temperatures of 308, 318, and 328 K, in the pressure range of (8-40) MPa were measured, as shown in Table 1 and Fig. 2. The solubility of TDA in $scCO_2$ was calculated as mole fraction (y_2) and g_{TDA} per L of expanded CO_2 gas (S). The experimental results were correlated using Bartle, and Mendez-Santiago and Teja equations.The solubility of TDA in $scCO_2$ increases with pressure while showing different trends at different temperatures. At 308 and 318 K, the solubility increases with pressure up to 15 MPa where it reaches a plateau. At 328 K the solubility increases with pressure up to 35 MPa and then a plateau is observed.

The solubility in $scCO_2$ is strongly influenced by the system pressure, which determines the density of the $scCO_2$ as a solvent [22]. Crossover points in Fig. 2 are observed for the different isotherms at about 14, 18 and 24 MPa. At the pressures less than the crossover points the solute is more soluble at the lower temperatures, but at the pressures higher than the crossover points the solute is more soluble at the higher temperatures. The crossover point is a consequence of competition between the $scCO_2$ density and TDA vapor pressure. At pressures lower than the crossover pressure, the density effect is dominant, leading to the decrease of the solubility of the solute as a function of temperature. At pressures higher than the crossover pressure, the density of the solvent becomes less effective and the vapor pressure plays a major role in increasing the solubility. The solubility of TDA increases with increasing pressure at constant temperature. Influence of pressure on the solubility is more significant at higher temperatures because of the effect of vapor pressure. Therefore, the solubility of TDA in $scCO_2$ increases with pressure.

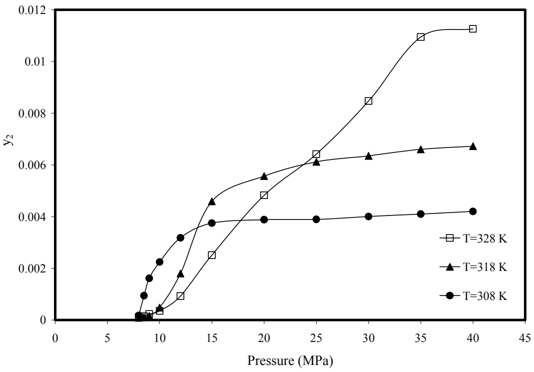

Fig. 2 Solubility of TDA (y_2) in the pressure range of (8-40) MPa and temperatures of 308 K (□), 318 K (●), and 328 K (Δ).

Temperature affects the solubility in two opposite ways; the density of the fluid decreases with increasing temperature, which leads to the lower solubility at the higher temperatures while the volatility of the solute increases with temperature and an increase in the solubility is observed at the higher temperatures. The density effect is dominant at the lower temperatures and the solubility increases at the lower temperatures. At the higher pressures, the density of CO_2 is not as sensitive to the pressure as it is at the lower pressures, and the volatility effect becomes dominant and the solubility increases at the higher temperatures. The solubility trend at 328 K is different and increased with pressure until 35 MPa.

The experimental results from the present study were correlated by two different density-based correlation models proposed by Bartle [23], and Mendez-Santiago and Teja [24]. The Bartle equation is given as:

$$Ln\left(\frac{y_2.p}{p_{ref}}\right) = A + C(\rho - \rho_{ref}) \tag{1}$$

where, A is given by equation 2, y_2 is the mole fraction solubility, p is the system pressure (MPa), A and C are constants, P_{ref} is the standard pressure (i.e. 0.1 MPa), ρ is the density of $scCO_2$, and ρ_{ref} is the reference density for which a value of 700 $kg.m^{-3}$ was used for calculations. The reason of using ρ_{ref} is to make the value of A much less sensitive to the data experimental error and to avoid the large variations caused by extrapolation to zero density [25].

$$A = a + \left(\frac{b}{T}\right) \tag{2}$$

TDA experimental solubility data were fitted by Equation 1, i.e. the Ln (y2.P/Pref) values versus ρ for the pressure range studied. The value of C, i.e. the slope of the line fitted into the data, is constant

Table 1. TDA solubility in mole fraction (y_2), in g_{TDA} per L of expanded CO_2 gas (S) and the density of $scCO_2$[a] (kg .m^{-3}) at temperatures of 308 K, 318. K and 328 K and pressure range of (8-40) MPa

	P (MPa)	100.y_2	100.S (g_{TDA}/L_{CO2})	$scCO_2$ Density (kg .m^{-3})
T=308 K	8.0	0.018 ± 0.002	0.33 ± 0.03	419.09
	8.5	0.094 ± 0.008	1.75 ± 0.15	612.12
	9.0	0.161 ± 0.012	3.00 ± 0.20	662.13
	10.0	0.225 ± 0.021	4.17 ± 0.38	712.81
	12.0	0.318 ± 0.036	5.91 ± 0.66	767.07
	15.0	0.375 ± 0.035	6.97 ± 0.65	815.70
	20.0	0.388 ± 0.025	7.22 ± 0.47	865.72
	25.0	0.389 ± 0.033	7.24 ± 0.62	901.23
	30.0	0.400 ± 0.042	7.45 ± 0.78	929.11
	35.0	0.410 ± 0.033	7.63 ±0.60	952.29
	40.0	0.420 ± 0.038	7.82 ± 0.70	972.26
T=318 K	8.0	0.008 ± 0.001	0.16 ± 0.02	241.05
	8.5	0.011 ± 0.002	0.21 ± 0.02	281.81
	9.0	0.015 ± 0.002	0.29 ± 0.03	337.51
	10.0	0.048 ± 0.006	0.89 ± 0.11	498.25
	12.0	0.180 ± 0.013	3.34 ± 0.24	657.74
	15.0	0.459 ± 0.046	8.54 ± 0.87	741.97
	20.0	0.556 ± 0.050	10.37 ± 0.94	812.69
	25.0	0.612 ± 0.032	11.41 ± 0.59	857.14
	30.0	0.635 ± 0.057	11.84 ± 1.07	890.33
	35.0	0.660 ± 0.066	12.31 ± 1.23	917.12
	40.0	0.672 ±0.047	12.50 ± 0.90	939.75
T=328 K	8.0	0.011 ±0.001	0.21 ± 0.01	203.64
	8.5	0.015 ± 0.002	0.27 ± 0.03	227.84
	9.0	0.023 ± 0.004	0.43 ± 0.07	255.55
	10.0	0.036 ±0.005	0.66 ± 0.07	325.07
	12.0	0.093 ± 0.013	1.72 ± 0.24	504.51
	15.0	0.251 ± 0.031	4.66 ± 0.50	635.50
	20.0	0.482 ± 0.041	8.98 ± 0.77	754.61
	25.0	0.641 ± 0.050	11.96 ± 0.94	810.65
	30.0	0.847 ± 0.077	15.83 ± 1.44	850.22
	35.0	1.094 ± 0.098	20.50 ± 1.84	881.17
	40.0	1.126 ± 0.090	21.10 ± 1.70	906.77

a Taken from http://webbook.nist.gov/chemistry/fluid/.

over the temperature range of (308-328) K as shown in Fig. 3. The error of the experimentally measured solubility and the solubility given by the Bartle equation was estimated by calculating the average absolute relative deviation (AARD) between the experimental and the calculated solubility data using the following equation: where, *n* is the number of solubility experimental data.

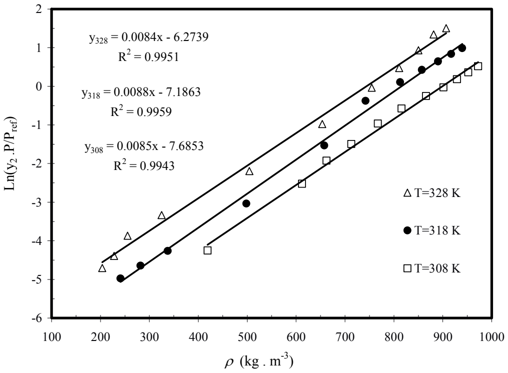

Fig. 3 Correlation plots of Ln (y_2.P/P_{ref}) vs. ρ (kg m^{-3}) for TDA in the pressure range of (8-40) MPa and the temperatures of 308 K (□), 318 K (●), and 328 K (Δ) using Bartle equation. The linear regression equations and the R^2 for different traces are shown on the graph.

$$AARD\ (\%) = \frac{1}{n} \Sigma \left| \frac{y_{2(\exp)} - y_{2(calc)}}{y_{2(\exp)}} \right| \times 100 \tag{3}$$

Finally, Mendez-Santiago and Teja model that is based on the simple theory of dilute solutions was used [24]. According to this model, all the mole fraction solubilities at different temperatures fit in a single straight line when plotted using equation 4. In this model, y_2 is the mole fraction solubility of the solute in the $scCO_2$; ρ_1 is the density of the $scCO_2$; T and P are the operating temperature and pressure; A, B, and C are constants obtained by a multiple linear regression of the experimental solubility data.

$$T \cdot Ln(y_2 \cdot P) = A + B\rho_1 + CT \tag{4}$$

Data in Table 1 was correlated as a function of the absolute temperature (T) and pressure (P) of the system, and the density of the $scCO_2$ (ρ) using the model of Mendez-Santiago and Teja . Then, Best-fit values of the model parameters *(*A = -9203 K*,* B = 2.805 K.L/g, and *C* = 21.74*)* for the solubility of TDA in $scCO_2$ are presented with the line equation of y = 2.8047 x – 9203.6, $R^2 = 0.9964$.

The two semi-empirical equations presented by Chrastil and Mendez-Santiago and Teja are commonly employed to correlate the solid solubility in $scCO_2$. However, the TDA solubility at different temperatures indicate that isotherms of 308, 318, and 328 K collapse to a single line and can linearly correlate the data so that A and B are independent of temperature as predicted by Mendez-Santiago and Teja model. While at these temperatures and pressures, the Chrastil equation did not correlate the solubility data of TDA as good as Mendez-Santiago and Teja model. For solubility data up to medium pressures of 20 MPa one can apply the Chrastil method, a purely phenomenological model, which is based on some rather physical arguments and gives a linear relation between the logarithm of the solvent density and solubility.

In Table 2, slope (C), intercept, R^2, and AARD (%) are given for the Bartle equation at different temperatures and the pressure range of (8-40) MPa. Because of having better correlation coefficients (R^2) obtained by the Mendez-Santiago and Teja model in comparison with the Bartle model we may concluded that our data is better correlated by the Mendez-Santiago and Teja model in the pressure range of (8–40) MPa. Finally, the high solubility of TDA in $scCO_2$ especially at high pressures and temperatures makes the system very attractive for the various separation processes listed in the introduction section.

Table 2. Intercept, slope (C) and AARD (%) of Bartle equation at TDA different temperatures and in pressure range of (8-40) MPa for the data shown in Fig. 3.

T (K)	n^a	C	Intercept	R^2	AARD^b (%)
308	11	0.0085	- 7.68	0.9943	13.63
318	10	0.0088	- 7.19	0.9959	12.86
328	10	0.0084	- 6.27	0.9951	9.07

[a] Number of data points used in the correlation.
[b] Average absolute relative deviation.

Conclusions

Solubility of TDA in scCO_2 was measured in the pressure range of (8–40) MPa at different temperatures of 308, 318, and 328 K. The data of different temperatures were correlated by semi-empirical Bartle equation and Mendez-Santiago and Teja model. Among which the Mendez-Santiago and Teja model was able to better correlate the solubility data. Generally, the solubility of TDA in scCO_2 may be considered high; especially at 328 K and pressures above 30 MPa.

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