Extraction of Maleic acid and Phthalic acid by Ion-Pair Formation Using Trioctylamine in Supercritical Carbon Dioxide

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Abstract

Using a continuous flow apparatus, extraction of maleic acid and phthalic acid by dissolved trioctylamine in supercritical carbon dioxide (scCO$_2$) from their mixture, have been performed at temperatures of 308, 318, and 328 K in the pressure range of (100-350) bar and flow rate of 0.2 mL/min liquid CO$_2$ flow rate. Since organic acids are polar compounds and can hardly be extracted by scCO$_2$, a reactant which increases the solubility of acids by an ion-pair formation reaction was used.

Trioctylamine were used as a reactant and acids were extracted by acid-amine ion pair formation. The solubility of acids in scCO$_2$ is very low. The extraction yield of maleic acid and phthalic acid at temperatures of 308, 318, and 328, increased with pressure up to 250 and 200 bar, respectively, where it reaches a plateau. The amount of extraction of maleic acid by trioctylamine in scCO$_2$ increased with pressure and was found higher than the amount of phthalic acid extracted. The amount of acid extracted was increased with temperature too.

The amount of extracted acids by dissolved trioctylamine in scCO$_2$ was much higher than the solubility of them in neat scCO$_2$. Moreover, the extraction selectivity of maleic acid to phthalic acid ($\alpha = y_m/y_p$) of 7.3 was achieved at 318 K and pressure of 250 bar. The extraction method was established as a selective and green method for dicarboxylic acids such as maleic and phthalic acid.

Introduction

Supercritical fluid extraction (SFE) has a great potential as an efficient and clean alternative method compared to the conventional methods of extraction. Supercritical carbon dioxide (scCO$_2$) is the most intensively used solvent due to its low critical point (P$_c$=73 bar, T$_c$=304 K), non-toxicity, inertness, and non-flammability, while remaining an inexpensive and environmentally acceptable substance [1]. The matter of replacing organic liquids with environmentally friendly and green solvents such as scCO$_2$ in various processes is an active area of research. Minimizing liquid waste generation, easy separation of solutes from extraction solvent and tunable solvating power are some of the advantages of using scCO$_2$ for extraction and separation of organic compounds from solid and liquid materials. However, since CO$_2$ is a nonpolar molecule and has a low dielectric constant, scCO$_2$ processing is limited by its poor ability to dissolve polar species [2].

Organic acids are widely used in food products and as starting materials for chemical synthesis [3,4,5]. Solubilities of organic acids in scCO$_2$ are very low, because organic acids are polar and CO$_2$ is nonpolar [6]. Direct extraction of acids with such a low solubility in scCO$_2$ is unlikely to be economically feasible. For increasing the solubility, polar entrainers or reactants can be usually added to the supercritical fluid phase, which increases the acid solubility.

Long-chain aliphatic amines are known to be efficient, selective, and reversible extractants for the separation of carboxylic acids [7,8]. In this work, we report our initial results regarding enhanced dissolution of organic acids such as maleic acid and phthalic acid in scCO$_2$ saturated with trioctylamine as an ion-pair forming reagent. Potential applications of this method for separation of the organic acids were also discussed.

A tertiary amine such as TOA was chosen as a base carrier because CO$_2$ does reacts with primary and secondary amines at low temperatures and pressures to form carbamates [9]. On the other hand, long-chain aliphatic tertiary amines are effective reactants for the separation of carboxylic acids from dilute aqueous solution. Monocarboxylic acids dissolved in an aqueous solution were extracted by trioctylamine (TOA) solution in hexane and tetrachloromethane as a nonpolar solvent and 1-octanol and

chloroform as protic solvents [10]. Extraction equilibrium features of some dicarboxylic acids have also been investigated systematically with TOA in different solvents [11,12,13,14].

Four different major mechanisms have been utilized for the extraction of acids using amine reactants namely anion exchange, ion-pair formation, H-bond formation, and solvation. Hence, extraction of carboxylic acid has in many cases an intermediate between ion-pair and H-bond [15]. Fourier-transform infrared spectroscopic analysis of TOA dissolved in the organic solvents revealed that TOA forms a 1:1 ion-pair association with succinic acid, malic acid, and maleic acid, and 1:1 and 1:2 ion-pair association with fumaric acid [16].

Recently, $scCO_2$ modified by suitable chelating agents has also been used to develop a new technique for the extraction of transition metal ions from various solid and liquid matrices. The most attractive features of this new technology include high solubilities of chelating agents and resultant metal complexes in $scCO_2$ and selectivity of the chelating agents [17]. Since tertiary amines do not react with $scCO_2$, its solubility was measured for its applicability for the reactive chemical separation using $scCO_2$ [18].

Commonly, organic acids are separated and quantified using high performance liquid chromatography (HPLC) [19,20,21,22,23,24] and capillary electrophoresis [25,26]. Although HPLC methods are frequently applied for the analysis of carboxylic acids, gas chromatography (GC) is often preferred, due to its inherent advantage of high resolution, rapid separation, low cost and easy linkage with sensitive detectors. Independent of the pre-concentration and clean-up step, when GC is considered as the separation technique the critical step of the analytical procedure is the derivatization of the analytes. Moreover, the extraction of maleic acid and phthalic acid by $scCO_2$ saturated with trioctylamine ($scCO_2$-TOA) is governed by acid-amine ion-pair formation. The dissociation temperature of the acid-amine ion-pair is high and therefore it could not be injected to GC without any derivatization step.

In this work, SFE followed by the derivatization of the acids in capillary glass tube and analysis with GC-FID was used for the extraction and determination of maleic acid and phthalic acid from their mixture. The effect of pressure and temperature on the amount of extraction, along with the optimization of the derivatization conditions was performed. The work is in progress for using the developed extraction method for the extraction of the acids from petrochemical wastes such as dioctylphthalate process molten phthalic anhydride (PA) and purge water.

MATERIALS AND METHODS

Phthalic acid with purity > 99% was purchased from Hopkin & Williams Co. Maleic acid with purity > 99%, TOA with purity > 93%, dibenzylether with purity > 99.5%, butanol with purity > 99% and with trifluoroacetic anhydride with purity > 99% 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 reagents were used without any further purification.

SFE Apparatus and procedure

The apparatus was used to perform SFE is shown schematically in Figure 1. The major components are the same as the setup reported in our previous works [18,27,28]. In each experiment 2.0 ± 0.1 g of TOA was placed in a three-port cylindrical cell (1st cell), which was filled with Pyrex wool to lower the cell dead volume and to increase the contact surface between the TOA and $scCO_2$. Both the first and the second cell had an inner diameter and length of 1.0 and 10.0 cm. The accuracy of the set flow rate of liquid CO_2 was within ± 2% and its flow rate stability was within ± 0.5%. The oven (model CO-2060 plus, JASCO, Japan) temperature was set within ± 0.1K.

At the beginning of each experiment, the system was kept at the desired temperature and pressure for 30 min (i.e. static condition) to reach equilibrium. The pressure was controlled by backpressure regulator (=BPR, JASCO, model BP 1580-81) to within ±1 bar.
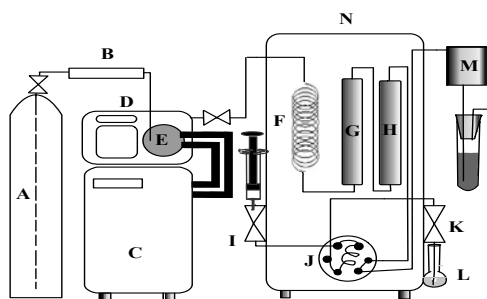
Fig. 1. Schematic diagram of scCO2 extraction system: (A) CO2 tank; (B) molecular sieve filter; (C) cooler; (D) high-pressure HPLC pump; (E) pump head cooler, (F) preheating coil, (G) SFE amine cell; (H) SFE acids cell; (I, K) two-way valves; (J) six-ports/two positions valve with 100 µL loop attached, (L) collecting vial; (M) back-pressure regulator; (N) thermo stated oven.

A 100 µL sampling loop was connected to a 6-port, two-position valve and was used to take samples during the extraction process. Then the loop was depressurized into the collection vial containing butanol through the exit valve that controls the sample depressurization. Finally, the entrance and exit valves were opened completely and the sample loop was washed with neat butanol that is collected into the collection vial. Each reported datum is an average of at least three and maximum six replicate measurements with the percent relative standard deviations (RSD) of generally less than 7%.

After finishing the extraction step, 5 µL of analytes and 2 µL of trifluoroacetic anhydride (TFAA) was injected into the capillary glass tube and mixed well with shaking. After a 20-min derivatization time in 463 K, the sample was injected into the GC.

GC analysis method

The analysis was carried out using a GC-FID. Nitrogen was used as the carrier gas at a constant head pressure of 15 kPa. The components were separated on a 15 m × 0.32 mm i.d., 0.1-µm film thickness OV-1 column (Mega, Legnano, Italy). The injection port temperature was set at 513 K and all injections were made in splitless mode. The column was initially maintained at 343 K for 1 min; subsequently, the temperature was increased to 523 K at a rate of 10 K/min (with 5 min hold).

RESULTS AND DISCUSSION
Derivatization

The derivatizations were performed using standard solutions of maleic and phthalic acid in butanol solvent at concentrations of about 100–5000 mg/L. A 10-µL aliquot of the standard solution of the analytes containing internal standard (i.e. dibenzyl ether) was injected into the capillary glass tube using a micro syringe and then a 4 µL of trifluoroacetic anhydride (TFAA) was added and well mixed by shaking. After derivatization in 463 K for 20 min, 2 µL of the sample was injected into the GC.

To optimize the derivatization conditions, three parameters, i.e. the amount of TFAA, the reaction time, and reaction temperature, were optimized. The effect of the reagent volume (1 to 6 µL TFAA), the derivatization time (from 5 to 30 min), and the derivatization temperature (323 to 493 K) on the yield of the esterification of the analytes was investigated. The derivatization reaction is complete in 20 min at 463 K. Moreover, the optimum time of 20 min was chosen as the reaction time and TFAA volume of 4 µL was chosen as the optimum volume. Finally, after each SFE experiment, derivatization was performed at 463 K for 20 min using a TFAA volume of 4 µL and 10 µL of analyte.

The effect of pressure on the extraction of maleic acid and phthalic acid using scCO₂-TOA

The solubility data of TOA in scCO₂ at different temperatures and in the pressure range of (80-400) bar were reported elsewhere [18]. In this work, the extraction of maleic and phthalic acids with scCO₂-TOA at different temperatures and pressures were investigated. The experimental results are listed in Table 1 in terms of the equilibrium mol fraction, y, and g of the solutes per liter of scCO₂, S. The amounts of maleic acid extracted with scCO₂-TOA at different temperatures of 308, 318, and 328 K increases with pressure up to 250 bar where it reaches a plateau. The amount of phthalic acid extracted

at different temperatures of 308, 318, 328 K increases with pressure up to 200 bar where it reaches a plateau.

Table 1 Amount of maleic acid and phthalic acid extracted in mole fraction (y), and in g acid per L of scCO$_2$ (S) at temperatures of 308, 318 and 328 K and pressure range of (100-350) bar.

Temperature (K)	Pressure (bar)	Maleic acid		Phthalic acid	
		$10^5 \times y$	$10 \times S$ (g/L)	$10^5 \times y$	$10 \times S$ (g/L)
308	100	7.00 ± 0.59	1.32 ± 0.11	4.14 ± 0.31	1.10 ± 0.08
	150	9.35 ± 0.65	2.01 ±0.14	3.85 ± 0.29	1.17 ± 0.09
	200	12.18 ± 0.39	2.78 ± 0.09	12.45 ± 0.68	4.02 ± 0.22
	250	94.46 ± 3.95	22.46 ± 0.98	12.95 ± 0.80	4.35 ± 0.27
	300	91.17 ± 2.37	22.48 ± 0.59	12.73 ± 0.61	4.41 ± 0.21
	350	90.05 ± 2.79	22.61 ± 0.70	12.31 ± 0.48	4.37 ± 0.17
318	100	10.98 ± 0.69	1.44 ± 0.09	4.03 ± 0.32	1.12 ± 0.06
	150	11.65 ± 0.61	2.28 ± 0.12	4.27 ± 0.25	1.18 ± 0.07
	200	20.06 ± 1.54	4.30 ± 0.33	13.63 ± 0.86	4.13 ± 0.26
	250	110.26 ± 5.58	24.94 ± 1.26	14.27 ± 1.01	4.56 ± 0.32
	300	118.94 ± 5.11	27.94 ± 1.20	14.20 ± 0.72	4.71 ± 0.24
	350	120.51 ± 5.79	29.17 ± 1.40	14.13 ± 0.82	4.83 ± 0.28
328	100	17.39 ± 0.70	1.49 ± 0.06	4.52 ± 0.72	1.12 ± 0.09
	150	13.51 ± 0.52	1.61 ± 0.09	4.93 ± 0.33	1.20 ± 0.80
	200	31.89 ± 1.45	6.35 ± 0.29	14.79 ± 0.82	4.19 ± 0.23
	250	133.95 ± 6.82	28.68 ± 1.23	15.35 ± 0.99	4.64 ± 0.30
	300	131.91 ± 3.83	29.60 ± 1.53	15.49 ± 0.92	4.91 ± 0.29
	350	139.43 ± 3.19	32.43 ± 0.79	15.07 ± 0.55	4.95 ± 0.18

The extraction of maleic and phthalic acid strongly depends on the operating pressure as shown in Table 1 and Figures 2-3. The solutes solubility increases with an increase in pressure at constant temperature. When the pressure increases, carbon dioxide density increases and the intermolecular mean distance between the solute and solvent molecules decreases and the solvating power of solvent increases [29]. Moreover, the solubility of TOA in scCO$_2$ increases with an increase in pressure [26] so with increasing the amount of TOA in scCO$_2$, the interaction between the acids and the solvent saturated from TOA will also be increased.
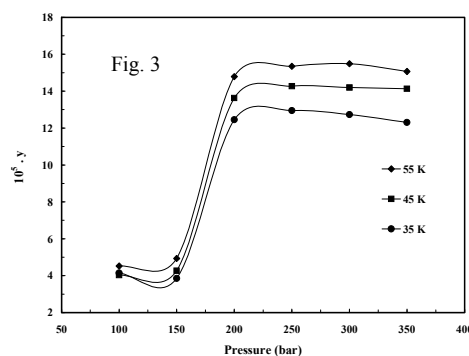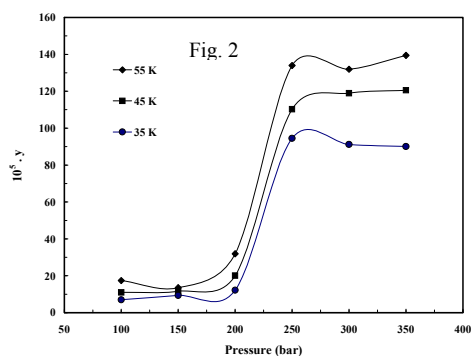

Fig. 2. Effect of pressure on the extraction of maleic acid in the pressure range of (100-350) bar and temperatures of 308 K (●), 318 K (■), 328 K (♦).
Fig. 3. Effect of pressure on the extraction of phthalic acid in the pressure range of (100-350) bar and temperatures of 308 K(●), 318 K (■), 328 K (♦)

The effect of temperature on the extraction of maleic acid and phthalic acid in scCO$_2$-TOA

According to the Figures 4-5, the extraction of maleic and phthalic acids increases with an increase in temperature. An isobaric increase of the temperature usually decreases the solvent density and increases the vapor pressure of the solute. Since, the extraction has increased with temperature the increase in the vapor pressure of solute has played a major role in the solubility of the solute in *scCO$_2$-TOA*. On the other hand, the solubility of TOA in scCO$_2$ increases with an increase in temperature [26]. The influence of pressure on the process of maleic and phthalic acid extraction by scCO$_2$-TOA is more than the temperature.
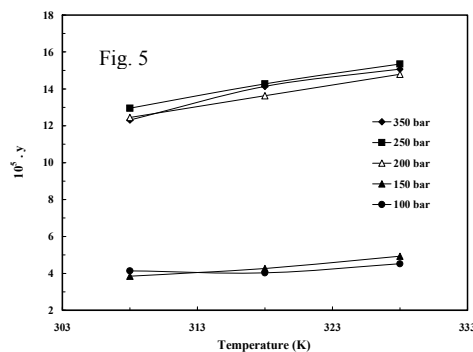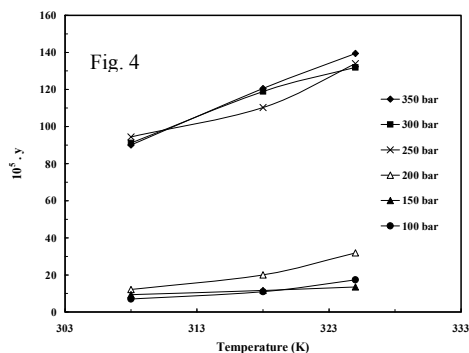
Fig. 7. Effect of temperature on the extraction of maleic acid in the pressure range of (100-350) bar.
Fig. 8. Effect of temperature on the extraction of phthalic acid in the pressure range of (100-350) bar.

Selectivity

The selectivity (α) of the scCO$_2$-TOA for a pair of components may be defined in terms of the ratio of the extracted solutes mole fraction as follows [30]:

$$\alpha = \frac{y_1}{y_2} \qquad (1)$$

where y_1 and y_2 are the mole fractions of the solutes extracted for more and less soluble components in the *scCO$_2$-TOA*, respectively. As shown in Table 1, the solubility of maleic acid is larger than that of phthalic acid at all conditions investigated. The selectivity of scCO$_2$-TOA for the solutes as a function of pressure is shown in Figure 6. At low pressures of (100-200) bar, the selectivity is low while at higher pressures, the selectivity increases sharply and leveled off to a constant value so that the extraction selectivity of maleic acid to phthalic acid of 7.3 was achieved at 318 K and pressure of 250 bar. On the other hand, as is shown in Figure 7, the selectivity increases smoothly with temperature. This result indicates that the selectivity of scCO$_2$-TOA for the extracted components in a mixture of organic solids is related primarily to the solute vapor pressure and only secondarily to intermolecular forces in the scCO$_2$ phase [31].
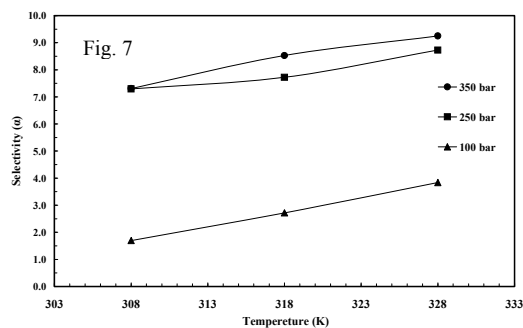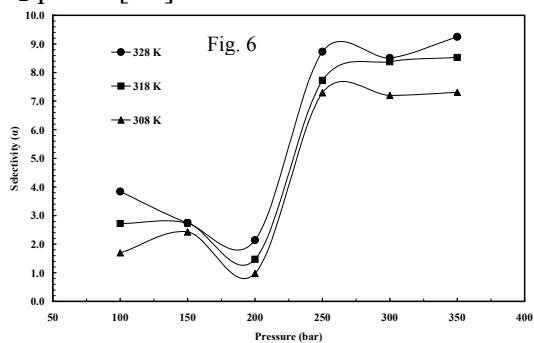

Fig. 6. Variation of the selectivity with pressure in temperature of 308 K (▲), 318 K (■), and 328K (●).
Fig. 7. Variation of the selectivity with temperature in the pressure of 100 bar (▲), 250 bar (■), and 350 bar (●)

Conclusion

The solubility of organic acid such as maleic and phthalic acid was very much increased in scCO$_2$ saturated from TOA as an ion-pair forming reagent. A new extraction method was proposed for the extraction of dicarboxylic organic acids by long chain tertiary aliphatic amines dissolved in scCO$_2$. The extraction data of maleic and phthalic acids by scCO$_2$-TOA are presented at 308, 318, and 328 K, in the pressure range of (100-350) bar. The highest value of maleic acid and phthalic acid extraction was obtained at 350 bar and 55$^{\mathrm{o}}$C as of 3.243 ± 0.074 and 0.495 ± 0.018 equilibrium mol fraction, respectively. Experimental results show that maleic acid has a higher solubility owing to its relatively

low melting point and higher vapor pressure. The experimental data showed that higher temperature and higher pressure is more favorable for the selective extraction of the dicarboxylic acids.

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