Solubility of Ethanamide and 2-Propenamide in Supercritical Carbon Dioxide. Measurements and Correlation[†]

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Solubilities of ethanamide (acetamide) and 2-propenamide (acrylamide) in supercritical carbon dioxide were measured at $T = (308.2, 318.2, \text{and } 333.2)$ K over the pressure range (9.0 to 40.0) MPa by a flow-type apparatus. The solubility of acetamide ($2.3 \cdot 10^{-4}$ to $31.3 \cdot 10^{-4}$) in the overall region of measurements is approximately twice that of acrylamide ($1.2 \cdot 10^{-4}$ to $16.3 \cdot 10^{-4}$). The solubility of both components increases with pressure, and the relative location of the crossover region is observed at about 12.0 MPa. The experimental data were correlated by using the Soave−Redlich−Kwong equation of state (EoS) with the one-fluid van der Waals mixing rule. In addition, the pure compound properties required for the modeling were also estimated.

Introduction

In pure form, both acetamide (ethanamide) and 2-propenamide (acrylamide) are white crystalline solids. Acetamide, the amide of acetic acid, is a product of the bacterial degradation of nitrile compounds such as acetonitrile[1] and is used in the varnish, cosmetics, explosives, textile, and pharmaceutical industries. Other diverse applications include its use as an additive in peroxides and as a raw material in organic synthesis.[2]

Acrylamide, a possible carcinogen, has been found in various heat-processed foods.[3] Many original papers have reported findings on the formation mechanism and possible reduction methods of acrylamide. In a recent contribution, the state-of-the-art of acrylamide formation and reduction in the Maillard reaction is summarized.[4] The review discusses primary mechanisms as well as reduction pathways including material and processing related ways and the use of exogenous chemical additives.

Starch undergoes chemical modification via its reaction with acrylamide, and this reaction has been thoroughly studied.[5] Other important reactions of the compound have also been examined, namely, selective Baylis−Hillman reactions between acrylamide and a range of aromatic aldehydes in different solvent media in which nucleophilic catalysts promote hydroalkoxylation preferentially.[6,7] The optimization of the reaction conditions has allowed achieving reasonable yields of the above reactions.

The importance of the two compounds and their applications results in part from the chemical structure of acetamide and acrylamide—they both have an amide bond, similar to the essential bond between amino acids in proteins.

This study is devoted to the experimental measurement and the thermodynamic modeling of the solubility of acetamide and acrylamide in supercritical carbon dioxide (SC CO_2), which, to the best of our knowledge, has not been reported in the literature until present.

The measurements were carried out in the temperature range (308 to 333) K and at pressures ranging from (9 to 40) MPa. The Soave−Redlich−Kwong cubic equation of state (SRK CEoS) with the one-fluid van der Waals mixing rule was applied to calculate the solubility of both components. In addition, the thermophysical properties of acrylamide and acetamide required for the modeling, but not available, were estimated and also reported.

Experimental Section

Chemicals. High purity CO_2 (99.995 % mass fraction purity) was supplied by Air Liquide (Portugal). Acetamide (> 98 mass %) and acrylamide (> 98 mass fraction purity %) were purchased from Sigma Aldrich.

Equipment and Procedure. The supercritical fluid extraction experiments were performed in a flow apparatus (Figure 1). This equipment allows carrying out studies at a temperature up to 393.2 K and pressures up to 60.0 MPa. A detailed description of the equipment is given elsewhere,[8] and thus, herewith a brief explanation will be presented only.

The liquid CO_2 flowing from the cylinder (G) is compressed to the desired pressure (Applied Separations, Spe-ed SFE) into the extractor (equilibrium cells), which are heated. About (13 to 16) g of the compound was introduced in the extractor for each experimental measurement. The bottom and top of the extractor contain two metal frits (2 μm), and its lower part was filled with propylene wool, which was also placed at the top to avoid the entrainment of any material. The uncertainties of the temperature and pressure measurements were ± 1 °C and ± 0.1 MPa, respectively. The gravimetric measurements were performed on an analytical balance with an uncertainty of ± 0.1 mg with coverage factor 2.

After equilibrium at the desired temperature and pressure was reached, samples were collected. The extracts were recovered in a system of two glass U tubes, at atmospheric pressure and a temperature controlled with an ice bath, through the depres-

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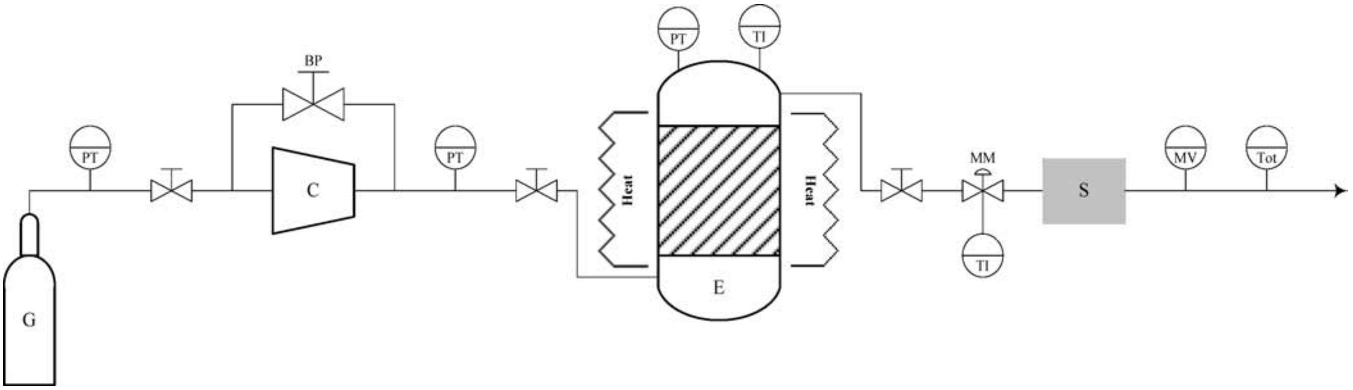


Figure 1. Diagram of the supercritical fluid extraction apparatus. G, cylinder of CO_2; C, compressor; E, extractor; S, separator; BP, back-pressure regulator; MM, micrometer valve; MV, flow meter; Tot, totalizer; TI, temperature indicator; PT, pressure indicator.

surization of the mixture of supercritical CO_2 + compound into valve MM. These tubes were weighed before and after the extraction.

The total volume of CO_2 was determined with a mass flow meter and totalizer (MV+Tot) from Alicat Scientific, model M-5 SLPM-D. The uncertainty associated with volume measurements was ± 0.5 %.

The conditions of the solubility studies were as follows: CO_2 flow rates of $9.65 \cdot 10^{-3}$ $g \cdot s^{-1}$ (linear velocity of $8.74 \cdot 10^{-3}$ $cm \cdot s^{-1}$, contact time 1950 s), pressures up to 40.0 MPa, and temperatures up to 323.2 K. The flow rate of the supercritical fluid through the extraction cell was checked to verify different contact times—from (640 to 2300) s during measurements of equilibrium solubilities—to ensure the saturation of the compound in the supercritical phase.

Solubility is obtained as the value of the mass of acetamide/acrylamide extracted versus the amount of CO_2 (volume measured at normal pressure and temperature). Three replicates were performed at each experimental condition, and the solubility was obtained as an average of these results. The average values of uncertainty of the solubility measurements for each isotherm were (2 to 4) %.

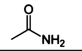
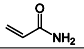
Experimental Results

The experimental solubilities of acetamide and acrylamide in SC CO_2, measured at T = (308.2, 313.2, and 323.2) K and p = (9 to 40) MPa, are summarized in Table 1. According to the experiments, the solubility of acrylamide and acetamide increases with pressure at constant temperature owing to an increase in the fluid density. The solubility isotherms for both compounds exhibit crossover behavior at around 12 MPa.

The existence of a crossover pressure in solid−SC fluid systems is an indication of the reliability and consistency of the experimental solubility data and is a result of the following: At constant pressure, below the crossover pressure (12 MPa in our case), the solid's solubility decreases as the density of carbon dioxide decreases with increasing temperature, which means that the temperature effect on density is more important than the temperature effect on the vapor pressure of acrylamide/acetamide. Above the crossover pressure, the increase in the vapor pressure of both solids with temperature has a more pronounced influence than the decrease of the density of the solvent.

The solubility of acetamide in the overall region of measurements is approximately twice that of acrylamide. The latter is a result of the difference in the sublimation pressure—the vapor pressure of acetamide is about an order of magnitude higher than that of acrylamide (Table 2).

Table 1. Solubility y for Acetamide (2) and Acrylamide (2)^{a,b} in SC CO_2 (1) from T = (308.2 to 323.2) K

		Acetamide 	Acrylamide 
T/K	p/MPa	$y_2 \cdot 10^4$	$y_2 \cdot 10^4$
308.2	9.0	7.543 ± 0.22	3.276 ± 0.16
	10.0	9.031 ± 0.35	3.971 ± 0.10
	12.0	10.96 ± 0.58	5.324 ± 0.11
	15.0	11.95 ± 0.26	6.710 ± 0.39
	17.5	12.25 ± 0.46	------
	20.0	13.46 ± 0.25	7.060 ± 0.15
	25.0	15.51 ± 0.20	8.704 ± 0.33
	30.0	15.77 ± 0.46	9.318 ± 0.21
	35.0	16.78 ± 0.72	9.410 ± 0.27
	40.0	18.04 ± 0.07	10.21 ± 0.25
313.2	9.0	3.998 ± 0.40	2.084 ± 0.10
	10.0	7.890 ± 0.30	3.901 ± 0.02
	12.0	11.54 ± 0.22	6.572 ± 0.12
	15.0	14.94 ± 0.79	7.448 ± 0.21
	17.5	15.25 ± 0.06	------
	20.0	16.81 ± 0.46	9.628 ± 0.27
	25.0	18.87 ± 0.30	10.85 ± 0.45
	30.0	19.25 ± 0.31	11.95 ± 0.53
	35.0	20.73 ± 0.46	12.51 ± 0.44
	40.0	20.85 ± 0.51	12.79 ± 0.60
323.2	9.0	2.383 ± 0.14	1.193 ± 0.04
	10.0	4.324 ± 0.16	2.392 ± 0.03
	11.0	8.683± 0.70	3.460 ± 0.17
	12.0	11.52 ± 0.20	5.146 ± 0.14
	15.0	16.92± 0.13	7.421 ± 0.24
	20.0	21.25 ± 0.28	11.04 ± 0.49
	25.0	23.55 ± 0.26	11.73 ± 0.48
	30.0	27.65 ± 0.94	14.67 ± 0.76
	35.0	28.14 ± 0.91	15.40 ± 0.90
	40.0	31.62 ± 1.03	16.31 ± 0.78

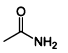
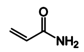
[a] Average values of mole fraction taken from triplicate runs. [b] ± Uncertainties refer to standard deviation.

Thermodynamic Modeling

Thermodynamic Framework. To compute the solubility (mole fraction) of the solid acetamide and acrylamide in the fluid phase (SC CO_2) at a specified temperature, pressure, and overall composition, an appropriate thermodynamic model is required.

The standard formulation of this problem is based on the equifugacity condition for the solute; that is, assuming an equation-of-state (EoS) model for the fluid phase and denoting by the

Table 2. Acetamide and Acrylamide Pure Componet Parameters

	Acetamide 	Acrylamide 
p_c/bar	66	57.3
T_c/K	761	776
ω	0.241	0.4863
p/bar (triple point)	$4.88.10^{-3}$	$2.26.10^{-3}$
V^S/cm^3·mol^{-1}	50.92	63.35
ΔH_{fus}/J·mol^{-1}	15500[a]	15330[a]
T_m/K	354.15[a]	357.65[a]
P_s^{subl}/bar at T=308.2 K	$1.1298 \cdot 10^{-4}$	$1.896 \cdot 10^{-5}$
P_s^{subl}/bar at T=313.2 K	$1.7950 \cdot 10^{-4}$	$3.291 \cdot 10^{-5}$
P_s^{subl}/bar at T=323.2 K	$4.3395 \cdot 10^{-4}$	$9.423 \cdot 10^{-5}$

[a] From ref 10.

Table 3. Binary Interaction Parameters (k_{ij}) and AARD for the Systems Acetamide + CO$_2$ and Acrylamide + CO$_2$ at the Temperatures of the Experiment

	acetamide + CO$_2$		acrylamide + CO$_2$	
T/K	k_{ij}	AARD/%	k_{ij}	AARD/%
308.2	0.1350	7.54	0.1251	8.00
313.2	0.1350	6.83	0.1240	13.5
323.2	0.1274	9.90	0.1340	15.5

superscript "S" the solid solute and by the superscript "F" the fluid phase

$$f^S(T, P) = f^F(T, P, \mathbf{y}, V) \tag{1}$$

where f^S is the fugacity of the solute in the pure solid phase; f^F is fugacity of the solute in the fluid-phase solution; $\mathbf{y} = (y_1, y_2, ..., y_{Nc})^T$ is the vector of fluid-phase mole fractions; and V is the molar volume of the fluid from the EoS model. Additional relationships that must be satisfied are the summation to one of the fluid-phase mole fractions.

There have been a number of efforts at introducing mathematical artifices for solid-phase fugacity within traditional fluid-phase equilibrium equation-of-state descriptions. The more common approach is to take a popular EoS and use it directly in solid−fluid equilibrium calculations by introducing a solid-phase fugacity function defined in terms of a fluid-phase reference state. In this study, we implement the fugacity of a hypothetical subcooled liquid phase, as the reference of the solid-phase fugacity. Thus, the solid-phase fugacity function, for a pure solute solid phase at temperature T and pressure P, defined in terms of a hypothetical liquid-phase fugacity as a reference state and disregarding the change in specific heat because of its negligible effect, is given as follows[9]

$$f^S = f^{SCL}(P, T) \exp\left(\int_{P_{subl}^s}^{P} \frac{V^S - V^{SCL}}{RT} dP + \frac{\Delta H_{fus}}{R}\left(\frac{1}{T_m} - \frac{1}{T}\right)\right) \tag{2}$$

Implicitly assuming that there are no solid−solid phase transitions and provided the solid specific volume at the subcooled liquid state V^{SCL} is weakly dependent on pressure, eq 2 can be written as follows

$$f^S = f^{SCL}(P, T) \exp\left(\frac{(V^S - V^{SCL})}{RT}(P - P_{subl}^S(T)) + \frac{\Delta H_{fus}}{R}\left(\frac{1}{T_m} - \frac{1}{T}\right)\right) \tag{3}$$

In eq 3, f^{SCL} is the fugacity of the pure subcooled liquid; ΔH_{fus} is the enthalpy of fusion; and $\Delta V_{fus} = V^S - V^{SCL}$ is the change in volume, all taken for the solute at its triple point. The fugacity of the pure subcooled liquid f^{SCL} is calculated from an EoS (in our case SRK CeoS).

Pure-Component Property Estimation. To calculate the fugacity of a pure solid solute according to eq 3, the following data are required: its fusion properties (enthalpy of fusion (ΔH_{fus}), melting temperature (T_m), ΔV_{fus}, and sublimation pressure (P_s^{subl})) and its critical parameters (T_c and P_c). For acetamide and acrylamide, some of the properties required are experimentally available (e.g., T_m, ΔH_{fus}),[10] while for those which are either not available or hypothetical the algorithm discussed in detail by Fornari[11] was followed to estimate them (Table 2).

Herewith we mark only the relevant main steps: The sublimation pressures at the temperatures of interest to the experiment were calculated from the Clapeyron equation, applying the data for the melting properties of acetamide and acrylamide; the solid volume was estimated applying the method proposed by Goodman et al.;[12] and the critical parameters were estimated applying the methods advocated by Cholakov et al.[13] and Wakeham et al.[14] Finally, the fugacity of the pure solute in the subcooled liquid phase, the triple point pressure, and V^{SCL} were all calculated from the EoS.

The thermodynamic model applied was the SRK CEoS with the one-fluid van der Waals mixing rule. The binary interaction parameters k_{ij} for the two solids with CO$_2$ were estimated for each temperature of the experiment from the best fit to the data measured in this work by a standard optimization procedure (Table 3). For the binary interaction parameters of acetamide and acrylamide obtained, there is no systematic change in the values with temperature (Table 3), which is consonant with the trend observed for other solid solutes with a supercritical solvent. Furthermore, it must be noted that the interaction parameters represent just one of the possible sets, as a local rather than a global method was employed in the optimization.

The average deviations (AARD) between the solubility values measured experimentally, y_i^{exp}, and those correlated by the model, y_i^{calc} are calculated according to the following

$$\text{AARD} = \left(\frac{100}{N}\right)\left(\sum_{j=1}^{N} \frac{|y_i^{exp} - y_i^{calc}|}{y_i^{exp}}\right) \tag{4}$$

where N is the number of data points. The values obtained are presented in Table 3.

The agreement between the experimentally measured and correlated solubilities in SC CO$_2$ for acetamide (Figure 2) and acrylamide (Figure 3) is acceptable particularly after the crossover pressure for the respective compound, where the

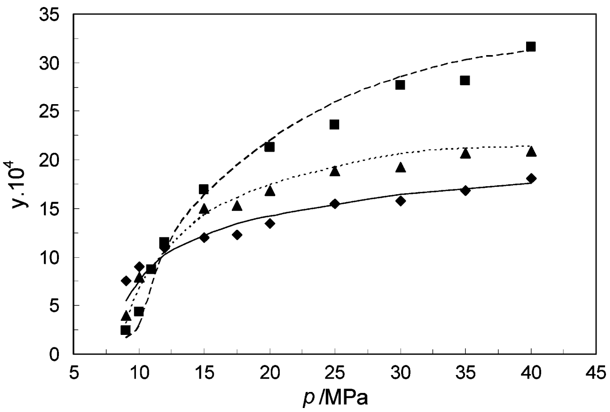


Figure 2. Solubility of acetamide in SC-CO_2. Symbols represent experimental solubility; lines represent the solubility, correlated by the SRK EoS. ◆, measured and —, correlated solubility at $T = 308.2$ K; ▲, measured and ·····, correlated solubility at $T = 313.2$ K; ■, measured and — — —, correlated solubility at $T = 323.2$ K.

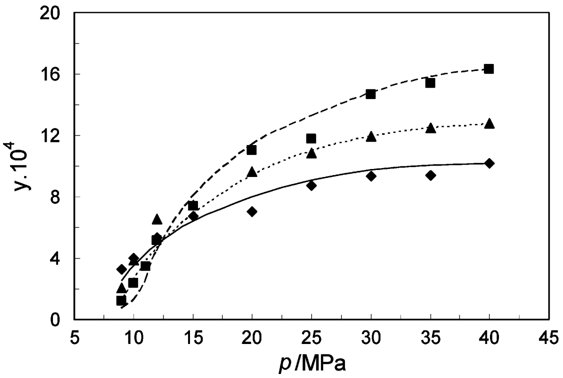


Figure 3. Solubility of acrylamide in SC-CO_2. Symbols represent experimental solubility; lines represent the solubility, correlated by the SRK EoS. ◆, measured and —, correlated solubility at $T = 308.2$ K; ▲, measured and ····, correlated solubility at $T = 313.2$ K; ■, measured and — — —, correlated solubility at $T = 323.2$ K.

experimental conditions are far from CO_2 critical point and where cubic EoSs perform better.

Conclusions

The solubilities of acetamide and acrylamide in SC-CO_2 at $T = (308 \text{ to } 323)$ K and $p = (9 \text{ to } 40)$ MPa were measured. The solubility of acetamide in the overall region of measurements is approximately twice that of the acrylamide and increases with pressure. The solubility isotherms of both compounds exhibit a cross over behavior at about 12 MPa.

The Soave−Redlich−Kwong EoS with the one-fluid van der Waals mixing rule was shown to be able to provide a good correlation of the solubility of acetamide and acrylamide in SC CO_2. The thermophysical parameters of both compounds, required by the modeling, for which there were no data available were estimated and reported.

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