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Solubility of the metal precursor Ni(NO$_3$)$_2$·6H$_2$O in high-pressure CO$_2$ + ethanol mixtures

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Abstract

The solubility of Ni(NO$_3$)$_2$·6H$_2$O in high-pressure CO$_2$ + ethanol mixtures was measured using a high-pressure variable-volume view cell from (308.2 to 353.2 K) and up to 25.0 MPa. This compound has been used previously as a Ni precursor in metal deposition experiments using supercritical CO$_2$. Ni(NO$_3$)$_2$·6H$_2$O was not soluble in pure CO$_2$ but the addition of ethanol into the system allowed the solubilisation of the hydrated salt in the mixture. Mole fraction of Ni(NO$_3$)$_2$·6H$_2$O varied from $1.67 \times 10^{-4}$ to $1.97 \times 10^{-3}$. At these salt concentrations, the phase diagram of the CO$_2$ + EtOH + Ni(NO$_3$)$_2$·6H$_2$O system resembled that of the CO$_2$ + EtOH binary system and, at the studied conditions, a vapour-liquid equilibrium was observed. For the higher ethanol concentrations, the bubble points closely matched those of the CO$_2$ + EtOH system. For the lower EtOH concentrations, however, much higher solubilisation pressures were required, due to the release of water molecules from the salt into the solution. Ni(NO$_3$)$_2$·6H$_2$O solutions were stable in high-pressure CO$_2$ + EtOH mixtures at the studied conditions.

Keywords: Supercritical Carbon Dioxide, Solubility, Hydrated Metal Salts, Ethanol, Modifier, CO$_2$-Expanded Liquids.
1. Introduction

The use of supercritical fluids and in particular supercritical CO\textsubscript{2} (scCO\textsubscript{2}) to replace the more toxic organic solvents in environmentally benign processes is of increasing interest nowadays. CO\textsubscript{2} is cheap, non-toxic, non-flammable and has moderate critical parameters ($T_c = 304.2$ K, $P_c = 7.4$ MPa), therefore it is considered a green solvent.\textsuperscript{1}

Knowledge of the high-pressure phase behaviour is essential in any application using scCO\textsubscript{2}. Prof. Cor Peters has successfully contributed throughout the years to the study and understanding of the thermodynamic properties of high-pressure systems and has also played a key role in the development of innovative high-pressure applications. His outstanding contribution involved the formation of many students and postdoctoral researchers. Other colleagues such as ourselves also benefited from his talks and from discussions in conferences and courses.\textsuperscript{2} C.P., J.A.R.R. and A.C. have enjoyed Cor Peters warm friendship for many years; it is an honour for us to participate in this issue celebrating his achievements.

High-pressure vapour-liquid equilibrium (VLE) measurements of CO\textsubscript{2} and alcohol systems are of interest due to their importance in the supercritical extraction of labile compounds, dehydration of alcohols using supercritical carbon dioxide and extraction of natural compounds.\textsuperscript{3} Supercritical CO\textsubscript{2} as well as many other non-polar fluids are not good solvents for polar solutes. A small amount of a cosolvent or modifier is added to the fluid in order to improve its solvation power.\textsuperscript{4} Alcohols, such as methanol or ethanol are often used to increase CO\textsubscript{2} polarity. If the amount of alcohol added is large enough, the system behaves such as an expanded liquid systems\textsuperscript{5} and keeps most of the solvation power of the
liquid solvent. Therefore, mixtures of CO$_2$ and methanol or ethanol can dissolve more polar compounds.

One process that can benefit from the use of high pressure CO$_2$ + ethanol mixtures is the deposition of metal and metal oxides on inorganic and polymeric supports using supercritical fluids.$^6, ^7$ The Supercritical Fluid Deposition (SCFD) technique involves the dissolution of a metal precursor in supercritical fluid, usually CO$_2$, and its adsorption onto the support. The metal precursor is then chemically or thermally decomposed on the support. The decomposition can be carried out after the depressurization or at supercritical conditions. Alcohols can also help in the reduction process.$^8$ Varying the experimental conditions, metal nanoparticles,$^9$ nanowires$^{10}$ or continuous supported films$^{11}$ have been produced. This technique offers many opportunities in the preparation of heterogeneous catalysts, ceramics, gas sensors and microelectronics, among others.

In our group, we have extensively investigated the deposition of Pd, Ru, Ni, Pt nanoparticles (NPs) on different inorganic supports.$^{12-16}$ The excellent catalytic properties of some of the materials produced were proved.$^{14, 16, 17}$ The method was also used to insert Ni nanoparticles into the pores of nanopatterned BaTiO$_3$ thin films for the preparation of multiferroics.$^{12}$

Organometallic precursors are the metal precursor commonly used, because of their high solubility in supercritical CO$_2$.$^{18}$ However, these compounds are generally expensive, toxic (due to their high volatility) and oftentimes difficult to manipulate as they can be light and/or air sensitive. In contrast, inorganic polar precursors such as metal nitrates and chlorides do not have some of these problems, being the most popular metal precursors used in the preparation of metal oxides and metallic materials by conventional techniques.
Metal nitrates and chlorides tend to form hydrates, which are not soluble in scCO$_2$ but are soluble in methanol or ethanol. These alcohols are highly miscible with CO$_2$ at moderate conditions. In this case, the solubilisation of hydrated metal nitrates or chlorides can be accomplished by adding a small amount of the alcohol to supercritical CO$_2$ which acts as a cosolvent or by using a CO$_2$-expanded solution of the precursor in the alcohol. The use of metal nitrates and metal chlorides dissolved in high-pressure CO$_2$ + alcohol mixtures has been extensively studied by Profs. Z. Liu and B. Han at Beijing National Laboratory (China).$^{19, 20}$ In our group, we have also used this approach to deposit Ru and Ni NPs on different substrates.$^{12, 13, 16}$ The transport properties of the hydrated metal salts in the CO$_2$ alcohol mixtures are highly favoured in comparison to those of the metal salt solutions in pure alcohol. Nevertheless, apart from the report by Ming et al. $^{21}$ on the reaction of hydrous inorganic metal salts in CO$_2$-expanded ethanol, the phase behaviour of these systems has not been previously studied. Furthermore, no quantitative measurements of these systems have been performed.

In this paper, we study the phase behaviour of the mixtures formed by Ni(NO$_3$)$_2$·6H$_2$O in high pressure CO$_2$ + ethanol mixtures using a high-pressure variable volume view cell. Phase behaviour measurements are reported from (308.2 to 353.2 K). These data are compared to VLE data for the CO$_2$ + ethanol and CO$_2$ + ethanol + H$_2$O systems available in the literature.

2. Experimental

2.1 Materials. The details of the reagents used in this work are given in table 1. These materials were used as received.
Table 1 Specifications of the chemicals used in this work.

<table>
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<th>Linear formula</th>
<th>CAS No.</th>
<th>Mw (g/mol)</th>
<th>Purity</th>
<th>Source</th>
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<tr>
<td>Carbon dioxide</td>
<td>CO₂</td>
<td>124-38-9</td>
<td>44.01</td>
<td>&gt;99.99</td>
<td>Air Liquide</td>
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<tr>
<td>Nickel(II) nitrate hexahydrate</td>
<td>Ni(NO₃)₂·6H₂O</td>
<td>13478-00-7</td>
<td>290.79</td>
<td>99.999</td>
<td>Sigma-Aldrich</td>
</tr>
<tr>
<td>Ethanol</td>
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<td>64-17-5</td>
<td>46.07</td>
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2.2. Apparatus and Procedures. Equilibrium measurements of Ni(NO₃)₂·6H₂O in CO₂ + ethanol mixtures were carried out using a high-pressure variable volume view cell built and designed at our laboratory, following the procedure previously described.²², ²³ Figure 1 shows a schematic design of the view cell and images of Ni(NO₃)₂·6H₂O + EtOH and CO₂ + EtOH + Ni(NO₃)₂·6H₂O solutions. The cell is a stainless steel high-pressure cylinder fitted with a sapphire window in one side. The volume of the cell is varied by moving a stainless steel piston placed on the opposite side, the maximum working volume being 15 cm³. The contents in the cell are illuminated and observed through the window using a Fiegert Endotech boroscope and a digital camera connected to a computer. The cell can be heated to 373 K using a silicone heating tape wrapped around the cylinder (Omegalux SRT051-040) connected to a Proportional Integral Derivative (PID) temperature controller (Microomega, model CN77322). A type J calibrated thermocouple inside the cell is used both as a control point and for measuring the temperature. The precision of the thermocouple is ±0.05 K and the stability of the thermostat during measurements is estimated to be ±0.2 K. The sample can be compressed (up to 30 MPa) or
decompressed by displacing the piston using a manual high pressure generator and water as hydrostatic fluid. The pressure is measured inside the cell using a relative transducer (Druck, model PTX7511-1) with an estimated error of ±(0.01 + 0.0015 P) MPa. This equipment has been previously used to measure the solubility of different Ni and Ru metal organic compounds in CO₂, both pure and modified with ethanol.²⁴, ²⁵

Figure 1. High pressure variable volume view cell and images of Ni(NO₃)₂·6H₂O + EtOH and CO₂ + EtOH + Ni(NO₃)₂·6H₂O solutions.

Solubility data were measured following the synthetic method by preparing a mixture of known composition and studying its phase behavior against pressure and temperature. Approximately 0.2 g of Ni(NO₃)₂·6H₂O was dissolved in 1.6 g of ethanol (2.0 cm³). From this solution, between 0.5 to 0.9 g was loaded into the cell using a syringe. For the measurements at high ethanol concentrations, an extra volume of pure ethanol was introduced into the cell. The concentration of the solution and the amount loaded into the

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cell were determined by weight using an analytical balance AND GR – 200 with a precision of ±0.001 g. Finally, liquid carbon dioxide was gravimetrically transferred into the cell by means of an auxiliary cell. Considering the precision of the weight measurements, the overall composition can be determined with an estimated error of 0.1%. Once the sample was loaded, the cell was kept at constant temperature and the sample was compressed to a single phase. The contents of the cell were agitated by a magnetic stirrer in order to assure homogeneity in the single phase. The pressure was then slowly decreased until the apparition of the second phase. Depending on the region of the phase diagram, the second phase appeared as a liquid phase (dew point) or a vapour phase (bubble point). The determination of this point was based on visual observation. At the studied compositions, no solid phase was observed. This process was reversed: the sample was pressurized to the homogeneous single phase and depressurized to the two-phase region repeatedly in order to get a precise pressure value for the pressure phase separation. Reproducibility in the pressure measurement was ±0.1 MPa.

Ni(NO$_3$)$_2$·6H$_2$O contains a large amount of crystallization water, which is released into the ethanol upon dissolution. In fact, the presence of water helps to dissolve the salt in the alcohol, which is required to be miscible with CO$_2$. To further assess the role that the water molecules play in the system, a particular solution of Ni(NO$_3$)$_2$·6H$_2$O in ethanol was dried using molecular sieves and mixed with CO$_2$. Molecular sieves (0.3 nm beads supplied by Merck) were activated in a conventional oven at 353 K for 24 hours. A given amount of molecular sieves following the manufacturer instructions was introduced into the solution and after 3 hours the solution was filtered and loaded into the cell following the procedure previously described. Phase behaviour measurements of the dried solution were performed.
3. Results and discussions

Ni(NO$_3$)$_2$·6H$_2$O was not soluble in pure CO$_2$ but the addition of ethanol into the system allowed the solubilisation of the hydrated salt in the mixture. Ni(NO$_3$)$_2$·6H$_2$O solutions of different ethanol concentration were used to cover a large ethanol concentration range. CO$_2$ mole fraction varied from 0.352 to 0.970, whilst ethanol mole fraction varied from 0.029 to 0.647. Ni(NO$_3$)$_2$·6H$_2$O mole fraction varied from $1.67 \times 10^{-4}$ to $1.97 \times 10^{-3}$ depending on the ethanol concentration.

Ni(NO$_3$)$_2$·6H$_2$O dissolved in ethanol and released the six crystallization water molecules into the medium. Upon addition of CO$_2$, the system could be considered as a quaternary system formed by CO$_2$, ethanol, H$_2$O, and Ni(NO$_3$)$_2$. The amount of water released into the system was estimated from the Ni(NO$_3$)$_2$·6H$_2$O concentration of the solution.

Solubility measurements were carried out at 308.2, 313.2, 323.2, 333.2, 343.2, and 353.2 K in the (5.2-25.0 MPa) pressure range. Ni(NO$_3$)$_2$·6H$_2$O solutions were stable at the studied conditions. The higher temperature used in this study, 353.2 K, is much lower than the decomposition temperature of 423 K previously reported for this salt in CO$_2$-expanded liquid systems.$^{21}$

Solubility data of Ni(NO$_3$)$_2$·6H$_2$O in scCO$_2$ modified with ethanol at the different conditions are given in Table 2. Figures 2-7 show the phase diagram of Ni(NO$_3$)$_2$·6H$_2$O in...
mixtures of CO$_2$ + EtOH at the different temperatures and compare these data to those of
the CO$_2$ + EtOH binary system previously reported at the same temperature.
Table 2. Solubilisation conditions for the different solutions of Ni(NO$_3$)$_2$·6H$_2$O in CO$_2$ + EtOH mixtures at high pressure and temperatures from 308.2 to 353.2 K.$^a$

<table>
<thead>
<tr>
<th>$x$ CO$_2$</th>
<th>$x$ EtOH</th>
<th>$x$ Ni(NO$_3$)$_2$·6H$_2$O</th>
<th>$P$ / MPa</th>
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<td></td>
<td></td>
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<td>308.2 K</td>
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<tr>
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<td>0.647</td>
<td>1.97 $10^{-3}$</td>
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<td>0.937</td>
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<td>0.945$^b$</td>
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<td>1.15 $10^{-3}$</td>
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<td>0.970</td>
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$^a$ Standard uncertainties $u$ are $u(T)/K = 0.2 , u(P)/MPa = 0.1, u(x) = 0.1%.$

$^b$ Sample prepared using molecular sieves.

A bubble point (BP) or a dew point (DP) was observed.

Solubilisation pressures for the composition $x$ CO$_2$ = 0.937, $x$ EtOH = 0.062 and $x$ Ni(NO$_3$)$_2$·6H$_2$O = 1.17 $10^{-3}$ at 308.2, 313.2 and 323.2 K were not measured due to the very slow solubilisation process. At the higher temperatures, solubilisation was much faster. For the higher CO$_2$ compositions phase equilibrium measurements at 343.2 K were also omitted.
Figure 2. Phase diagram of the CO$_2$ + EtOH + Ni(NO$_3$)$_2$·6H$_2$O system at 308.2 K plotted as function of CO$_2$ mole fraction (◇) and comparison with the phase diagram of the binary system CO$_2$ + EtOH at the same temperature:(○) Chin *et al.* 26 and (□) Tanaka *et al.* 27. Ni(NO$_3$)$_2$·6H$_2$O mole fraction values vary from 1.67 $10^{-4}$ to 1.97 $10^{-3}$ and are given in Table 2.
Figure 3. Phase diagram of the CO$_2$ + EtOH + Ni(NO$_3$)$_2$·6H$_2$O system at 313.2 K plotted as function of CO$_2$ mole fraction (◊) and comparison with the phase diagram of the binary system CO$_2$ + EtOH at the same temperature (○) Chin et al. $^{26}$ and (□) Secuianu et al. $^{27}$. (◆) Solution prepared adding molecular sieves. Ni(NO$_3$)$_2$·6H$_2$O mole fraction values vary from $1.67 \times 10^{-4}$ to $1.97 \times 10^{-3}$ and are given in Table 2.
Figure 4. Phase diagram of the CO$_2$ + EtOH + Ni(NO$_3$)$_2$·6H$_2$O system at 323.2 K plotted as function of CO$_2$ mole fraction (◊) and comparison with the phase diagram of the binary system CO$_2$ + EtOH at the same temperature: (○) Chen et al. $^{28}$, (□) Joung et al. $^{29}$ and (△) Suzuki et al. $^{30}$. Solution prepared adding molecular sieves. Ni(NO$_3$)$_2$·6H$_2$O mole fraction values vary from 1.67 $10^{-4}$ to 1.97 $10^{-3}$ and are given in Table 2.
Figure 5. Phase diagram of the CO$_2$ + EtOH + Ni(NO$_3$)$_2$·6H$_2$O system at 333.2 K plotted as function of CO$_2$ mole fraction (◇) and comparison with the phase diagram of the binary system CO$_2$ + EtOH at the same temperature: (○) Knez et al. $^{31}$ and (◇) Secuinanu et al. $^{32}$. Solution prepared adding molecular sieves. Ni(NO$_3$)$_2$·6H$_2$O mole fraction values vary from $1.67 \times 10^{-4}$ to $1.97 \times 10^{-3}$ and are given in Table 2.
Figure 6. Phase diagram of the system CO$_2$ + EtOH + Ni(NO$_3$)$_2$·6H$_2$O system at 343.2 K plotted as function of CO$_2$ mole fraction (◊) and comparison with the phase diagram of the binary system CO$_2$ + EtOH at the same temperature: (○) Wu et al. $^{33}$ and (□) Joung et al. $^{29}$. (◆) Solution prepared adding molecular sieves. Ni(NO$_3$)$_2$·6H$_2$O mole fraction values vary from $1.67 \times 10^{-4}$ to $1.97 \times 10^{-3}$ and are given in Table 2.
Figure 7. Phase diagram of the system CO$_2$ + EtOH + Ni(NO$_3$)$_2$·6H$_2$O system at 353.2 K plotted as function of CO$_2$ mole fraction (○) and comparison with the phase diagram of the binary system CO$_2$ + EtOH at the same temperature: ○ Wu et al. $^{33}$, □ Secuianu et al. $^{32}$ and △ Knez et al. $^{31}$. (▲) Solution prepared adding molecular sieves. Ni(NO$_3$)$_2$·6H$_2$O mole fraction values vary from 1.67 $10^{-4}$ to 1.97 $10^{-3}$ and are given in Table 2.

At high pressure, the system studied either formed one single phase or split upon depressurization into a vapour and a liquid phase in equilibrium showing the behaviour of a bubble or a dew point, depending on concentration, pressure and temperature.

Figure 8a shows a schematic representation of the CO$_2$ + EtOH binary phase diagram above the critical point of CO$_2$. Bubble and dew points merge in the critical point. Due to
the small concentration of Ni(NO$_3$)$_2$·6H$_2$O in comparison to those of CO$_2$ and EtOH, a similar behaviour was observed for the CO$_2$ + EtOH + Ni(NO$_3$)$_2$·6H$_2$O system. In the same figure, images of the view cell in a typical experiment show (b) two phases at low pressure, (c) one phase at higher pressure, and (d) a bubble and (e) a dew point upon depressurization.

**Figure 8.** (a) Schematic representation of the CO$_2$ + EtOH binary phase diagram at a temperature above the critical temperature of CO$_2$. Images taken from the view cell in a typical CO$_2$ + EtOH + Ni(NO$_3$)$_2$·6H$_2$O experiment show: (b) two phases at low pressure, (c) one phase at higher pressure, (d) a bubble point and (e) a dew point.

At large EtOH concentrations, bubble points were observed at every temperature. The pressure conditions were very similar to those of the binary CO$_2$ + EtOH system, due to the low concentration of the salt into the system. At these conditions in the one-phase region, the system behaved as a CO$_2$-expanded liquid mixture rather than as a supercritical fluid mixture.

At much lower ethanol concentrations, however, the system behaved differently and, at every temperature, large deviations from the binary system were observed. Differences were much larger at the higher temperatures. Figure 9 shows images of the contents of the
cell in an experiment with $\text{CO}_2 + \text{EtOH} + \text{Ni(NO}_3\text{)}_2 \cdot 6\text{H}_2\text{O}$ at very low EtOH concentration. The composition of the mixture was: $x \text{CO}_2 = 0.941$, $x \text{EtOH} = 0.057$, $x \text{Ni(NO}_3\text{)}_2 \cdot 6\text{H}_2\text{O} = 1.16 \times 10^{-3}$. The upper phase was rich in CO$_2$ and EtOH and exhibited a very mild green colour whilst the lower one, which was darker green coloured, was rich in H$_2$O and Ni(NO$_3$)$_2$. For this composition, the system did not form a single phase even at 353.2 K and 25.0 MPa. The system was not pressurized further to avoid breaking of the O-rings at high temperature. This pressure is much larger than that required to get single phase conditions in the CO$_2$ + EtOH binary system at a similar composition.

**Figure 9.** Images from the view cell for a typical experiment at low EtOH concentration showing two phases at pressure conditions much higher than those of the binary system CO$_2$ + EtOH. The upper phase is rich in CO$_2$ and EtOH, whilst the lower liquid phase is composed mostly by H$_2$O and Ni(NO$_3$)$_2$. The composition of the mixture was: $x \text{CO}_2 = 0.941$, $x \text{EtOH} = 0.057$, $x \text{Ni(NO}_3\text{)}_2 \cdot 6\text{H}_2\text{O} = 1.16 \times 10^{-3}$. For the lower EtOH compositions reported in the table, the aqueous phase was very hard to dissolve and very high solubilisation pressures were required in order to reach single-phase conditions. Depressurization from the single phase led to the appearance of a liquid phase at most conditions. However, it became difficult to distinguish between bubble and dew points. In this region, the solubilisation pressures were much higher than those
found for the CO$_2$ + EtOH binary system. The low solubility of water in CO$_2$ increased the equilibrium pressures. In this region, only four compositions were measured at pressures below 30.0 MPa (upper pressure limit of the cell).

**Figure 10.** Phase diagram for the CO$_2$ + EtOH + H$_2$O ternary system at 313.2 K and different pressures $^{34}$: (■) 10 MPa, (●) 20 MPa and (▲) 30 MPa, and experimental compositions studied for the CO$_2$ + EtOH + Ni(NO$_3$)$_2$·6H$_2$O system at 313.2 K (★). Right image shows an enlargement of the region of lower ethanol concentration. Ni(NO$_3$)$_2$·6H$_2$O mole fraction values vary from 1.67 x $10^{-4}$ to 1.97 x $10^{-3}$ and are given in Table 2.

Figure 10 shows the phase diagram of the ternary system CO$_2$ + EtOH + H$_2$O at 313.2 K and 10, 20 and 30 MPa, exhibiting the binodal curves separating the two and one-phase regions together with the experimental compositions studied for the CO$_2$ + EtOH + Ni(NO$_3$)$_2$·6H$_2$O system. The concentration of Ni(NO$_3$)$_2$ has not been considered in the calculation, whilst the amount of water has been determined from the amount of salt. Enlargement in the region of lower EtOH concentration shows the proximity of the experimental compositions to the binodal line. Although in relation to the binodal curve for
the CO$_2$ + EtOH + H$_2$O system most compositions lie in the one phase region, experimentally the larger pressures required for complete solubilisation of the system for compositions poor in ethanol suggests a slight shift of the phase diagram in this region due to the presence of the salt. This effect is more pronounced at high temperature.

To further study the role of water in the system, in one experiment water was removed from the system by adding molecular sieves to the initial Ni(NO$_3$)$_2$·6H$_2$O solution. The composition of the mixture was very similar to that shown in Figure 9, which did not lead to one phase. At these conditions, the solubilisation pressure for the salt was lower than that measured without molecular sieves and close to that of the binary system CO$_2$ + EtOH. At some temperatures, solubilisation pressures were still slightly higher than those of the binary system, which could be due to the incomplete water removal or most likely to the presence of the salt, noticeable in this concentration range.

Ni(NO$_3$)$_2$·6H$_2$O can be successfully dissolved in CO$_2$ + EtOH mixtures. Although the concentration of Ni(NO$_3$)$_2$·6H$_2$O in the mixture may seem rather low, large quantities of the nickel salt can be dissolved at very mild conditions, particularly at the large EtOH concentration range. This mixture can be used in metal deposition experiments.

4. Conclusions

Ni(NO$_3$)$_2$·6H$_2$O is not soluble in pure CO$_2$ but can be dissolved in high-pressure CO$_2$ + ethanol mixtures. Solubility of Ni(NO$_3$)$_2$·6H$_2$O in CO$_2$ + ethanol mixtures was studied at temperatures from (308.2 to 352.2 K) and pressures up to 25 MPa using a view cell. At these temperatures, the solutions were stable and did not decompose. Mole fraction of Ni(NO$_3$)$_2$·6H$_2$O varied from $1.67 \times 10^{-4}$ and $1.97 \times 10^{-3}$. At each temperature, for most compositions the phase diagram closely matched that of the binary system CO$_2$ + EtOH due
to the small concentration of the salt. However, at the lower EtOH concentrations, the presence of water in the compound increased significantly the solubilisation pressures. The Ni concentrations used in these experiments are high enough to perform metal deposition experiments in CO₂. From a practical point of view, in order to solubilise Ni(NO₃)₂·6H₂O in CO₂ + ethanol mixtures, it is recommended using EtOH concentrations above 0.1 mole fraction in order to reach complete miscibility at moderate pressures.

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References


308.2 to 353.2 K up to 25.0 MPa

One phase

Ni(NO₃)₂·6H₂O + CO₂ + EtOH

Bubble point