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Liquid/Solid Extraction of Acetylacetone Chelates with Supercritical Carbon Dioxide

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Synopsis. The solubilities of the acetylacetone chelates in supercritical CO_2 (SC-CO_2) at 333 K and 9.8—29.4 MPa were strongly influenced by the extraction pressure, and by the nature of the metals and the number of acetylacetone ligands in the chelates. It was found that acetylacetone chelates could be extracted selectively by SC-CO_2 treatment because of significant differences in their solubilities in SC-CO_2.

Supercritical CO_2 (SC-CO_2) extraction, a remarkable extraction method that utilizes specific properties of SC-CO_2,[1,2] has been used chiefly to study organic substances, such as coffee,[3] hops,[4] seed oils,[5] and organic pollutants.[6] While we have been studying the extraction of fish oils from mackerel[7] and the extraction of selectively unsaturated fatty acid methyl esters[8] by this method, we are interested in determining its ability to extract metal chelates. Few inorganic compounds have been investigated by this method because of their low solubilities in SC-CO_2; however metal chelates, which contain organic ligands, should be readily extracted with SC-CO_2. Furthermore, the nature of the metals and the ligands in metal chelates should be reflected in the differences in their solubilities in SC-CO_2, and metal chelates should be extracted selectively by SC-CO_2 treatment.[9] Acetylacetone (acac) chelate, which has been employed for separating metals by solvent extraction,[10] was suitable for investigating these abilities. In this report, liquid/solid extraction of acetylacetone chelates using SC-CO_2 was carried out at 333 K and at 9.8—29.4 MPa. The possibility of selective extraction of acetylacetone chelates was also investigated.

Experimental

Materials: Acetylacetone chelates were of extra pure grade purchased from Tokyo Kasei Kogyo Co., Ltd. Liquid CO_2 of commercial grade was used as solvent.

Extraction: A flow diagram of the extraction apparatus is shown in Fig. 1. Liquid CO_2 was introduced into a diaphragm pump (3) and compressed to the desired pressure. The extraction pressure was controlled by a back-pressure regulator (4). Temperature was controlled within ±1 K. A 25 g sample of acetylacetone chelate (or a mixture of chelates) was charged in a 0.5 L-extractor (6) equipped at both ends with sintered stainless steel filters and extracted at pressures of 9.8—29.4 MPa and 333 K. The extracted solution was flashed to atmospheric pressure across a heated metering valve (8), and the extract was accumulated in a receiver (9). The amount accumulated was determined by weighing, and the corresponding volume of CO_2 was measured with a wet-flow totalizer (10). The flow rate of CO_2 was adjusted to at 1 L (gas) min^{-1} under atmospheric pressure by a control valve (8).

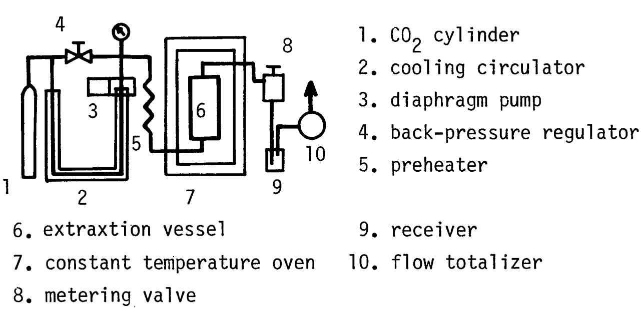

Fig. 1. Supercritical CO_2 extraction apparatus.

Analytical Methods: The compositions of the extracts obtained were determined by atomic absorption analysis using a Shimazu AA-610S atomic absorption/flame spectrometer.

Results and Discussion

Solid/Liquid Extraction of Acetylacetone Chelates: The solubilities (milligram of extract obtained per liter of CO_2 consumed) of the chelates in SC-CO_2 at 333 K and 9.8—29.4 MPa are presented in Fig. 2. The solubilities increased greatly with increase in the pressure. For example, the solubility of $In(acac)_3$ in SC-CO_2 at 29.4 MPa was about 800 times that at 9.8 MPa, and about 2.3 times that at 19.6 MPa: this is probably due to the increase of the SC-CO_2 density which closely relates to its dissolving capacity.[11] At 29.4 MPa, in tris(acetylacetonato) chelates, $In(acac)_3$ and $Ga(acac)_3$ were highly soluble (2.63 and 3.01 mg L^{-1}, respec-

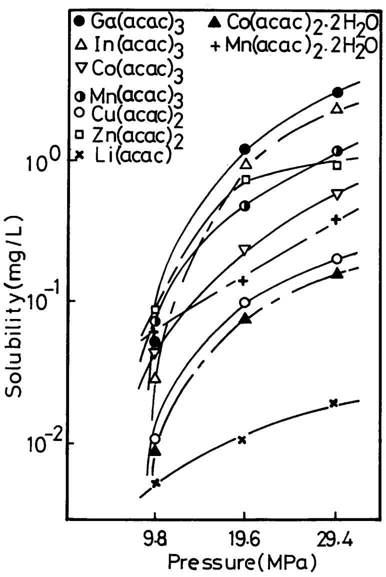

Fig. 2. Solubilities of acetylacetone chelates in supercritical CO_2 during initial 6.5 h at 333 K.

tively), compared with $Mn(acac)_3$ and $Co(acac)_3$ (1.26 and 0.62 mg L^{-1}, respectively). In bis(acetylacetonato) chelates the solubility of $Zn(acac)_2$ was 1.01 mg L^{-1}, while the solubilities of $Mn(acac)_2 \cdot 2H_2O$, $Co(acac)_2 \cdot 2H_2O$ and $Cu(acac)_2$ were only 0.40, 0.25 and 0.21 mg L^{-1} at 29.4 MPa, respectively. From these results the solubilities appear to be strongly influenced by the nature of the metals and the coordinated water in the chelates. The solubilities of $Co(acac)_3$ and $Mn(acac)_3$ were about 2.5 and 3.2 times greater than those of $Co(acac)_2 \cdot 2H_2O$ and $Mn(acac)_2 \cdot 2H_2O$ respectively, and the bis(acetylacetonato) chelates used were much less soluble than the tris(acetylacetonato) chelate used. Li(acac) was poorly soluble (0.01 mg L^{-1} at 29.4 MPa). These results suggest that the solubilities of acetylacetone chelates in $SC\text{-}CO_2$ increased with an increase in their affinities for $SC\text{-}CO_2$, which corresponded to an increase in the number of acetylacetone ligands in the chelates.

Extraction of the Mixtures of Acetylacetone Chelates: In order to investigate the possibility of selective extraction on the basis of these results, a mixture of $In(acac)_3$ having large solubility and bis(acetylacetonato) chelates having relatively low solubilities was used. The extraction of $In(acac)_3$, from a mixture of 5 g each of $Co(acac)_2 \cdot 2H_2O$, $Cu(acac)_2$, $Mn(acac)_2 \cdot 2H_2O$ $Zn(acac)_2$ and $In(acac)_3$ was carried out at 333 K, and at 19.6 and 29.4 MPa. As shown in Fig. 3, extraction curves show an increase in extraction efficiency with an increase in pressure. The total amount of the extract obtained at 29.4 MPa increased linearly at a rate of about 2.00 mg L^{-1} (CO_2 consumed) until 2 m^3 of CO_2 was consumed. At higher CO_2 consumption the rate decreased to about 0.05 mg L^{-1}. This fact indicates that some chelates can be extracted preferentially in the straight line portion of the extraction curve below 2 m^3 CO_2 consumption. The composition of the fractions obtained at each sampling point are given in Fig. 4. $In(acac)_3$ was selectively extracted at a ratio of about 75—87% in the early fractions at 29.4 MPa. After this CO_2 consumption value, the proportion of $In(acac)_3$ in the fractions decreased sharply, in contrast to the proportion of $Cu(acac)_2$ which increased sharply to maximunm of 90%. The proportion of $Co(acac)_2 \cdot 2H_2O$ was 2—9% in all fractions obtained during the extraction. That of $Zn(acac)_2$ was 8—14% in initial fractions, and then decreased to below 3%. $Zn(acac)_2$ was not extracted above 4 m^3 CO_2 consumption. Little $Mn(acac)_2 \cdot 2H_2O$ was detected in the extracts. Analogous results were also obtained at 19.6 MPa. Although some of the findings are not consistent with the results obtained when the chelates were extracted individually (cf. Fig. 2), the reasons for these phenomena were not apparent. The degree of chelate extraction in Fig. 5 is expressed as a percent extraction of the amount of the chelates extracted to the amount of the chelates supplied (g). The percent extractions of $Cu(acac)_2$ and the mixture of the chelates were only about 15 and 20%, respectively, but that of $In(acac)_3$ amounted to about 72%, until 9 m^3 of CO_2 was consumed. Furthermore, the total amount of $In(acac)_3$ extracted below 2 m^3 CO_2 consumption was equal to 91% of that extracted below 9 m^3 CO_2 consumption. These facts indicate that $SC\text{-}CO_2$ is a selective solvent for $In(acac)_3$ in the presence of several other bis(acetylacetonato) chelates.

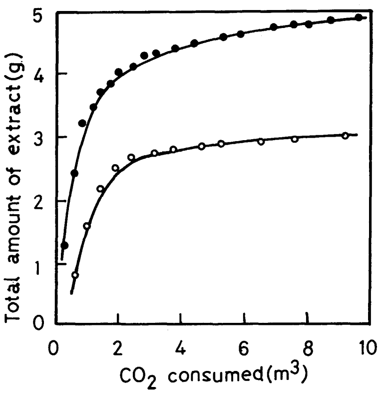

Fig. 3. Yields of chelates extracted from the mixture of 5 g each $Co(acac)_2 \cdot 2H_2O$, $Cu(acac)_2$, $Mn(acac)_2 \cdot 2H_2O$, $Zn(acac)_2$ and $In(acac)_3$ with supercritical CO_2 at 333 K, and at 29.4 (●) and 19.6 (○) MPa.

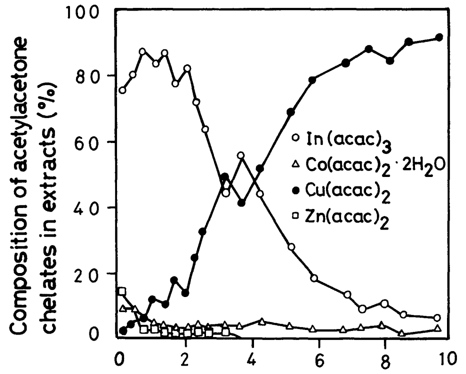

Fig. 4. Compositions of chelates in fractions obtained with supercritical CO_2 at each sampling points at 333 K and 29.4 MPa.

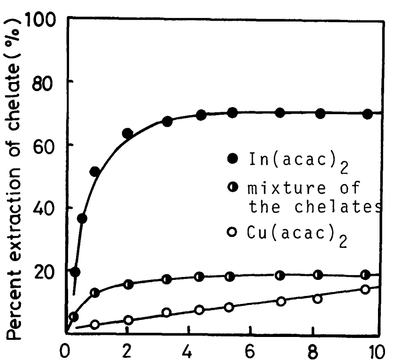

Fig. 5. Degrees of chelate extraction with supercritical CO_2 from the mixture of the acetylacetone chelates at 333 K and 29.4 MPa.

As described above, it is apparent that acetylacetone chelates can be extracted selectively with SC-CO_2 treatment because of significant differences in their solubilities in SC-CO_2. Although these selectivities are not sufficient, addition of the third substance as organic solvents to SC-CO_2,12) or employment of other ligands in place of acetylacetone may enable us to improve the selectivity of extraction of chelates with SC-CO_2.

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