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Mixing Properties of the (Mn,Ca)CO_3 Solid Solution at 25°C: a Calorimetric Study

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INTRODUCTION.

Manganese (II) is a divalent toxic-metal cation that can be conveyed in excessive amounts in natural waters as a residue of steel and packaging industries. In waste waters, the precipitation of intermediate members of the calcite-rhodochrosite series ($CaCO_3$-$MnCO_3$) has been reported as a possible process for the abiotic removal of Mn^{2+} (Bamforth et al., 2006).

However, the interference of ordered kutnahorite as a stable stoichiometric phase between the pure $CaCO_3$ and $MnCO_3$ endmembers implies a limited Ca^{2+}-Mn^{2+} miscibility in the calcite-rhodochrosite solid solution at ambient conditions.

In this work we present calorimetric measurements of the heat of precipitation of various $Mn_xCa_{1-x}CO_3$ solid-phase compositions at 25 °C with the aim to evaluate in a quantitative way (i) the excess free energy of mixing (ΔG^E) of the calcite-rhodochrosite solid solution and (ii) the extent of the miscibility gap.

EXPERIMENTAL.

The precipitation experiments were carried out in a fully silvered Dewar flask of a PARR 6755 solution calorimeter equipped with a PARR 6772 high-precision thermometer. The Dewar flask was fulfilled with 100 ml of a $MnCl_2$-$CaCl_2$ aqueous solution of different Mn^{2+}/Ca^{2+} ratios. A 10 ml 0.5 M Na_2CO_3 solution was poured into a glass cell that was sealed with a detachable Teflon® dish. The cell was finally immersed into the Dewar and forced to a continuously rotating motion by an external electric motor. As soon as thermal equilibrium was achieved, the glass cell was opened and the reactants were mixed into the Dewar flask. The heat of precipitation was determined by the PARR 6772 temperature-measuring system.

The heat of dilution of a 10 ml 0.5 M Na_2CO_3 solution in 100 ml of deionized water was previously determined. The heat of dilution of the $MnCl_2$-$CaCl_2$ aqueous solutions was found to be negligible.

The precipitates formed in these experiments were separated from the aqueous solution using a 0.65 µm filter, dried in an oven at 40 °C, and powdered in order to be analyzed by powder X-Ray diffraction. All the precipitates were confirmed to be homogeneous members of the calcite-rhodochrosite solid solution (Fig. 1). The indexing of the main reflections and the calculation of the unit cell parameters were performed using the computer program X'Pert Plus version 1.0.

The amount of moles of the precipitated solid solution and the solid-phase compositions expressed as the mole fraction of rhodochrosite ($X_{rho} = 1 - X_{cal}$) were determined by analyzing the remaining aqueous solutions in an iCAP 6000 (Thermo) plasma spectrometer.

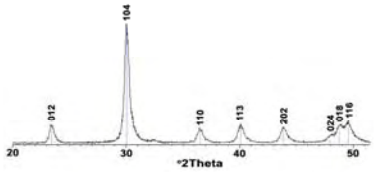

fig 1. A typical diffractogram of a $Mn_xCa_{1-x}CO_3$ solid solution member (X_{rho} = 0.38).

RESULTS AND DISCUSSION.

Excess Free Energy of Mixing.

The enthalpy of mixing (ΔH^m) was calculated as the difference:

$$\Delta H^m = \Delta H_{SS} - \Delta H_{MM} \qquad (1)$$

where ΔH_{SS} is the enthalpy of precipitation determined from the calorimetric measurements and ΔH_{MM} is the enthalpy of precipitation of an equivalent mechanical mixture of the pure $CaCO_3$ and $MnCO_3$ endmembers.

The enthalpy of the mechanical mixture varies as a function of the solid-phase

initial concentrations (M)				
$CaCl_2$	*$MnCl_2$*	*X_{rho} (±0.01)*	*ΔH_{SS} (kJ·mol^{-1})*	*ΔH^m (kJ·mol^{-1})*
0.050	*0.000*	*0.00*	*8.83 ± 0.50*	*—*
0.050	*0.005*	*0.11*	*9.58 ± 0.37*	*0.38 ± 0.37*
0.050	*0.010*	*0.22*	*10.52 ± 0.82*	*0.95 ± 0.80*
0.050	*0.015*	*0.30*	*11.50 ± 0.49*	*1.65 ± 0.47*
0.050	*0.020*	*0.38*	*11.93 ± 0.22*	*1.82 ± 0.22*
0.050	*0.025*	*0.42*	*12.23 ± 0.35*	*1.96 ± 0.36*
0.050	*0.030*	*0.52*	*12.82 ± 0.35*	*2.21 ± 0.30*
0.050	*0.035*	*0.58*	*13.12 ± 0.39*	*2.31 ± 0.43*
0.050	*0.040*	*0.66*	*13.66 ± 0.63*	*2.56 ± 0.60*
0.050	*0.050*	*0.74*	*13.99 ± 0.77*	*2.61 ± 0.75*
0.040	*0.050*	*0.80*	*13.95 ± 0.50*	*2.38 ± 0.52*
0.030	*0.050*	*0.86*	*12.55 ± 0.35*	*0.79 ± 0.33*
0.015	*0.050*	*0.89*	*12.62 ± 0.35*	*0.75 ± 0.33*
0.010	*0.050*	*0.93*	*12.02 ± 0.58*	*0.03 ± 0.57*
0.000	*0.050*	*1.00*	*12.25 ± 0.30*	*—*

Table 1. *Concentrations of parent solutions and solid-phase compositions. Columns 4 and 5 show the enthalpy of precipitation and the enthalpy of mixing of the obtained solid-solution members. The ± symbol stands for the standard deviation (σ).*

palabras clave: Calcite, Kutnahorite, Solid Solution, Excess Free Energy of Mixing.

keywords: Calcita, Kutnahorita, Solución Sólida, Exceso de la Energía Libre de Mezcla.

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composition according to:

$$\Delta H_{MM} = X_{rho} \cdot \Delta H_{rho} + X_{cal} \cdot \Delta H_{cal} \qquad (2)$$

where ΔH_{rho} and ΔH_{cal} are the enthalpies of precipitation of pure $MnCO_3$ and $CaCO_3$ respectively.

The initial concentrations of the aqueous solutions, the solid-phase composition, and the enthalpies of precipitation (ΔH_{SS}) and mixing (ΔH_{MM}) are shown in Table 1. Each experiment was performed in quintuplicate. Therefore, the values of the parameters displayed in Table 1 correspond to the average of five similar experimental runs.

In Fig. 2, the ΔH^m values (in kJ·mol^{-1}) are plotted against the composition of the precipitated solid-phases. The solid line represents a fitting curve ($R^2 = 0.88$) according to the Guggenheim's expansion series that is given by:

$$\begin{aligned}\Delta H^m = {} & R \cdot T \cdot X_{rho} \cdot X_{cal} \cdot [3.93 + \\ & + 1.85 \cdot (X_{rho} - X_{cal}) - \\ & - 2.00 \cdot (X_{rho} - X_{cal})^2]\end{aligned} \qquad (3)$$

where R is the gas constant and T is the absolute temperature in K.

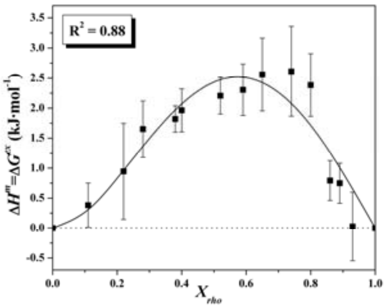

fig 2. The experimental values and the fitting line of the excess enthalpy of mixing obtained for the precipitated solid phases. The error-bars correspond to the standard deviation (σ) assigned to the ΔH^m *values.*

Despite the relatively high degree of the experimental error, the ΔH^m curve clearly demonstrates positive enthalpy of mixing for the whole compositional range. This positive deviation suggests a non-ideal solid solution with a miscibility gap for a series of intermediate $Mn_xCa_{1-x}CO_3$ compositions. (Note that in the present precipitation experiments the supersaturation is very high and the intermediate compositions can crystallize in a metastable way).

Having in mind that the enthalpy of mixing of any ideal solid solution is equal to zero ($\Delta H^{m,id} = 0$), and that $\Delta H^m = \Delta H^{ex} + \Delta H^{m,id}$, for this case $\Delta H^m = \Delta H^{ex}$; therefore, the ΔH^m values shown in Table 1 and the ones corresponding to the excess enthalpy of mixing are equivalent. No ordering or departure from ideal randomness has been detected in the analyses of the diffraction peaks, so that, in a first approximation, the excess entropy of mixing (ΔS^{ex}) has been assumed to be probably negligible. Therefore, the excess Gibbs free energy of mixing ($\Delta G^{ex} = \Delta H^{ex} - T \cdot \Delta S^{ex}$) of the disordered precipitates can be considered equal to ΔH^{ex}.

Miscibility gap.

The extend of the miscibility gap in the (Mn,Ca)CO_3 solid solution was determined using the common tangent points of the free energy of mixing (ΔG^m) function (Glynn & Reardon, 1990):

$$\Delta G^m = \Delta G^{ex} + \Delta G^{m,id} \qquad (4)$$

where $\Delta G^{ex} = \Delta H^m$. The term $\Delta G^{m,id}$ represents the free energy of mixing of an equivalent ideal solid solution that is given by:

$$\begin{aligned}\Delta G^{m,id} = {} & R \cdot T \cdot [X_{\mathrm{rho}} \cdot \ln(X_{rho}) + \\ & + X_{cal} \cdot \ln(X_{cal})]\end{aligned} \qquad (5)$$

The graphical representation of the free energy of mixing and the limits of the miscibility gap are shown in Fig. 3. The results suggest that most of the intermediate members of the calcite-rhodochrosite SS-AS system have to be considered as unstable with respect to a mechanical mixture with composition $(Mn_{0.13}Ca_{0.87})CO_3$ - $(Mn_{0.98}Ca_{0.02})CO_3$.

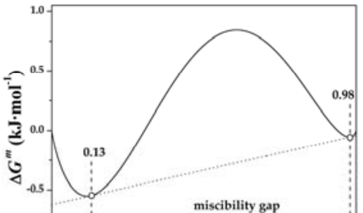

fig. 3. Free energy of mixing of the (Mn,Ca)CO_3 *solid solution (solid curve). The common tangent (dotted line) and the limits of the miscibility gap (vertical dashed lines) are also represented.*

Despite the predicted miscibility gap, the complete series of the calcite-rhodochrosite solid solutions have been experimentally precipitated (Table 1). Such a disagreement has been extensively reported in the bibliography (e.g. Böttcher, 1998) and has been satisfactory interpreted on the basis of kinetic contributions (Mucci, 2004). It is possible that most of the $Mn_xCa_{1-x}CO_3$ solids that crystallize under surface or low-metamorphic conditions correspond to metastable cation-disordered solids.

The Stability Field of Kutnahorite.

Although McBeath et al. (1998) have depicted negative values for the ΔG^E function at intermediate compositions (that was designated to the kutnahorite ordering), the excess energy of mixing determined in present study does not provide any evidence upon the formation of an ordered phase near $X_{rho} = 0.5$. The lack of such evidences at 25 °C has been ascribed to kinetic factors that may suppress the ordering process and lead to metastable equilibrium states (Boynton, 1971).

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