Mixing properties in the continuous solid solution of the system $AgNO_3$–$NaNO_3$

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Abstract

The binary phase diagram for $AgNO_3$–$NaNO_3$ has been previously reinvestigated and shows, in particular, a continuous subsolidus solid solution. The mixing enthalpies in this solid phase determined by solution calorimetry at 474 K are presented here. The results are fitted by the Van Laar model.

INTRODUCTION

The phase diagram and the thermodynamic properties both represent the same general physiochemical phenomenon, i.e. the relative stability of the phases in the composition and temperature ranges. The phase diagrams are investigated experimentally, for example, by differential thermal analysis or X-ray diffraction techniques. The thermodynamic properties are determined by calorimetric and potential methods such as the partial vapor pressure or the concentration cell e.m.f. measurements. The coherency of these two kinds of data is checked by means of computation programs. The simplest ones compare the free energies calculated from the thermodynamic properties of the various phases and draw a phase diagram which can be compared with the experimental determination. More developed calculations fit together the experimental thermodynamic data and the phase diagram investigations. It is emphasized that the best computation program cannot furnish good results if experimental data are bad or lacking. For the monoalkaline nitrates, for example, recent compilations in the system KNO_3–$NaNO_3$ gave different results [1–3].

We are interested here in the Silver nitrate–sodium nitrate system. Many investigations into this phase diagram are reported in the literature (see, for example, refs. 4–8). The mixing properties of the liquid phase have been determined by Kelppa et al. for the enthalpy [7] and by Ketelaar and

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Dammars-Deklerk for the free enthalpy [6]. Our recent redetermination of the phase diagram has shown the existence of a continuous solid solution just below the solidus line [9, 10]. As part of our study of the monoalkaline nitrate ($NaNO_3$, KNO_3, $CsNO_3$) and silver nitrate systems [9–12], the results of the experimental determination of the mixing enthalpy in this solid solution are presented here.

EXPERIMENTAL

The measurement method

The mixing enthalpies of the continuous solid solution $(Ag_x,Na_{1-x})NO_3$ were determined by solution calorimetry. The composition of the solvent corresponds to the composition of the ternary eutectic in the system $CsNO_3$–KNO_3–$NaNO_3$ [13]. A dissolution temperature of 474 K was chosen. The three following reactions were performed inside an isothermal calorimeter

$$x AgNO_3 + S = (AgNO_3)_x,S \tag{1}$$

$$(1 - x)NaNO_3 + S = (NaNO_3)_{1-x},S \tag{2}$$

$$(Ag_x,Na_{1-x})NO_3 + S = (Ag_x,Na_{1-x})NO_3,S \tag{3}$$

for x varying from 0.5 to 1, the concentration range over which the solid solution is stable at the chosen dissolution temperature. The mixing enthalpy $\Delta_m H$ of the solid solution $(Ag_x,Na_{1-x})NO_3$ at the dissolution temperature referred to the pure nitrates at the same temperaure is given by a combination of the different enthalpies, $\Delta_s H_1$, $\Delta_s H_2$, $\Delta_s H_3$, corresponding to reactions (1), (2) and (3), so that

$$\Delta_m H = \Delta_s H_1 + \Delta_s H_2 - \Delta_s H_3$$

if no interaction between the solute species occurs in the solvent. In other words the enthalpy of the reaction

$$(AgNO_3)_x,S + (NaNO_3)_{1-x},S = (Ag_x,Na_{1-x})NO_3,S \tag{4}$$
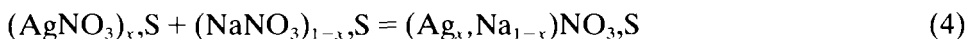
must remain zero. In order to verify this condition, the dissolution enthalpies at infinite dilution of $NaNO_3$ (respectively $AgNO_3$) in the pure solvent and in the solvent containing $AgNO_3$ (respectively $NaNO_3$) have been compared. In the two cases the results are identical; therefore, the assumption $\Delta_s H_4 = 0$ is correct at infinite dilution.

To overcome the experimental difficulty of dissolving exact quantities of $x AgNO_3$ and $(1 - x)NaNO_3$, the thermodynamic cycle under investigation is written at infinite dilution: for each composition the partial dissolution enthalpy is measured for several concentrations of the solute in the bath. Thus, small amounts of the solute are successively dissolved in the same

bath. Only the extrapolated infinite solution enthalpy is used in the following calculations. The mixed enthalpy will then be given by

$$\Delta_m H = x \Delta_s H^{\infty}_{AgNO_3} + (1 - x) \Delta_s H^{\infty}_{NaNO_3} - \Delta_s H^{\infty}_{(Ag_x,Na_{1-x})NO_3} \qquad (5)$$

At the chosen dissolution temperature the solid solution β is stable in the composition range $0.45 < x_{AgNO_3} < 1$. For lower concentrations in silver nitrate this structure is stable at higher temperatures. For pure sodium nitrate, it extends from 549 K to 579 K; thus, the partial dissolution enthalpy which is measured for this compound is relative to the low-temperature phase, α [10]. A correction is then applied to this data by removing the enthalpy of transition $\Delta_{tr} H_{\alpha-\beta}$ of the sodium nitrate at 474 K which is calculated by

$$\Delta_{tr} H(T_c) = \Delta_{tr} H(T_r) + \int_{T_r}^{T_c} [C_{p_\beta}(T) - C_{p_\alpha}(T)]\, dT \qquad (6)$$

where T_c is the temperature of the calorimeter and T_r is the equilibrium temperature of the transition.

This correction is relatively large compared with the expected mixing enthalpies. Therefore, it must be determined carefully. For this reason, the enthalpy of transition and the heat capacities have been recently redetermined: $\Delta_{tr} H(474\ K) = 3369\ J\ mol^{-1}$ [14].

Experimental device and procedure

The dissolution experiments were performed in high-temperature Tian–Calvet twin calorimeter. The experimental design has already been largely described in the literature [15, 16]. Two cylindrical thermopiles, as identical as possible, made of PtRh13%–Pt thermocouples, are set inside an isothermal alumina block. The thermal effects are produced in one of the sensors which are connected together in opposition. The temperature of the calorimetric block is electronically controlled at a constant value by means of an electric furnace. The temperature of the reaction cell is measured with a PtRh10%–Pt thermocouple to ±1 K. The thermal effect occurring during the reaction is recorded on an analog plotter.

Figure 1 shows the calorimetric equipment, which was built in our laboratory. Two platinum crucibles G are introduced in the bottom of the two quartz tubes C which are inserted into the two thermoelectric sensors. At the beginning of a run the solute is placed on the platinum plate H just above the surface of the bath. The plate is fastened by means of three platinum rods to the alumina tube with a refractory cement.

When thermal equilibrium is reached in the calorimeter, the plate is introduced into the bath by a translatory motion of the calorimeter equipment A–D–F–H. The dissolution begins and goes on for about 30 minutes. The vertical motion of the plate inside the thermopile produces a
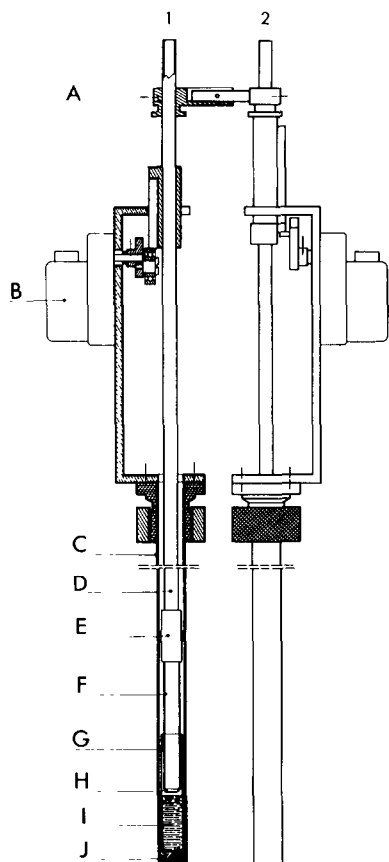
Fig. 1. Calorimetric setup: A, metallic junction pieces; B, electric motors which permit translatory motion and, if necessary, the stirring of the alumina tubes, D; C, quartz tube; E, alumina cement joining the alumina tube and the platinum rods F which support the plate H before the dissolution (the sample is placed on the plate); G, platinum crucible containing the solvent I.

thermal effect which must be measured separately during a "blank run". Such a run follows each dissolution. This thermal effect is minimized by an appropriate adjustment of the position of the plate towards the open surface of the bath.

The calorimeter was calibrated periodically in the same configuration as that used during the dissolutions. The calibration consists of producing known thermal effects in the bath. The area under the thermogram is proportional to the amount of the thermal effect. The proprotional factor depends principally on the temperature and the calorimetric configuration. The calibrating thermal effect is the enthalpic variation of pure platinum balls between two well-known temperatures; the ambient temperature T_a which is determined at ± 0.05 K before each drop into the bath through the alumina tube, and the temperature of the calorimeter T_c. The thermal effect

is obtained by integration of the following heat capacity relation $(J\,mol^{-1}\,K^{-1})$ [17]

$$C_p = 24.5526 + 4.96594 \times 10^{-3}T + 1.20828 \times 10^{-7}T^2 + 15948T^{-2}$$

$$\Delta H = n \int_{T_a}^{T_c} C_p(T)\,dT$$

where n is the amount of platinum (mol) in the ball, measured previously by weighing on an electronic precision balance. For each bath, a group of drops was performed. After studying the discrepancy, the mean value was calculated. The calibrating factor is 0.787 ± 0.025 mW μV^{-1}.

RESULTS AND DISCUSSION

The starting materials were pure nitrates (99.998% minimum for the solid solution samples and 99.8% minimum for the bath) from Aldrich ($CsNO_3$ and $AgNO_3$) and Prolabo ($NaNO_3$ and KNO_3). The samples and the bath were prepared by weighing (Mettler AT250) in suitable propor- tions and melting in a platinum crucible. In order to ensure the homo- geneity of the bath, the compositions were far removed from the ternary eutectic that is homogenized in the liquid state.

The dissolution reactions are relatively fast. For each selected solid solution composition, a lot of samples were dissolved in the same bath, such that the maximum of the solute concentratoin was less than 5 mol.%. The plot of the partial dissolution enthalpies versus the solute concentration in the bath is always a straight line, as shown in Fig. 2. The extrapolations to
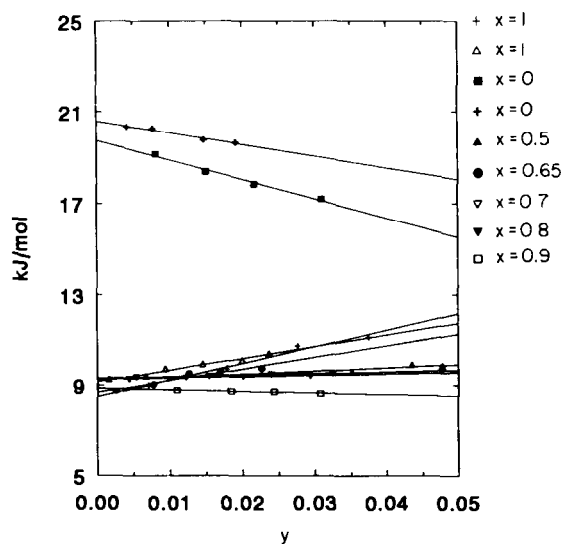

Fig. 2. Dissolution enthalpies of the solid solutions $(Ag_x,Na_{1-x})NO_3$ at 474 K in the $(Na,K,Cs)NO_3$ ternary eutectic: x, molar fraction of $AgNO_3$ in the solid solution; y, molar fraction of the solute $(AgNO_3)_x(NaNO_3)_{1-x}$ in the bath.

TABLE 1

Partial dissolution enthalpies at infinite dilution of the solid solutions $(Ag_x, Na_{1-x})\, NO_3$ at 474 K; the standard deviation σ is calculated by $[\Sigma\,(y - y_i)^2/(n - 2)]^{1/2}$

x	$\Delta_s H^{\infty}_{diss}$ (J mol^{-1})	σ (J mol^{-1})
0.00	20083	118
0.50	9205	300
0.65	8786	133
0.70	9205	23
0.80	9205	13
0.90	8786	22
1.00	8786	180

zero concentration in the bath give the partial dissolution ethalpies at infinite dilution, which are reported in Table 1, with the corresponding standard deviation σ given by $[\Sigma\,(y - y_i)^2/(n - 2)]^{1/2}$, n being the number of data for each composition.

From these data, the mixing enthalpies in the solid solution referred to the pure nitrates in the same structure β, can be deduced with the equation

$$\Delta_m H = x \Delta_s H^{\infty}_{AgNO_3} + (1 - x)\Delta_s H^{\infty}_{NaNO_3} - \Delta_s H^{\infty}_{(Ag_x, Na_{1-x})NO_3} - (1 - x)\Delta_{tr} H_{NaNO_3}$$

deduced from eqns. (5) and (6). The results are reported in Table 2 and Fig. 2. In order to estimate a global inaccuracy of the experimental data, for the two pure nitrates two series of five runs were performed using four different baths sampled from the single ternary eutectic mixture. In each case, two distinct extrapolations at infinite dilution were determined with a reproducibility of ± 420 J. This major value is also affected by the extrapolated data corresponding to the solid solution concentrations. The solid solution presents a positive deviation from ideality and a shift of the

TABLE 2

Mixing enthalpies in the solid solutions $(Ag_x, Na_{1-x})NO_3$ referred to the pure nitrates in the same structure at 474 K

x	$\Delta_m H$ (J mol^{-1})
0.00	0
0.50	3546
0.65	2775
0.70	1960
0.80	1167
0.90	793
1.00	0

maximum to the sodium-rich concentration range. It can be observed that, within the error margin, the solution referred to pure silver nitrate and the solid solution at $x = 0.5$ are ideal.

The shift can be related to the difference between the volumes of the cations. In fact, the parameters of the rhombohedral unit cells of the pure nitrate are very close: $a = 4.15$ Å, axial angle $75°31'$ for sodium nitrate; and $a = 4.13$ Å, axial angle $78°0'$ for silver nitrate. In the Van Laar model for a binary mixture AB, the mixing enthalpy can be written as a function of the partial mixing enthalpy at infinite dilution ΔH_A^∞, the concentration x_B and the volume ratio of the species ($\mu = V_A/V_B$). Moreover, the ratio of the enthalpies at infinite dilution equals the volume ratio μ

$$\Delta_m H = \Delta H_A^\infty \frac{x_B(1 - x_B)}{x_B + (1 - x_B)\mu}$$

$$\frac{\Delta H_A^\infty}{\Delta H_B^\infty} = \frac{V_A}{V_B} = \mu$$

The literature data for the ionic radius of sodium are in good agreement. For our purposes, we use $r_{Na} = 0.97$ Å [18] and $r_{Na} = 0.98$ Å [19]. For the silver ion, a larger discrepancy is observed. Newns and Staveley [19] gave 1.13 Å and ref. 18, 1.26 Å. The following fits of the experimental data are represented in Fig. 3 and in Table 3. With respect to the maximum position, the best fit seems to be given with an ionic radius for silver of 1.26 Å. The
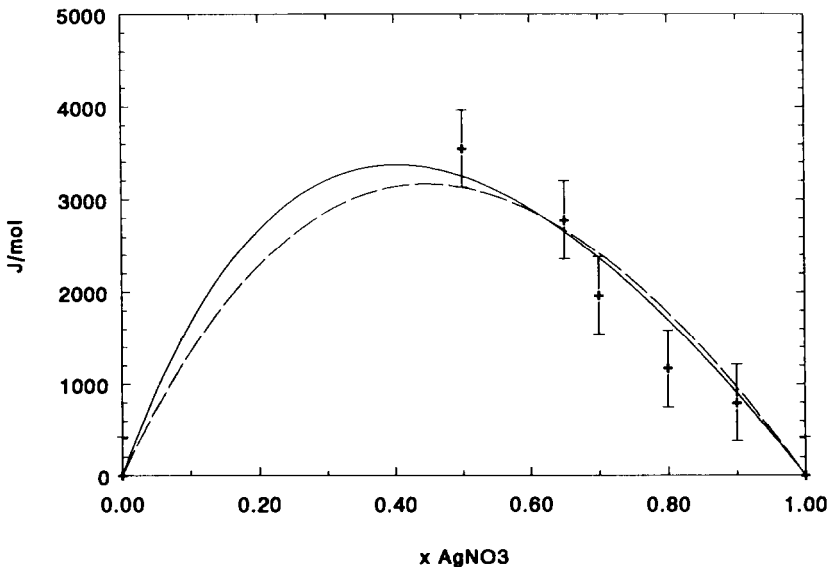

Fig. 3. Mixing enthalpy in the solid solution $(Ag_x,Na_{1-x})NO_3$ at 474 K. The stability range at this temperature is $0.45 < x < 1$. The curves represent two fits of the data with a Van Laar equation: $\mu = 0.456$, solid line; $\mu = 0.652$, broken line.

TABLE 3

The calculation of the enthalpies at infinite dilution of $AgNO_3$ and $NaNO_3$ in the solid solutions $(Ag_x,Na_{1-x})NO_3$ at 474 K

r_{Na} (Å)	r_{Ag} (Å)	μ	$\Delta_{Na}H^\infty$ (kJ mol^{-1})	$\Delta_{Ag}H^\infty$ (kJ mol^{-1})
0.98	1.13	0.652	10.33	15.84
0.97	1.26	0.456	9.45	20.72

maximum mixing enthalpy ($\approx$kJ mol^{-1}) is of the same order of magnitude as the correcting factor, due to the reference state change of $NaNO_3$ ($\approx$2 kJ mol^{-1} at this composition). This stresses the importance of an exact as possible knowledge of heat capacity variations corresponding to this transition. The mixing enthalpies at infinite dilution for the sodium and silver nitrates which are then deduced can be affected to the same extent by such an inaccuracy. The corresponding value for the silver nitrate is higher by about 5–10 kJ mol^{-1} than that of the sodium nitrate.

No direct evidence for the existence of the solid solution is available in the X-ray diffraction literature. This is largely due to the high diffracting power of the silver, making the detailed resolution of the structure difficult by this technique. Nevertheless, mixed crystals between $NaNO_3$ and $AgNO_3$ have been observed by Bridgman, (as mentioned in ref. 19). The recent redetermination of the phase diagram [9, 10] and this study represent the only thermodynamic observations of this solid solution.

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