Solubility of Nickel Chloride in Molten Sodium Tetrachloroaluminate saturated with Sodium Chloride over the Temperature Range 200–400 °C

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Interesting thermodynamic data have been obtained from experiments in molten sodium tetrachloroaluminate. The solubility of NiCl₂ in chlorobasic (NaCl-saturated) NaAlCl₄ has been studied over the temperature range 200–400 °C, leading to the result that the apparent standard enthalpy change for the dissolution of NiCl₂ in this system is independent of temperature over this range. This is normally only the case in simple solvents and/or where free ions are formed. A model is presented which accounts for the observations.

As part of our phase studies in the NaCl-AlCl₃ and NaCl-AlCl₃-NiCl₂ systems, we have investigated the temperature dependence of the solubility of nickel chloride in molten sodium tetrachloroaluminate (NaAlCl₄). NaAlCl₄ is an ionic solid (m.p. $\approx 156 \,^{\circ}\text{C})^1$ which can be prepared from an equimolar mixture of NaCl and AlCl₃. The solubility of NiCl₂ in NaAlCl₄ is of particular interest to those involved in ZEBRA^{\dagger} cell² technology; such cells utilise an NaAlCl₄based molten electrolyte and a solid Ni|NiCl₂ positive plate. Under normal circumstances, the liquid electrolyte in ZEBRA cells is (chloro)basic,^{3,4} with an excess of NaCl solid present at all times. Our experiments were therefore carried out using NaCl-saturated NaAlCl₄; the solubility of NaCl in NaAlCl₄ has previously been determined over the desired temperature range,⁵ the values being of the order of 0.1 mol kg⁻ ¹ (see Table 1).

The solubility of NiCl₂ in NaAlCl₄ is known to be small⁶ compared with that of NaCl, although numerical data covering a range of temperatures have been reported only very recently.⁷ Studies of NiCl₂ solubility with varying melt composition do not appear to have been published, although we are aware of such studies involving other transition-metal chlorides.^{8,9} The fact that relatively few solubility studies have been undertaken is likely to be due to the very long equilibration times involved. In addition, the solubilities of other transition-metal chlorides in sodium tetrachloro-aluminate are known⁴ to be extremely composition (at which a strikingly sharp minimum of solubility has been observed).^{8,9}

Solid NaAlCl₄ was prepared to order by Merck, using Analar grade AlCl₃ and NaCl, followed by pre-electrolysis to remove electroactive contaminants and filtration to remove suspended matter. The samples thus provided possessed a suitably low moisture content for use in our experiments. The molten NaAlCl₄ was again filtered immediately prior to use using a high-temperature filtration system operated within a thermostatted molten salt bath containing 10 1 of KNO₃-NaNO₃-NaNO₂ at eutectic composition. The waterclear molten NaAlCl₄ was then transferred to a doublecontained Pyrex solubility cell (also situated in the salt bath) which was maintained under a positive inert atmosphere of White Spot oxygen-free nitrogen (BOC Ltd.), which was dried using sulfuric acid traps. Failure to ensure that atmospheric moisture is adequately excluded results in the formation of insoluble Al_2O_3 which is particularly troublesome if the solid remains suspended in solution for a long period of time. An excess of NaCl (ICI vacuum dried, >99.9%) was then added to the cell and left to equilibrate for several days. NiCl₂ was prepared¹⁰ by the dehydration of NiCl₂ \cdot 6H₂O using thionyl chloride (SOCl₂). The purest samples obtained were found to contain 44.5 mass% Ni (compared with 45.3 mass% for pure NiCl₂), it being extremely difficult to achieve complete dehydration. The Ni analysis was carried out by means of a complexometric titration using EDTA. An excess of NiCl₂ was then added to the solubility cell and allowed to equilibrate using the nitrogen flow system to agitate the melt continuously. Depending on the temperature, the equilibration time required (judged by visual observation of the melt colour/intensity) could be as long as three weeks.

Once equilibration was deemed to be complete, the gas inlet tube was raised above the level of the melt and the solid particles allowed to settle. Several days invariably elapsed before a clear melt could be obtained, although this was difficult to judge in the intensely coloured (blue) solutions obtained at the highest temperatures. Samples of melt (1-2 g) were then extracted using a long-handled Pyrex spoon, solidified in a stainless-steel dish and weighed immediately. The solid samples were then dissolved in distilled water and made up to known volumes prior to analysis. Ni analysis was carried out by means of flame atomic absorption spectroscopy (FAAS) using a Perkin-Elmer 2380 atomic absorption

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Table 1 Comparison of experimental solubility of NiCl₂ in NaCl-saturated NaAlCl₄ with that of NaCl in NaAlCl₄ (data from ref. 5) in the range 200-400 $^{\circ}$ C

	$m(\text{NiCl}_2)/m^{\Theta}$			$m(Na^+)/m^{\Theta}$ in	
t/°C	series 1	series 2	series 3	$m(NaCl)$ /m ^{Θ}	NaCl-sat. NaAlCl₄
200	2.95×10^{-4}		2.34×10^{-4}	0.05	5.26
250		7.41×10^{-4}	6.31×10^{-4}	0.09	5.30
300	1.51×10^{-3}	1.20×10^{-3}	1.32×10^{-3}	0.15	5.36
350	2.14×10^{-3}		2.75×10^{-3}	0.22	5.43
400	5.30×10^{-3}	5.09×10^{-3}	4.18×10^{-3}	0.32	5.53

spectrophotometer measuring at 232 nm. Two sets of Ni standard solutions were employed (with and without a large excess of sodium ions) in order to determine whether or not matrix effects would give rise to misleading results. In the event, no interference was observed. The concentrations of Ni thus obtained were then converted to give the solubility of NiCl₂ in NaCl-saturated NaAlCl₄ in units of mol kg⁻¹.

Three sets of data were obtained for each of five temperatures in the range 200-400 °C, giving rise to a degree of scatter in the data points. Erroneously high values (due to inclusion of suspended solid matter in the sampling process) were then rejected on the basis of additional sodium analysis (using a Corning 400 Flame Photometer) from which the NaCl content of the melt was determined. Since inclusion of suspended solid matter leads to erroneously high values of both NiCl₂ and NaCl content, comparison of the resulting NaCl content with the solubility data given in ref. 5 indicated which samples had included solid matter. Use of this technique to test for under-saturation is not generally feasible since NaCl attains saturation in a far shorter period of time than NiCl₂. Table 1 shows the remaining data obtained over three sets of experiments.

It is apparent from Table 1 that, under the (chloro)basic conditions employed in our experiments, $NiCl_2$ is around two orders of magnitude less soluble than NaCl in $NaAlCl_4$. The solubility of $NiCl_2$ is known⁶ to fall further as the basicity of the solvent is reduced; a pronounced minimum in solubility is observed when the $AlCl_3$: NaCl ratio is exactly 1 : 1.

Fig. 1 illustrates the linear relationship between $\ln[m(NiCl_2)/m^{\odot}]$ and inverse absolute temperature [curve (b)]. The equation corresponding to the line of best fit is:

$$\ln\left(\frac{m(\text{NiCl}_2)}{m^{\Theta}}\right) = (1.38 \pm 0.64) - \frac{(4560 \pm 360)K}{T} \qquad (1)$$

where the ranges quoted correspond to 95% confidence limits and the standard deviation of the fit is 0.12.

This result is somewhat unusual for a system as apparently complicated as the one under investigation, and it implies that the apparent standard enthalpy change for the dissolution of NiCl₂ in NaCl-saturated NaAlCl₄ ($\Delta H_{\text{NiCl}_2}^{\ominus}$) is independent of temperature over the range studied. From the graph,

$$\Delta H_{\text{NiCl}_2}^{\Theta} = -R \left(\frac{\partial \ln[m(\text{NiCl}_2)]}{\partial T^{-1}} \right)_{p, \text{ sat.}}$$

= 37.9 ± 2.9 kJ mol⁻¹ (2)

The data provided in ref. 5 also conform to a linear relationship between $\ln[m(\text{NaCl})/m^{\Theta}]$ and inverse absolute temperature, from which the value $\Delta H_{\text{NaCl}}^{\Theta} = 23.0 \pm 2.2 \text{ kJ mol}^{-1}$



Fig. 1 Comparison of plots of (a) $\ln[m(\text{NiCl}_2)m(\text{Na}^+)^2/m^{\ominus 3}]$ and (b) $[m(\text{NiCl}_2)/m^{\ominus}]$ vs. 1/T

J. CHEM. SOC. FARADAY TRANS., 1993, VOL. 89

is derived. This is understandable since the system is simpler; the NaAlCl₄ itself does not vary in composition with temperature and the solute dissolves to form free ions. In our experiments, however, the solvent (NaCl-saturated NaAlCl₄) has a chloride molality which does vary with temperature. In addition, Ni²⁺ is too polarising a cation to exist as a free ion in solution and thus complex formation is expected. It is believed¹¹ that at least two distinct nickel complexes are present in chloroaluminate melts, one of which is known to be NiCl²⁻₄. Since free chloride ions (the activity of which varies with temperature) are almost certainly involved in complex formation/equilibria, an explanation of the linearity of Fig. 1 is not immediately obvious. However, an interpretation may be presented on the basis of a simple model for the dissolution processes involved.

In the molten state, the stoichiometric compound NaAlCl₄ is a charge-ordered ionic liquid containing discrete Na⁺ and AlCl₄⁻ ions. The latter disproportionate to a significant extent¹² as follows:

$$2\mathrm{AlCl}_{4}^{-} \rightleftharpoons \mathrm{Al}_{2}\mathrm{Cl}_{7}^{-} + \mathrm{Cl}^{-} \tag{I}$$

The equilibrium constant for reaction (I) has been measured, as a function of temperature.^{12,13} Calculations (not presented here) show that negligible error arises if we take the chloride ion concentration in NaCl-saturated NaAlCl₄ to be the same as the NaCl solubility; the contribution arising from the disproportionation of $AlCl_4^-$ is less than 1% of the total at all temperatures in the range of our experiments.

At a specific temperature and assuming ideal behaviour, the dissolution of NaCl to form free ions is given by the equilibrium constant

$$K_1 = \frac{m(\mathrm{Na}^+)m(\mathrm{Cl}^-)}{m^{\Theta 2}}$$
(3)

the activity of solid NaCl being equal to unity by definition. In this expression, $m(Cl^-)$ is equal to the solubility of NaCl, which is relatively small but varies quite markedly with temperature (see Table 1). In contrast, $m(Na^+)$ is greater than the solubility of NaCl by an amount 5.214, which is the sodium ion molality in the pure solvent NaAlCl₄. In consequence, the fractional change in $m(Na^+)$ with temperature is much smaller than that for $m(Cl^-)$.

The simplest model for NiCl₂ dissolution is that in which $NiCl_4^{2-}$ is assumed to be the only nickel species formed in solution. Spectroscopic evidence indicates that this is undoubtedly the major nickel complex in this system; the additional complexes are certainly present in such low concentrations that conclusive spectral evidence for their existence has not been presented in the literature. $NiCl_4^{2-}$ is formed according to the equilibrium

$$NiCl_2(s) + 2Cl^- \rightleftharpoons NiCl_4^{2-}$$
 (II)

Assuming ideal behaviour, the equilibrium constant in this case is

$$K_{2} = \frac{[m(NiCl_{4}^{2-})/m^{\Theta}]}{[m(Cl^{-})/m^{\Theta}]^{2}}$$
(4)

Substitution for $m(Cl^{-})$ using eqn. (3), and rearrangement, gives

NiCl₂ solubility =
$$m(NiCl_4^{2^-}) = \frac{K_2 K_1^2 m^{\Theta_3}}{m(Na^+)^2}$$
 (5)

Thus, in terms of this model, a plot of $\ln[m(\operatorname{NiCl}_4^2 -)m(\operatorname{Na}^+)^2/m^{\ominus 3}]$ vs. 1/T should be a straight line. This plot is shown in Fig. 1, curve (a). On comparison of the two curves, it is seen that the inclusion of the term $m(\operatorname{Na}^+)^2$ makes very little difference to the rectilinearity of the plot, having regard to the scatter in the experimental results; the slopes of curves (a) and (b), with 95% confidence limits, are

respectively -4710 ± 370 K and -4560 ± 360 K. This small difference in slope is attributable to the fact that the fractional change in $m(Na^+)$ is small over the temperature range of interest (see Table 1). For curve (a), we may write

$$\Delta H_{\text{NiCl}_{2}}^{\Theta} = -R \left(\frac{\partial \ln[m(\text{NiCl}_{4}^{2})]}{\partial T^{-1}} \right)_{p, \text{ sat.}}$$

$$= -R \left(\frac{\partial \ln K_{2}}{\partial T^{-1}} \right)_{p, \text{ sat.}} - 2R \left(\frac{\partial \ln K_{1}}{\partial T^{-1}} \right)_{p, \text{ sat.}}$$

$$+ 2R \left(\frac{\partial \ln[m(\text{Na}^{+})]}{\partial T^{-1}} \right)_{p, \text{ sat.}}$$

$$= \Delta H_{2}^{\Theta} + 2\Delta H_{\text{NaCl}}^{\Theta} + 2R \left(\frac{\partial \ln[m(\text{Na}^{+})]}{\partial T^{-1}} \right)_{p, \text{ sat.}}$$
(6)

Thus, the apparent standard enthalpy change for the dissolution of NiCl₂ in NaAlCl₄ saturated with NaCl is the sum of three enthalpy terms, the last of which, although temperature dependent, is small compared with the other two (we estimate that the mean value of $-2R \partial \ln[m(Na^+)]/\partial T^{-1}$ is 1290 J mol⁻¹ over the temperature range of interest). Thus, the linearity of curve (b) of Fig. 1 is explained on the basis of this model. Implicit in the above treatment is the neglect of activity coefficients (or, more exactly, of their temperature dependence).

We have compared our results with data on the same system reported recently by Redey *et al.*⁷ The data at temperatures below 300 °C are in agreement with those presented here only in terms of the order of magnitude, and considerably more scatter is apparent. Above 300 °C, however, they report that the solubility rises very steeply, which may indicate that suspended solid NiCl₂ was included in their sampling process.

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3819