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Equilibrium Studies of Nickel(II) Thiocyanate Complexes in Molten Dimethylsulphone

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The equilibrium between a tetrahedral and an octahedral nickel(II) thiocyanate complex was studied spectrophotometrically in molten dimethylsulphone. The effects of variation of temperature and concentrations of the cations, K^+ and Bu_4N^+, on the equilibrium were determined. The results indicate that there is a complex interaction between the coordination sphere and the outer cationic sphere and that the heat of reaction is dependent on the relative concentrations of the two cations.

Introduction

It has been found [1–3] that the spectra of various Ni(II) complexes in melts are often extremely sensitive to temperature and to the nature of the cations present in solution. For example, the spectra of dilute solutions of $NiCl_2$ in chloride melts vary with the relative amounts of Li^+ and K^+ present in the solution [1, 2]. Also, while Ni(II) is known to be octahedrally coordinated in molten KSCN [5, 6], there appears to be a tetrahedrally coordinated species present as well in molten dimethylsulphone [3]. The relative amounts of the octahedral and tetrahedral Ni(II) species depend upon the temperature and the relative concentrations of K^+ and Bu_4N^+ in the solution. These results can be qualitatively explained according to models suggested by Smith [7] and by Gruen and McBeth [1, 8]. The smaller the cation is the greater its ability to stabilize a highly negatively charged complex (in solution, though not in the solid-state [9]) and hence a high concentration of small cations tends to produce a high concentration of the octahedrally coordinated species (preferential stabilization of pseudo-halide bonding modes by counterions in the solid-state has been observed [10]). A finding from the study of de Haas [3] is that plots of the logarithm of the absorbance of solutions of $Ni(NCS)_2$ in molten dimethylsulphone containing KSCN and Bu_4NSCN *vs.* the reciprocal of the temperature are linear. We have carried out a more extensive investigation of the equilibrium between tetrahedral and octahedral nickel(II) thiocyanate complexes in molten dimethylsulphone with a view to subsequent determination of the kinetics and mechanism of the reaction, and an explanation of the linearity of the $\ln\epsilon$ *vs.* T^{-1} plots is proposed.

Experimental

Koch–Light reagent grade chemicals were used in this investigation. The salt, $Ni(NCS)_2 \cdot 2H_2O$ was prepared in the manner described by de Haas [3]. All materials were handled only in a dry box under nitrogen. Concentration ranges employed were (at 110 °C): [Ni(II)], 4–10 $\times 10^{-3}$ *M*; $[K^+]$, 0.2–0.8 *M*; and $[Bu_4N^+]$, 0.2–0.8 *M*. For samples with mixed cations, the values of $\alpha = [Bu_4N^+]/([Bu_4N^+] + [K^+])$ used were in the range 0.1–0.8. The temperature range investigated was 108° to 150 °C.

A Zeiss PMQ3 spectrometer modified for measuring spectra at high temperatures [4] was used to measure the absorbances of the solutions. The samples were contained in 1 cm quartz cells placed in a furnace, the temperature of which was controlled by a Eurotherm SCR proportionating temperature controller. Spectra were determined from 400 nm to 800 nm in order to monitor changes in the absorption as functions of wavelength. Absorbance values were obtained at a wavelength of 620 nm at which there is a maximum in the spectrum of the tetrahedral nickel(II) species.

Results and Discussion

Under no conditions in molten dimethylsulphone could a solution containing either a pure tetrahedral or a pure octahedral nickel(II) thiocyanate complex be obtained. In all cases a mixture of the two was obtained. For every solution studied, plots of the logarithm of the absorbance, A, *vs.* the reciprocal of the temperature were linear.

Examples of plots of $\log\epsilon$ *vs.* T^{-1} where $\epsilon = A/N_0$ and N_0 is total Ni concentration for solutions containing both K^+ and Bu_4N^+ are given in Figure 1, with linear plots pertaining. However, the values of the slopes are not the same but vary with the value of α. Table I lists ΔH^0 values calculated from the slopes of plots of the type illustrated in Figure 1 for various α values. As can be seen ΔH^0 appears to decrease with

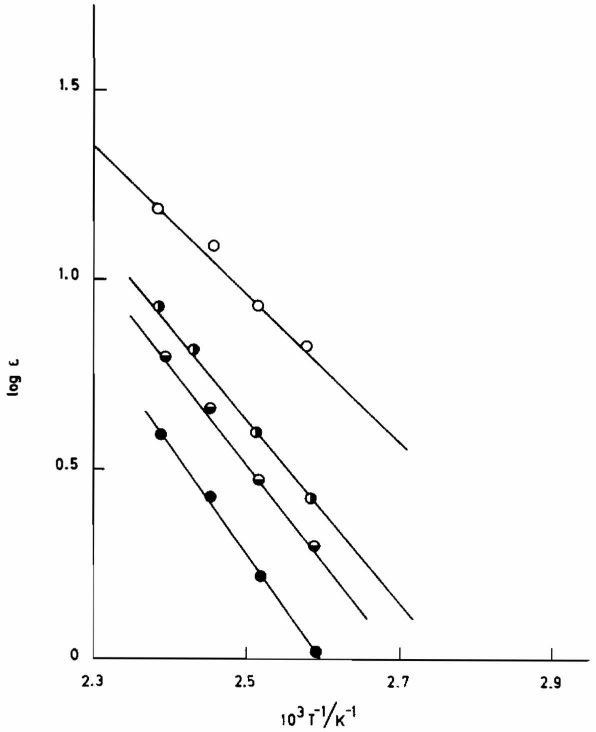

Fig. 1. Plot of log ϵ *vs.* 10^3 T^{-1} for various $\alpha = [Bu_4N^+]/([Bu_4N^+] + [K^+])$. ●, $\alpha = 0.2$; ⊖, $\alpha = 0.4$; ◑, $\alpha = 0.6$; ○, $\alpha = 0.8$, and $\epsilon = A/[Ni^+]$ where A is absorbance.

TABLE I. Measured ΔH^0 Values for Different Values of α.

α	ΔH^0 kJ mol^{-1}
0.2	25.6
0.4	22.7
0.6	22.0
0.8	16.4

increasing α values. The value of 19.7 kJ/mol found by de Haas [3] lies well within the range of values found in this investigation.

The linearity of plots of log ϵ *vs.* T^{-1} is explained as follows. The equilibrium constant for the reaction

$$T + 2L \rightleftarrows O_h \qquad (1)$$

may be written as

$$K = \frac{[O_h]}{[T]\,[L]^2} \qquad (2)$$

where $T = Ni(NCS)_4^{2-}$, $O_h = Ni(NCS)_6^{4-}$, and $L = SCN^-$. The absorption coefficient, ϵ, of a solution of mixed T and O_h is given by

$$\epsilon = \frac{[T]}{[O_h] + [T]}\epsilon_T + \frac{[O_h]}{[O_h] + [T]}\epsilon_0 \qquad (3)$$

where ϵ_T is the absorption coefficient of T and ϵ_0 the absorption coefficient of O_h. Since,

$$M_0 = [O_h] + [T] \qquad (4)$$

where M_0 is the total nickel concentration, then equation (3) may be written as

$$\epsilon = \frac{(M_0 - [O_h])(\epsilon_T)}{M_0} + \frac{[O_h]}{M_0}\epsilon_0$$

or

$$\epsilon = \epsilon_T + \frac{[O_h](\epsilon_0 - \epsilon_T)}{M_0} \qquad (5)$$

and equation (2) and equation (4) can be combined and rearranged to give

$$[O_h] = \frac{M_0 K[L]^2}{1 + K[L]^2} \qquad (6)$$

Substituting equation (6) into equation (5) gives

$$\epsilon = \epsilon_T + \frac{(\epsilon_0 - \epsilon_T)K[L]^2}{1 + K[L]^2}$$

or

$$\epsilon = \frac{\epsilon_T + \epsilon_0 K[L]^2}{1 + K[L]^2} \qquad (7)$$

At 620 nm, ϵ_0 is very small compared with ϵ_T and, hence,

$$\epsilon \cong \frac{\epsilon_T}{1 + K[L]^2} \qquad (8)$$

Since $[O_h] > [T]$ under the conditions used in this investigation, it follows from (2) that $K[L]^2 > 1$ and hence

$$\epsilon \cong \frac{\epsilon_T}{K[L]^2} \qquad (9)$$

Since

$$K = \exp[\Delta S^0/R]\exp[-\Delta H^0/RT] \qquad (10)$$

then

$$\epsilon \cong (\epsilon_T/[L]^2)\exp[-\Delta S^0/R]\exp[\Delta H^0/RT] \qquad (11)$$

Equation (11) explains the linear plots of lnϵ *vs.* T^{-1} and predicts that the slopes of the plots are equal to $\Delta H^0/R$.

The small cation, K^+, tends to stabilize the highly charged O_h species much more than the large cation, Bu_4N^+, because the former, on average, can get much closer to the O_h species. It also, of course, undoubtedly stabilizes the T species more as well, but the effect is not as marked because the charge is not as great. The effects are illustrated in Figure 2 where T_N and O_N represent the species surrounded only by Bu_4N^+; T_K and O_K represent the species surrounded only by K^+, ΔH_N^0 is the standard enthalpy of reaction if only Bu_4N^+ cations are present, and ΔH_K^0 is the standard enthalpy of reaction if only K^+ ions are present.

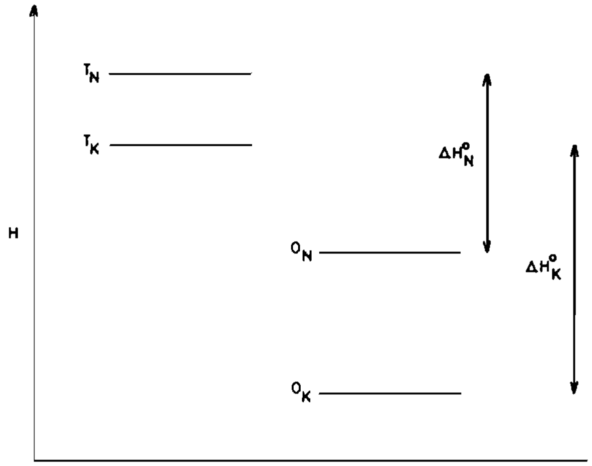

Fig. 2. Enthalpy diagram showing relative stabilities of O_h and T complexes. T_N and O_N represent the species surrounded only by Bu_4N^+; T_K and O_K represent the species surrounded only by K^+, ΔH^0_N is the standard enthalpy of reaction if only Bu_4N^+ cations are present, and ΔH^0_K is the standard enthalpy of reaction if only K^+ ions are present.

In solutions containing mixed cations, the effect on the enthalpies of reaction is somewhere between the two extremes illustrated in Figure 2. If it is assumed that the probability of a species being in contact with a given cation is directly proportional to the concentration of that cation and that the enthalpy of reaction varies linearly with the proportion of the two cations (*i.e.* if there is a 1:1 ratio of Bu_4N^+ and K^+, then the enthalpy of reaction is $(\Delta H^0_N + \Delta H^0_K)/2)$, then the observed enthalpy of reaction is given by

$$\Delta H^0 = \frac{[K^+]}{[Bu_4N^+] + [K^+]}\Delta H^0_K + \frac{[Bu_4N^+]}{[Bu_4N^+] + [K^+]}\Delta H^0_N \qquad (12)$$

or

$$\Delta H^0 = (1 - \alpha)\Delta H^0_K + \alpha\Delta H^0_N \qquad (13)$$

Hence,

$$\Delta H^0 = \Delta H^0_K + \alpha(\Delta H^0_N - \Delta H^0_K) \qquad (14)$$

Equation (14) cannot be expected to apply quantitatively, since it is unlikely that the probability of a cation being in contact with another species is directly proportional to its concentration, since energy differences between the two cations also affect the probability through the Boltzmann factor. However, this simple interpretation explains semi-quantitatively the observed increasing value of ΔH^0 with decreasing values of α.

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