Thermodynamics of Formation of Na^+(cryptand[2.2.1])·Na^- from the Metal and Complexant

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Abstract

The e.m.f. of the cell Pt|Na(s)|$Na^+\beta$-alumina|Na^+(C221)·Na^-(sat),C221(sat)|Pt in which C221 represents cryptand[2.2.1] was measured as a function of temperature from −75 to +5 °C in diethylether and diethylether–trimethylamine mixtures. The thermodynamic results for the reaction 2Na(s) + C221(l) → Na^+(C221)·Na^-(s) are: $\Delta G^\circ_{298} = -12.3 \pm 0.6$ kJ mol^{-1}, $\Delta H^\circ = -37 \pm 3$ kJ mol^{-1} and $\Delta S^\circ = -83 \pm 8$ J mol^{-1} K^{-1}. As was the case for Na^+(C222)·Na^- (U. Schindewolf, L. D. Le and J. L. Dye, *J. Phys. Chem., 86* (1982) 2284) the enthalpy change is fairly close to that predicted from a modified Born–Haber cycle but the magnitude of the entropy change is much smaller than predicted.

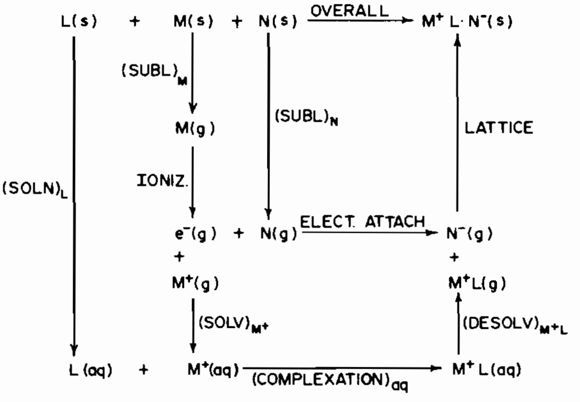

Fig. 1. Modified Born–Haber cycle used to estimate ΔH° and ΔS° for the formation of alkalides and electrides from the metal(s) and complexant (refs. 19 and 26).

Introduction

Since the preparation of the first sodide salt in 1974 [1, 2], we have synthesized and characterized a large number of crystalline salts (alkalides) that contain Na^-, K^-, Rb^- or Cs^- as counter-ions to complexed alkali metal cations [3–25]. Estimates of the stability of alkalides by use of a modified Born–Haber cycle [7, 19, 26] indicate that all are enthalpy stabilized but entropy destabilized. The two effects very nearly balance at ambient temperatures so that ΔG° for the formation reaction

$$M(s) + N(s) + \text{complexant} \longrightarrow M^+(\text{complexant})\cdot N^- \qquad (1)$$

in which M and N can be either the same or different alkali metals, is too close to zero to permit a reliable assessment of stability. It was thought, however, that differences in the estimated thermodynamic quantities would be more reliable. Only for a single compound, Na^+(C222)·Na^- **, have measured thermodynamic properties been obtained [13]. Although the measured enthalpy change for reaction (1) (with M = N = Na, complexant = C222) was within two standard deviation estimates of the predicted value, the measured entropy change of −90 ± 8 J mol^{-1} K^{-1} was very different from the predicted value of −197 J mol^{-1} K^{-1}. The measured value of ΔG°, −7.1 ± 0.6 kJ mol^{-1}, was therefore 28 kJ mol^{-1} more negative than predicted. Attempts to reconcile the large difference between predicted and observed entropies of reaction have not been successful [26]. In this paper we report thermodynamic measurements on a second sodide, Na^+(C221)·Na^- which is predicted [26] to the about 10 kJ mol^{-1} more stable than the 'parent' compound, Na^+(C222)·Na^-.

The estimation of ΔH° and ΔS° for reaction (1) is based on a combination of experimental data and model calculations, as indicated in Fig. 1. Although lack of data on the thermodynamics of solution of the complexant in water and of complexation of the cation by L can introduce uncertainty in some cases, the major sources of error are the model calculations of the solvation enthalpies and entropies of M^+(g) and M^+L(g) and the lattice enthalpies and entropies of $M^+L\cdot N^-$. Errors in these calculations are expected to have the same sign and be of comparable magnitude for different compounds, so that estimated *differences* in ΔH°, ΔS° and ΔG° should be more

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**IUPAC names are: cryptand[2.2.2], 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane, abbreviation C222; cryptand[2.2.1], 4,7,13,16,21-pentaoxa-1,10-diazabicyclo[8.8.5]tricosane, abbreviation C221.

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reliable than absolute values. Of course, differences in structure that are not accommodated by the simple spherical models will introduce uncompensated errors.

The reliability of the thermodynamic estimates described above could be tested by e.m.f. measurements on other alkalides. However, the number of compounds that can be studied at present is limited by the availability of only a sodium electrode, so that the complexed cation must contain Na^+, and the anion must be Na^-. The only known alkalide [12] other than $Na^+(C222)\cdot Na^-$ that meets these criteria is $Na^+(C221)\cdot Na^-$, the subject of this paper. In adapting the cycle of Fig. 1 to the present case, it should be noted that the ligand C221 is a liquid that readily undercools. The absence of a change in the slope of the plot of e.m.f. versus T indicates that no significant effects due to the phase transitions are present.

The thermodynamics of the reaction

$$2Na(s) + C221(l) \longrightarrow Na^+(C221)\cdot Na^-(s) \qquad (2)$$

can be studied by determining the e.m.f. of the cell

$$Pt|Na(s)|Na^+\beta\text{-alumina}|Na^+(C221)\cdot Na^-(sat),C221(sat)|Pt \qquad (3)$$

as a function of temperature. As long as the solution is saturated in both the salt and the (liquid) complexant, the e.m.f., E, is independent of the nature of the solvent [13] and is related to ΔG_2° by

$$\Delta G_2^\circ = -2FE \qquad (4)$$

in which F is the Faraday. The variation of E with temperature yields ΔH_2° and ΔS_2°.

Experimental

The construction of a reversible sodium–β-alumina electrode has been described in detail [27–29] as has the preparation of crystalline $Na^+(C221)\cdot Na^-$ [12, 26]. A diagram of the cell is given in ref. 13. The cell was loaded with 100–500 mg each of cold (−50 °C) solid $Na^+(C221)\cdot Na^-$ and C221 in a nitrogen-filled glove bag.

The compound $Na^+(C221)\cdot Na^-$ is difficult to crystallize, probably because of its very high solubility in the 'usual' recrystallization solvent mixtures of dimethylether and either trimethylamine or diethylether. When mixtures of n-pentane with either 2-aminopropane or trimethylamine were used, gold-colored crystals formed at −78 °C. When solvent free crystals were warmed to about −30 °C the color changed to blue–green with a coppery sheen and the crystals appeared to soften or melt, losing their sharp edges.

After loading the cell with the sodide and complexant, it was evacuated to ~1 × 10^{-5} torr and a few ml of a mixture of diethylether and trimethylamine were distilled into the cell. The choice of solvent is dictated by the desire to have a relatively concentrated solution to decrease the cell resistance and the e.m.f. stabilization time while insuring the presence of excess compound and complexant. Experiments were carried out over the temperature range −78 to +5 °C. Higher temperatures were avoided to maintain saturation and prevent decomposition.

When first used with a new mixture, more than 10 h were required for stable potentials to develop, probably because of slow conditioning of the electrodes. During this period, cell potentials up to 500 mV were observed, which changed drastically with time and when the cell was shaken. Once stability was achieved, however, the potentials were independent of time and agitation, and gave reproducible results. When the temperature was reduced, the potential first dropped below the equilibrium value because of supersaturation, but stabilized after a few minutes with shaking. Similarly, when the temperature was increased, the potential first exceeded the equilibrium value and then decreased to give a stable reading. This behavior provides confidence that correct equilibrium values of the e.m.f. were measured. As expected, the cell e.m.f. depended on temperature but was independent of the composition of the solvent mixture.

Results and Discussion

The variation of the e.m.f. with temperature is shown in Fig. 2. A weighted least-squares fit of a straight line to all of the data yielded $\Delta H_2^\circ = -36 \pm 1$ kJ mol^{-1}, $\Delta S_2^\circ = -80 \pm 4$ J mol^{-1} K^{-1} and $(\Delta G_2^\circ)_{298} = -12.3 \pm 1.0$ kJ mol^{-1}. A more realistic estimate of the accuracy of the thermodynamic quantities is obtained [13] by fitting straight lines to the data from each experiment and then evaluating

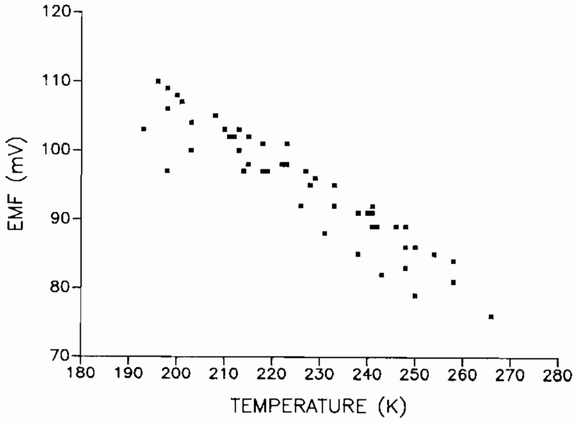

Fig. 2. Electromotive force vs. temperature for the cell $Pt|Na(s)|Na^+\beta\text{-alumina}|Na^+(C221)\cdot Na^-(sat.),C221(sat.)|Pt$.

the weighted average values of ΔH_2°, ΔS_2° and ΔG_2°. The values obtained in this way were: $\Delta H_2^\circ = -37 \pm 3$ kJ mol^{-1}, $\Delta S_2^\circ = -83 \pm 8$ J mol^{-1} K^{-1} and $\Delta G_{298}^\circ = -12.3 \pm 0.6$ kJ mol^{-1}. The uncertainties listed are standard deviation estimates. Note that the values of ΔH°, ΔS° and ΔG_{298}° refer to the formation of the solid compound rather than the melt, since they are obtained from data at temperature below the melting point of the sodide. This should have little effect on ΔG° but would change both ΔH_{298}° and ΔS_{298}° for the actual reaction at this temperature, since the product would be liquid.

The values predicted from a Born–Haber type cycle [19, 26] for this compound are: $\Delta H_2^\circ = -31$ kJ mol^{-1}, $\Delta S_2^\circ = -140$ J mol^{-1} K^{-1} and $\Delta G_2^\circ = +10.5$ kJ mol^{-1}. Thus, as with $Na^+(C222){\cdot}Na^-$, the predicted entropy change is much more negative than that observed. If one uses the observed values for $Na^+(C222){\cdot}Na^-$ together with the estimated differences on the basis of the Born–Haber cycle, one obtains the predicted values: $\Delta H_2^\circ = -28$ kJ mol^{-1}, $\Delta S_2^\circ = -33$ J mol^{-1} K^{-1}, $\Delta G_2^\circ = -18$ kJ mol^{-1}. The result is not very encouraging for difference calculations. While the estimates based on the model of closest-packed charged spheres show that alkalides can be stable, the model does not seem to be capable of quantitatively correct predictions, even of differences in the thermodynamic quantities. Evidently, differences in packing geometry between the two sodides studied are important. Part of the discrepancy may result from uncertainties in the estimates used in the Born–Haber type cycle depicted in Fig. 1. For example, the enthalpy and entropy of solution of liquid C211 in water are unknown, so the values for solid C222 were used. We do not, however, expect such errors to be large enough to remove the discrepancy between the experimental and estimated thermodynamic values.

The results show that, were it not for irreversible thermal decomposition of the cryptand, the sodide, $Na^+(C221){\cdot}Na^-$ would be stable to decomplexation up to ~450 K. In fact, the compound softens and melts below room temperature and the blue liquid that forms tends to decompose irreversibly. Work is underway [30] on sodides which utilize macrocyclic tertiary amines that are remarkably stable to reduction by Na^- at and above room temperature.

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