Spectrochemistry of Solutions, Part 23.[1] Changes of Enthalpy and Entropy in the Formation of Contact Ion Pairs: A Vibrational Spectroscopic Appraisal using Thiocyanate and Azide Solutions**

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Summary. The vibrational spectra of solutions have been analyzed to assess both qualitatively and quantitatively the changes in enthalpy and entropy for ion pair formation in solutions of LiNCS, $Mg(NCS)_2$, and LiN_3 in liquid ammonia, dimethylformamide, dimethylsulphoxide and acetonitrile. Contrary to predictions both the ΔH_{ass} and ΔS_{ass} terms are all positive in the cases examined, indicating that the driving force in the ion association process derives from solvent-solute restructuring, and not the energy of the interaction between the cation and anion. This characteristic of contact ion pair formation is likely to be found to be applicable over a wide range of solvents. The following specific values of the thermodynamic parameters at 298 K have been obtained: LiNCS/*DMF*, $\Delta G = -1.3$ (1) kJ mol^{-1}, $\Delta H_{ass} = +1.8$ (5) kJ mol^{-1}, $\Delta S_{ass} = +10$ (2) J mol^{-1} K^{-1}; LiNCS/*DMSO*, $\Delta G = +0.9$ (2) kJ mol^{-1}, $\Delta H_{ass} = +0.3$ (3) kJ mol^{-1}; $Mg(NCS)_2$/*DMF*, $\Delta G_{ass} = -4.0$ (3) kJ mol^{-1}, $\Delta H_{ass} = +15$ (4) kJ mol^{-1}, $\Delta S = +64$ (17) kJ mol^{-1}; LiN_3/*DMSO*, $\Delta G_{ass} = -2.5$ (3) kJ mol^{-1}, $\Delta H_{ass} = +4.9$ (9) kJ mol^{-1}, $\Delta S_{ass} = \sim +25$ (10) J K^{-1} mol^{-1}.

Keywords. Enthalpy; Entropy; Vibrational spectra; Ion pairs; Electrolyte solutions.

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Eine vibrationsspektroskopische Studie an Thiocyanat- und Azid-Lösungen

Zusammenfassung. Um die Enthalpie- und Entropieänderungen bei der Bildung von Kontaktionenpaaren sowohl quantitativ als auch qualitativ zu bestimmen wurden Schwingungspektren von Lösungen von LiNCS, $Mg(NCS)_2$ and LiN_3 in flüssigem Ammoniak, Dimethylformamid, Dimethylsulphoxid and Acetonitril untersucht. Im Gegensatz zu Vorhersagen sind die Enthalpie- und Entropie in allen untersuchten Fällen positiv. Diese Tatsache deutet daraufhin, daß die treibende Kraft des Assoziationsprozesses die Umstrukturierung der Lösung und nicht die Wechselwirkungsenergie zwischen Kation und Anion ist. Diese Eigenschaft der Kontaktionenpaarbildung ist wahrscheinlich auf eine große Anzahl von Lösungsmitteln übertragbar. Folgende, spezifische Werte wurden für die

thermodynamischen Parameter ermittelt: LiNCS/DMF, $\Delta G = -1.3$ (1)kJ mol^{-1}, $\Delta H_{ass} = +1.8$ (5)kJ mol^{-1}, $\Delta S_{ass} = +10$ (2)J mol^{-1}K^{-1}; LiNCS/$DMSO$, $\Delta G = +0.9$ (2)kJ mol^{-1}, $\Delta H_{ass} = +0.3$ (3)kJ mol^{-1}; Mg (NCS)$_2$/DMF, $\Delta G_{ass} = -4.0$ (3)kJ mol^{-1}, $\Delta H_{ass} = +15$ (4)kJ mol^{-1}, $\Delta S = +64$ (17)kJ mol^{-1}; LiN$_3$/$DMSO$, $\Delta G_{ass} = -2.5$ (3)kJ mol^{-1}, $\Delta H_{ass} = +4.9$ (9)kJ mol^{-1}, $\Delta S_{ass} = \sim +25$ (10)J K^{-1} mol^{-1}.

Introduction

In earlier reviews of our work with electrolyte solutions in liquid ammonia we asserted our belief that one of the best ways of investigating the constitution of the equilibria between the specific ion associates in a given solution is by measurement and analysis of the vibrational spectra of the solute ions of that solution [2, 3]. This experimental approach has also been recognised by other workers. For instance Irish et al., reported extensively on the presence, and the stabilities, of ion pairs in 2:2 and 2:1 electrolyte solutions in water [4−6], and 1:1 electrolyte solutions in non-aqueous solvents [7, 8]. From analyses of Raman spectra they also showed that the degree of contact ion-pairing in aqueous 1:1 electrolyte solutions is very low; e.g., $K_{ass} \sim 6 \cdot 10^{-2}$ mol^{-1} dm^3 in a 6 mol dm^{-3} NaNO$_3$ solution [7]. Chabanel and coworkers [9] have worked extensively on the phenomena of both ion pairing and ion aggregation in aprotic media, as also have Corset and his collaborators [10−13].

Quantitative measurements of ion pairing in solution have normally been made by measurement of a bulk property of the solution such as conductance. The property measured in such experiments is a total collective ion association constant encompassing all electrostatically interacting species in the solution capable of influencing the bulk property measured. Thus $^T K_{ass} = {}^T\{M^+ \, .. \, {}^-X\}_{ip}/\{M^+\}_T\{X^-\}_T$, where subscript and superscript (T) indicates "total" activities, and $^T\{M^+ \, .. \, {}^-X\}_{ip}$ is the activity of the collective total of all the different forms of ion associate in the solution.

If vibrational spectroscopy is used to probe specific structural types of ion associate it is sometimes possible to establish the parameters which define the individual equilibria relating to their formation from the "free" solvated ions or other ion associates. Thus in a solution system containing a number of different types of ion associate it is theoretically possible to define a set of equilibrium constants analogous to the stepwise stability constants used to define metal cation-ligand equilibria. This is possible in cases where component bands attributable to individual ion associates in the solution can be resolved from the solution spectrum and measured; providing absorbance/concentration relationships are linear.

Relatively few quantitative data for ion association equilibria are available from spectroscopy. However, it is already clear from the literature that there can sometimes be agreement, and sometimes disagreement, between equilibrium constants obtained spectroscopically for a specific ion association step (K_{ass}) on the one hand, and those obtained from conductance and other bulk measurement methods ($^T K_{ass}$) on the other. Close agreement between K_{ass} and $^T K_{ass}$ implies that one, and one species only, must dominate the ion pairing process. Generally for 1:1 electrolytes in liquid NH$_3$ we have found substantial divergence between the magnitudes of K_{ass} and $^T K_{ass}$: from conductance [14, 15] and activity [16] studies $^T K_{ass}$ $\sim 10^3$ mol^{-1} dm^3, whilst indications from several thousands of Raman spectra sug-

gest that $K_{ass} \sim 1 - 25\,mol^{-1}\,dm^3$ for the formation of the 1:1 contact ion pair. Clearly for the NH_3 solutions the spectra measure the pairing equilibrium for the formation of a discrete individual ion associate whereas, within the overall equilibrium system measured by conductance, many other interacting ion-ion species exist each of which makes its own specific contribution to $^TK_{ass}$.

Agreement between $^TK_{ass}$ and K_{ass} was observed by Janz and Müller [16] for $AgNO_3$ in acetonitrile (AN). Analyses of their Raman spectra gave $K_{ass} = [Ag^+ .. ^-NO_3]/[Ag^+][NO_3^-] = 84(\pm 14)\,mol^{-1}\,dm^3$ which coincides with the overall ion association constant, $^TK_{ass} = 70(\pm 1)\,mol^{-1}\,dm^3$, obtained from the conductance data of Yeager and Kratochvil [18]. Accordingly it is inferred in this case that both methods measure the formation of the same dominant species, namely the contact ion pair $[Ag^+ .. ^-NO_3]°$.

From the facts available in the literature it might be tempting to argue that contact ion pairs are dominant among associated species if the dielectric constant ε of the medium is high and the Bjerrum critical distance is low, as in AN where $\varepsilon = 37$. Support for such an argument can be provided by the spectra of LiNCS solutions in dimethylsulphoxide $(DMSO)$ where $\varepsilon = 48$ and a two-band infrared spectrum appears to indicate a simple one-step equilibrium between a contact ion pair $[Li^+ .. ^-NCS]°$ and the "free" solvated cations and anions [19]. Conversely when the dielectric constant of the solvent is between medium and low, as with liquid NH_3 (ε lies between 13 and 27 depending on temperature), the ion association equilibria consist of a complex array of different ion associates [2, 3]. However with the data available at the present time any attempt to categorise these phenomena so simply would be unwise. For instance, for LiNCS solutions in AN it is now known that the degrees of formation of both contact (cip) and solvent-shared (ssip) ion pairs are high: $\log K_{ass}$ (cip) = 3.87 and $\log K_{ass}$ (ssip) = 3.05 [20].

Clearly more than just the dielectric-dependent electrostatic forces of attraction between the charged ions must be taken into account, and Chabanel has recently made some attempts to do this [9, 21]. Very important must be the donor and acceptor strengths of the solvent molecule as measured by its Donor Number [22] and Acceptor Number [23]. The donor and acceptor properties of the constituent ions must also not be disregarded. Because the interactive forces between the component ions of a solution, and also the solvent itself, are so complex much more information than is available at present time must be acquired to enable interpretations to be made. An area where data are particularly sparse is in the thermodynamic parameters for individual ion pair and ion aggregate formation. The Gibbs's energy changes (ΔG_{ass}) are important but it is also vital to know the corresponding component values of the changes in enthalpy (ΔH_{ass}) and entropy (ΔS_{ass}). It is Chabanel and his coworkers who have so far made the most serious attempts to quantify some of these thermodynamic parameters from spectroscopic data. For example they have reported values for the changes in enthalpy (ΔH_{ass}) and entropy (ΔS_{ass}) associated with the formation of contact ion pairs in DMF solutions of LiNCS [24], and $DMSO$ solutions of alkali cyanates [25]. They also usefully concentrated their attention to the formation of higher ionic aggregates, e.g., dimers and tetramers, such as $(Li^+ .. ^-NCS)_2$ and $(Li^+ .. ^-NCS)_4$ in various ethers [24, 26, 27], 1,3-dioxolane (DXL) [28], and THF [28, 29]; further anion-cation aggregation often appears to be aided in solvents with low dielectric constants and fairly high Donor Numbers. However, this paper does not set out to consider

the equilibrium steps to higher aggregate formation, it is concerned only with the process of formation of 1 : 1 contact ion pairs.

To obtain these parameters it is necessary to collect and analyse carefully the spectra of solutions of a given salt (i) at various concentrations to establish the ion association constants, K_{ass}, and hence the change in Gibbs' energy (ΔG_{ass}), and (ii) over a range of temperatures to obtain the changes in ΔS_{ass} and ΔH_{ass}. To obtain worthwhile data the temperature in the measuring cell must be carefully controlled but, even with accurate temperature control this route to values of ΔS_{ass} and ΔH_{ass} is generally regarded as being somewhat imprecise, especially in respect of the ΔS_{ass} term. However, the principal aim set out in this paper has not been to define precise numerical values of ΔS_{ass} and ΔH_{ass}. It has been to establish the *signs* associated with the thermodynamic terms in order that the directional contributions of ΔH_{ass} and ΔS_{ass} towards the formation of a specific 1 : 1 contact ion pair can be established beyond doubt. We are confident that our experimental procedures and results achieve these aims.

Experimental Part

The most important practical requirement in the work was the control and measurement of the temperature within the thin layer of solution located in the spectrometer beam. It might be assumed that this could be achieved simply by circulating a thermostatting fluid through the body of the cell. However, there is no such simple experimental answer. Thermostatting is difficult because the liquid is "sandwiched" between two closely spaced ($12 - 50\,\mu m$) insulating CaF_2 crystal windows. However, an even more serious problem arises from the increase in solution temperature resulting from the absorption of radiation over the whole range emitted by the spectrometer source. This is a particularly severe experimental handicap because, with successive coadditions of spectra on a Ratio Recording Spectrometer, the sample has to be located in the lightpath for long periods of time, e.g., 30 to 90 min, while spectra are being recorded. We have effectively eliminated this problem.

In our method [30] the solute spectrum is obtained by computer-subtraction of the spectrum of the solvent from that of the solution; both measured under identical conditions. Absorption of radiation over the whole range emitted by the source, except for that under examination, is eliminated by a medium band pass multidielectric filter situated directly in front of the sample. For this work the filter eliminated all radiation except that between $1\,950\,cm^{-1}$ and $2\,400\,cm^{-1}$. Although absorption of radiation by both solution and solvent must still occur within this narrow region the resultant temperature changes are very small and, because they are equal, they are effectively eliminated in the subtraction process. Using a pathlength of $25\,\mu m$ a typical sample had a background absorption due to the solvent of ~ 0.3. Thus good quality solute spectra were obtained at concentration/pathlength combinations which produced optical densities between 0.4 and 1.2. Because multiple scanning and spectrum coaddition was always used to improve S/N ratios, the same number of scans under identical spectrometer conditions was made for all the solutions of a particular series.

The Raman method might, at first sight, appear to be more favourable than the infrared. (1) Because glass or silica can be used as a window material there is no need for specially designed cells with specific window materials to suit either the chemical characteristics of the solution or the wavenumber range. (2) The quality of resolution obtained in electrolyte solution spectra is usually much better in the Raman than in the infrared. Unfortunately, however, the single beam nature of the Raman method is a serious disadvantage for quantitative work because it is impossible to replicate sample positions and laser alignments on the spectrometer over a given set of samples. Unless a suitable reference Raman emission band exists in the spectrum of a solution quantitative work must involve the addition of some compound as an internal reference. In our case such a procedure would interfere with the ion association processes under study. None the less by using the Raman method

it is still possible to obtain a semi-quantitative appraisal of the relative proportions of component species in a solution.

It is from the infrared spectra that we can best gain quantitative data. The cell for liquid NH_3 solutions has already been described [30]. All the cells used in this work, for all solvents and solutes, had CaF_2 windows with the same dimensions. Pathlengths were varied with PTFE spacers. Except for the cell used with liquid NH_3 solutions the cell body was constructed from stainless steel drilled out to enable temperature control of the sample by a through-flow of thermostatted water; cells were maintained to within $\pm 0.05°C$ of the required temperature.

Spectra. Infrared spectra were recorded at preset temperatures between 273 K and 333 K on a Philips HP9545 Ratio Recording Spectrometer using optimum spectrometer conditions to minimize spectrum distortion. Normally 16 consecutive spectrum scans were collected digitally and coadded at equal slow scan rates; resultant S/N ratios of ca. 500 : 1 were sought. Raman spectra were recorded on an old Coderg PHO, now updated to provide digital data at $0.125\,cm^{-1}$ intervals and spectrum coaddition [31, 32], at the slowest available scan rate $(1\,cm^{-1}/min)$ with spectrometer settings chosen to minimize spectrum distortion; 4 to 9 coadditions were needed to achieve good S/N ratios. Because the baselines of the spectra of all the pure solvents are flat in the regions studied the profile of the $v(C-N)$ and $v(N_3)$ regions of the Raman spectra of the solutions are regarded as those of the solutes.

Curve Analyses. Spectra were resolved into their component bands using VIPER [33, 34]. The derivative and smoothing program TREAT [34] was used as a resolution aid; the 2nd, and sometimes the 4th, derivatives of the spectra were used to establish the positions of underlying bands.

Liquid NH_3 solutions. Pure anhydrous liquid NH_3 (ex ICI Ltd) was transferred to a cylinder containing a charge of solid $NaNH_2$. Pure dry NH_3 gas was distilled from this into a vacuum line. Solutions in liquid NH_3 were prepared by condensation of this gaseous NH_3 on to the preweighed salts in a graduated tube. From this measuring tube the solutions were transferred directly to the sample cells.

DMSO, DMF, AN Solvents. Analytical grade solvents were dried for one or two weeks over molecular sieve (4 Å). They were then distilled at reduced pressure under N_2 gas immediately before use. All solutions of *DMSO, DMF,* and *AN* were made and introduced into sealed spectrometer cells in a glove bag under dry N_2 in the presence of P_4O_{10}.

LiNCS. Pure AR grade salt was used immediately after drying under high vacuum at 385 K for at least 24 h.

LiN_3. NaN_3 (6.5 g) and $LiSO_4 \cdot H_2O$ (7.1.g) were dissolved in water (35 cm³). After addition of pure ethanol (175 cm³) the solution was filtered, and the filtrate and washings evaporated to near dryness. LiN_3 crystals were dried at 353 K before two recrystallisations from pure ethanol. The salt was dried in vacuo for 24 h before use in the presence of P_4O_{10}.

$Mg(NCS)_2$. The pure hydrated salt was slowly heated to 350 K in a vacuum oven prior to two recrystallisations from pure anhydrous liquid NH_3. The crystals were then dried in vacuo for at least 24 h in the presence of P_4O_{10}.

Results and Discussion

Ion-ion interactions in a solution containing a multiatomic anion can often be identified and quantified by the resolution and measurement of the bands which underly the spectral profiles of the regions of the spectra specific to the stretching and bending vibrations of the constituent atoms of an anion. The positions of bands due to "free" solvated anions are always invariant and independent of the associating cocation, the temperature and the concentration. In marked contrast the parameters of bands due to ion pairs are variable; their positions depend on the associating cation, and their intensities depend on the concentration and the temperature of the solution. Figure 1 illustrates the $v(C-N)$ stretching region of
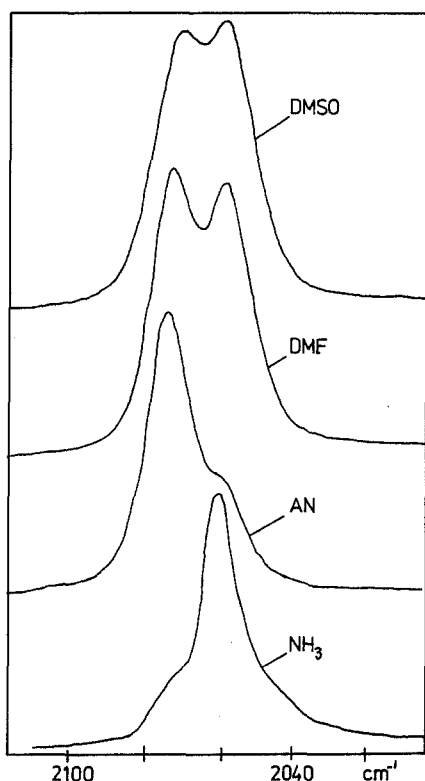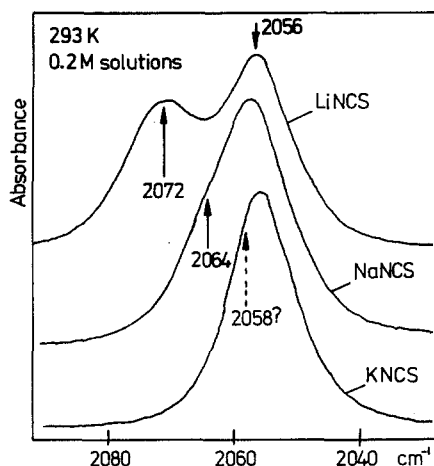
Fig. 1. The $\nu(C-N)$ stretching region of the infrared spectra of LiNCS in *DMSO, DMF, AN,* and liquid NH_3

Fig. 2. The $\nu(C-N)$ stretching region of the infrared spectra of LiNCS, NaNCS, and KNCS in *DMF*

the infrared spectra of LiNCS in four different solvents. Figure 2 shows how the position of the band due to the 1 : 1 contact ion pair shifts from $2\,073(\text{Li})\,\text{cm}^{-1}$ to $2\,064(\text{Na})\,\text{cm}^{-1}$ to $2\,058(\text{K})\,\text{cm}^{-1}$ in NCS^- solutions in *DMF*. For a 1 : 1 contact ion pair the cation-dependent shift from the "free" anion band, $\Delta\nu$, can be as little as 1 or $2\,\text{cm}^{-1}$ or, as in the case of LiCN solutions in NH_3, as great as $40\,\text{cm}^{-1}$. For solutions in NH_3 the magnitude of this shift, $\Delta\nu$, generally follows the orders, $\text{Li}^+ \gg \text{Na}^+ > \text{K}^+ > \text{Rb} > \text{Cs}^+$, and $\text{Mg}^{2+} \gg \text{Ca}^{2+} > \text{Sr}^{2+} > \text{Ba}^{2+}$.

By analyzing spectra like those illustrated in Fig. 1 into their component band parameters we are able to establish at least the order of magnitude of the stoichiometric ion association constant, $K_{ass} = [\text{Li}^+ .. \ ^-\text{NCS}]°/[\text{Li}^+][\text{NCS}^-]$ for a contact ion pair. Similarly solutions of LiN_3 and $Mg(NCS)_2$ give rise to spectra from which the contact ion pairing processes between cation and anion can be examined. Sometimes, however, the spectra behave in a more complicated way as in the case of LiNCS in *AN*, and LiN_3 in *DMF*, where more than two component bands indicate contributions from other species such as solvent-shared ion pairs (or outer sphere complexes) and ionic aggregates [19, 35]. Results from some specific examples follow.

Table 1. Band resolution parameters from VIPER-fitting of the $\nu(C-N)$ stretching region of the IR spectra for LiNCS/*DMF* solutions at 298 K. Pathlengths 50 mmol dm⁻³ (98 μm), 100 mmol dm⁻³ (98 μm), 200 mmol dm⁻³ (48 μm), 400 mmol dm⁻³ (25 μm), 800 mmol dm⁻³ (25 μm)

Concn. /mmol dm⁻³	Band 1					Band 2				
	Height	Position /cm⁻¹	F.W.H.H. /cm⁻¹	Gaussian fraction	Area	Height	Position /cm⁻¹	F.W.H.H. /cm⁻¹	Gaussian fraction	Area
50	0.395 (2)	2055.53 (3)	12.86 (10)	0.28 (4)	7.9 (9)	0.081 (1)	2071.87 (5)	13.97 (7)	0.05 (8)	1.8 (8)
100	0.704 (1)	2055.62 (2)	12.90 (4)	0.27 (4)	14.1 (3)	0.202 (1)	2071.56 (4)	13.31 (8)	0.53 (11)	4.1 (3)
200	1.243 (3)	2055.63 (1)	12.73 (11)	0.24 (5)	24.6 (11)	0.557 (3)	2071.20 (1)	13.94 (10)	0.58 (8)	11.9 (4)
400	1.055 (2)	2055.79 (1)	13.26 (4)	0.31 (5)	21.7 (11)	0.748 (2)	2071.27 (3)	14.16 (6)	0.56 (8)	16.3 (3)
800	0.861 (3)	2055.88 (3)	13.76 (4)	0.32 (7)	18.4 (8)	0.916 (1)	2071.33 (2)	14.53 (2)	0.56 (1)	20.4 (4)

LiNCS *in DMF*

The spectra of the alkali metal thiocyanates in *DMF* shown in Fig. 1 can be analyzed into two component bands: positions are LiNCS, $2\,072\,cm^{-1}$, $2\,056\,cm^{-1}$; NaNCS, $2\,064\,cm^{-1}$, $2\,056\,cm^{-1}$; KNCS, $2\,056\,cm^{-1}$; and CsNCS, $2\,056\,cm^{-1}$.

Spectral resolution of a quality suitable for quantitative assessment is obtained only in the case of the LiNCS solutions where the band separation Δv is ca. $16\,cm^{-1}$. The data obtained from these spectra (an example is given in Table 1) were good and reliable and, in view of the methods employed, led to reasonable constancy in the values of the association constant. Our K_{ass} values are in reasonable agreement with that of $K_{ass}=2.4\,mol^{-1}\,dm^3$ previously obtained by Chabanel [36]. There appears to be, however, a small continuous trend in the value of K_{ass} with changing concentration: viz.,

[LiNCS]/mol dm^{-3}	K_{ass}/mol^{-1} dm^3
0.10	3.7 (2)
0.15	3.3 (2)
0.20	3.3 (2)
0.40	3.0 (2)
0.80	2.9 (2)

A similar change in K_{ass} with concentration for solutions of LiAsF$_6$ in *DMF* was explained by Inoue, Petrucci and Xu [37] in terms of the small change in K_{ass} resulting from the change in the dielectric constant, ε, of the medium as the concentration of dissolved salt is increased. In view of the similar trend in the results we have obtained for LiNCS in *DMF* that explanation seems to be eminently reasonable. The values of K_{ass} for a $0.2\,mol\,dm^{-3}$ solution of LiNCS at six temperatures between 278 K and 338 K yielded a good linear plot of $\log K_{ass}$ versus $1/T$ (Fig. 3); $\Delta G = -1.3$ (1) kJ mol^{-1}, $\Delta H_{ass} = +1.8$ (5) kJ mol^{-1} and $\Delta S_{ass} = +10$ (2) J mol^{-1} K^{-1}. The positive values of both the enthalpic and the entropic terms should be noted.

LiNCS *in DMSO*

The low value of $K_{ass} = 0.7\,mol^{-1}\,dm^3$ for contact ion pair formation in solutions of LiNCS in *DMSO* was obtained from the infrared spectra. On changing the

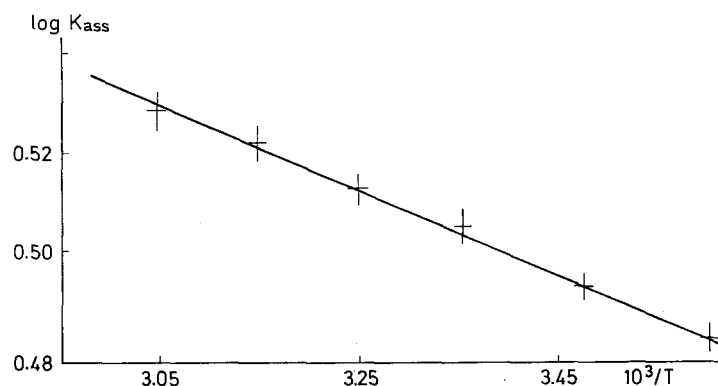**Fig. 3.** Plot of log K_{ass} versus $1/T$ for contact ion pairing between Li$^+$ and NCS$^-$ in a *DMF* solution at $0.2\,mol\,dm^{-3}$

temperature between 298 K and 338 K the small changes in the spectral profiles indicate very little change in the equilibrium position between "free" ions and 1 : 1 contact ion pairs. The bands are broad and fairly featureless, and accordingly resolution errors are high.

The peak of the band centred at ca. $2\,070\,cm^{-1}$ shifts slightly to lower frequency as the temperature is increased but if the principal contribution from this band is assumed to be due to a 1 : 1 contact ion pair a three point plot of $\log K_{ass}$ versus $1/T$ leads to a very small $+ve$ value of ΔH_{ass}. Because of the small values of both ΔG_{ass} and ΔH_{ass} it is unrealistic even to claim knowledge of the sign of ΔS_{ass}: $\Delta G_{ass} = +0.9$ (2) $kJ\,mol^{-1}$, $\Delta H_{ass} = +0.3$ (3) $kJ\,mol^{-1}$.

LiNCS in AN

We have already reported on this solution system in detail [20]. Although the $v(C-N)$ stretching region of the infrared spectra appears to be a two-band system detailed examination over a range of concentrations shows that the spectrum is much more complex. If a three-band structure is applied to analyse the profiles bands can be assigned to the "free" NCS^- at $2\,056\,cm^{-1}$, the 1 : 1 contact ion pair at $2\,073\,cm^{-1}$ and the solvent-shared ion pair at ca. $2\,061\,cm^{-1}$. At first sight the intensities of the bands at $2\,073\,cm^{-1}$ and $2056\,cm^{-1}$ appear to move in opposite directions of intensity versus temperature compared with all the other solutions we have studied. However, this observation cannot be used on its own without taking into account the substantial contribution to ion association which comes from the formation of solvent-shared ion pairs: $\log K_{ass}$ (cip) $\sim 3.87\,mol^{-1}\,dm^3$, and $\log K_{ass}$ (ssip) $\sim 3.05\,mol^{-1}\,dm^3$. A further feature not yet properly explained is that the band-positions are temperature-dependent. Possibly more species, not yet accounted for, exist in the system. Alternatively these band-shifts may be due to upper stage transitions, "hot bands", of the linear thiocyanato-species.

Although much more work is necessary on this solution system to explain the finer detail it now appears that when the contribution from solvent-shared ion pair formation is taken into account the contribution to the spectrum due to contact ion pairing increases relative to that of "free" NCS^- anion as the temperature is increased. Thus it is a fair qualitative assumption that ΔH_{ass} (cip) is $+ve$. Accordingly the ΔS_{ass} (cip) term must also be $+ve$.

Mg(NCS)₂ in DMF

The two-band spectra of the $v(C-N)$ region of Mg, Ca, Sr, and Ba thiocyanates in DMF can all be analyzed to show that the higher frequency band due to the contact ion pair steadily increases in intensity as the temperature is increased, relative to the band at $2\,056\,cm^{-1}$ due to the "free" NCS^- anion. However, it is from these $Mg(NCS)_2/DMF$ solutions from which some of our best quantitative data so far have been established. Measurements at 6 temperatures between 293 K and 338 K yielded a good linear plot of $\log K_{ass}$ versus $1/T$: at 298 K $\Delta G_{ass} = -4.0$ (3) $kJ\,mol^{-1}$; $\Delta H_{ass} = +15$ (4) $kJ\,mol^{-1}$; $\Delta S = +64$ (17) $kJ\,mol^{-1}$.

Mg(NCS)₂ in Liquid NH₃

For these solutions only Raman spectra are available. Consequently the conclusions are from qualitative results only. Normally the $v(C-N)$ region of the Raman

spectra of NCS⁻ solutions in liquid NH_3 is broad and rather featureless. However three well-resolved bands are observed in the spectra of $Mg(NCS)_2$ in liquid NH_3: $2087.3\,cm^{-1}$ (1 : 1 contact ion pair), $2061\,cm^{-1}$ (solvent-shared ion pair), and $2056\,cm^{-1}$ (free NCS⁻). The better resolution of the features underlying the $v(C-S)$ stretching region, ca., $736\,cm^{-1}$, is a good supportive aid to these assignments.

The overriding important factor to emerge is that the intensity of the band at ca. $2087\,cm^{-1}$ due to the contact ion pair decreases in intensity relative to the remainder of the spectrum as the temperature is raised. Thus once again, in this example of the formation of a monopositive contact ion pair K_{ass} (cip) (= $[Mg^{2+}\,..\,^{-}NCS]^+/[Mg^{2+}][NCS^-]$) increases with increasing temperature and ΔH_{ass} is markedly +ve.

LiN₃ in NH₃, DMF, and DMSO

Figure 4 illustrates how the spectrum of LiN_3 in liquid NH_3 is well-resolved compared with the spectra of NaN_3 and KN_3. Each of these consists of three underlying bands (relative areas/intensities are in parentheses):

LiN_3, $2043.4\,cm^{-1}$ (15%), $2014.5\,cm^{-1}$ (78%), $2001.5\,cm^{-1}$ (7%);

NaN_3, $2027.3\,cm^{-1}$ (30%), $2014.5\,cm^{-1}$ (62%), $1998.1\,cm^{-1}$ (8%);

KN_3, $2020.8\,cm^{-1}$ (40%), $2014.1\,cm^{-1}$ (51%), $2002.0\,cm^{-1}$ (9%).

The band of highest frequency in the spectrum of each solution is due to a 1 : 1 contact ion pair. The bands at ca. $2014\,cm^{-1}$ are due to "free" solvated N_3^-, and those at ca. $2000\,cm^{-1}$ arise from an upper stage transition of "free" N_3^-.

A reduction of concentration from 500 to $50\,mmol\,dm^{-3}$ has little effect on the relative intensities of the bands but the equilibrium between "free" anions and contact ion pairs is significantly affected by temperature. This is highlighted in the
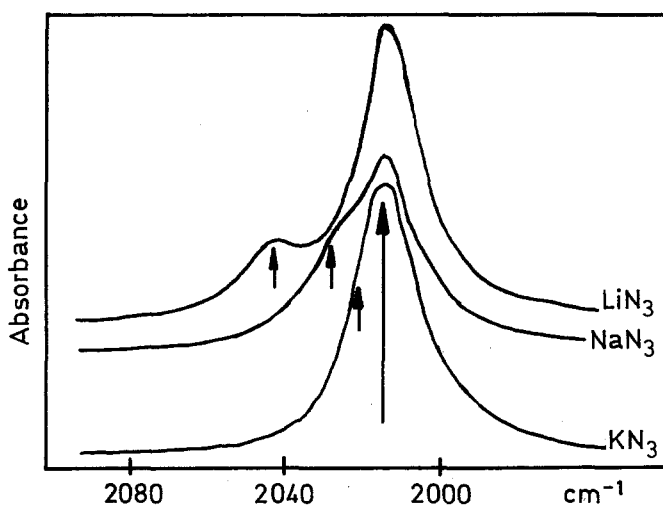

Fig. 4. The $v(N_3)$ antisymmetric stretching region of the infrared spectra of LiN_3, NaN_3, and KN_3 solutions in liquid NH_3 at ca. $0.3\,mol\,dm^{-3}$

$v_1(N_3)$ region of the Raman spectra of a solution of LiN_3 in liquid NH_3 which gives rise to a Raman spectrum containing three underlying components at $1337\,cm^{-1}$, $1330\,cm^{-1}$ and $1320\,cm^{-1}$ [38]. As the temperature is raised from 200 K to 273 K the area (intensity) of the band at $1337\,cm^{-1}$ due to the 1 : 1 contact ion pairs, $[Li^+ .. ^-N_3]°$, increases. Simultaneously the band at $1320\,cm^{-1}$, due to "free" unassociated N_3^-, decreases in area (intensity). The low intensity band at $1330\,cm^{-1}$ ($>5\%$ total area) is probably due to solvent-shared ion pairs. Hence again in this example the association constant for the contact ion-pairing process, $K_{ass} = [Li^+ .. ^-N_3]/[Li^+][N_3^-]$, rises as the temperature rises indicating a $+ve$ change in ΔH_{ass}.

LiN_3 in DMSO

Analyses of the infrared spectra of LiN_3 in NH_3, *DMF*, and *DMSO* show that K_{ass} is solvent-dependent in the order $NH_3 > DMF > DMSO$. It might not be unreasonable to attempt to interpret this observation in terms of a direct relationship between the degree of ion association and the dielectric constant of the solvent; viz., at 293 K for NH_3 $\varepsilon \sim 18$, for *DMF* $\varepsilon = 37$, and for *DMSO* $\varepsilon = 48$.

The infrared spectra of LiN_3 in *DMSO* closely resemble those observed for the liquid NH_3 solutions; 3 features at $2036\,cm^{-1}$, $1999\,cm^{-1}$, and $1985\,cm^{-1}$. The bands at $1999\,cm^{-1}$ and $1985\,cm^{-1}$ are both due to "free" N_3^-: the latter of these (ca. 5% of the total relative intensity of the two bands) is due to an upper stage transition. The band at $2036\,cm^{-1}$ is the one due to the 1 : 1 contact in pair, $[Li^+ .. ^-N_3]°$.

The data for K_{ass} for 1 : 1 contact ion pair formation at temperatures between 293 K and 343 K lead to the following thermodynamic parameters for a solution of $0.200\,mol\,dm^{-3}$ at 298 K [35]: $\Delta G_{ass} = -2.5$ (3) $kJ\,mol^{-1}$, $\Delta H_{ass} = +4.9$ (9) $kJ\,mol^{-1}$, and $\Delta S_{ass} \sim +25$ (10) $J\,K^{-1}mol^{-1}$. This again is a good example of an enthalpy-opposed contact ion pairing process which must acquire its driving energy from factors manifested as a positive entropy change.

LiN_3 in DMF

We found the $v_{as}(N_3)$ region of the infrared spectra of LiN_3 solutions in *DMF* to be composed of 6 bands; $2081\,cm^{-1}$, $2043\,cm^{-1}$, $2034\,cm^{-1}$, $2008\,cm^{-1}$, 1998 cm^{-1}, and $1984\,cm^{-1}$. At first sight interpretation appears difficult. Corset proposed [12, 13] that N_3^- solutions of alkali metals in solvents like *DMF* contain ion triplets such as $[Li^+ .. N_3^- .. {}^+Li]^+$. Furthermore contributions to the spectrum can be expected from solvent-shared ion associates. To compound the problem the N_3^- anion and the contact ion pair $[Li^+ .. ^-NCS]°$ are both linear and, as with the NCS^- anion, upper stage transitions are to be expected. However, by following the changes in relative intensity with changes in concentration and temperature (between 298 K and 348 K), we have assigned the bands at $2044\,cm^{-1}$ and $1999\,cm^{-1}$ to the contact ion pair and the "free" N_3^- anion respectively.

The overall impression gained from a qualitative appraisal of intensity changes of these two bands with temperature is that, at a given concentration, the intensity of the band at $2044\,cm^{-1}$ increases as the temperature rises, whilst that of the band at $1999\,cm^{-1}$ due to free N_3^- anion decreases. This indicates that ΔH_{ass} and ΔS_{ass} for the process of formation of the contact ion pair are both $+ve$.

General Discussion

The purist might levy criticism on this work for a number of reasons based on the various assumptions, and certain omissions, which have been necessary. Some of these can be listed as follows. (i) To calculate K_{ass} and ΔG_{ass}, like other workers before us [4−8, 24−26, 39], it was assumed that all the species in a system give rise to bands with similar intensity coefficients. Perhaps this is not unreasonable in view of the fact that numerical data have been obtained from what are effectively 2-species systems. Even if this assumption does not hold the extinction coefficients of the bands concerned will always be in a constant ratio with each other. (ii) The Beer-Lambert Law applies to the system. (iii) The dielectric constant of the solvent remains near the same value over the temperature range studied. This assumption is perhaps a fair one for *AN*, *DMSO*, and *DMF* but it is a more serious problem with liquid NH_3 where ε changes from ~ 27 at $200\,K$ to ~ 15 at $310\,K$. The qualitative assessments made concerning liquid NH_3 solutions have been made from Raman spectra taken at the lower end of this temperature range where the problem is less severe.

Perhaps the greatest cause for concern should be in the failure to apply appropriate activity coefficients to the data. Firstly activity coefficient data are unavailable. Secondly the calculation of unreliable coefficients would not be acceptable; calculations are unreliable because of the high degree of nonideality of all of the solutions examined and the lack of appropriate formulae, especially at the high solution concentrations used in the work. Thirdly it is impossible to overcome the activity problem practically by the use of an ionic background at constant ionic strength to maintain constant activity coefficient values; excess "spectator" ions would perturb the specific processes being investigated.

From our wide survey of Raman and infrared spectra of many electrolyte solutions in liquid NH_3 solutions we can now confidently state that a general rule exists that the intensity of the band associated with the 1 : 1 contact ion pair increases (compared with the remainder of the spectrum) with increase in the temperature of the solution, i.e., contact ion pair formation in liquid NH_3 appears universally to be an *endothermic* process.

In the case of liquid NH_3 solutions where there is a large change in dielectric constant of the solvent medium with temperature it might be argued that this phenomenon results from the change of dielectric constant with temperature. However, it is at temperatures above $273\,K$ where the dielectric constant of NH_3 can be regarded as being low with a relatively large proportional change for a temperature change over a specific interval. At temperatures below $273\,K$ the dielectric constant moves into the medium range. Thereafter its relative change over a given temperature interval becomes much less significant. None the less the increase in 1 : 1 contact ion pair formation with temperature is still observed in the lower temperature region. It is clear therefore that changes observed in K_{ass} with temperature reflect the thermodynamics related to the formation of the contact ion pair to a much greater degree than they reflect the changing dielectric properties of the medium.

From the relatively small number of solutions studied so far in the solvents NH_3, *AN*, *DMF*, and *DMSO* a general rule is emerging, i.e., 1 : 1 contact ion pair formation is enthalpy opposed. In all the cases studied there is a small but favourable

Table 2. Thermodynamic parameters for ion pairing processes from spectroscopic measurements

Solvent	Salt	K_{ass}	ΔG_{ass}	ΔH_{ass}	ΔS_{ass}	Ref.
Contact Ion Pairs						
DMSO	LiNCO	110	−11.5	+1.2	+43	[25]
DMSO	NaNCO	46	−9.5	+3.2	+43	25
DMSO	KNCO	16	−6.9	+0.5	+25	25
DMF	LiNCS	2.4	−6.6	+3.5	+34	[24, 26]
NH_3	TlNO$_3$	110	−11.5	+26	+126	42
LiNCS Dimers						
THF	LiNCS	0.24		+23	+66	28
THF	NaNCS	45		+1	+37	28
THF	KNCS	∼60		−3	∼2	28
DXL	LiNCS	0.45		+19	+5	28
DXL	NaNCS	40		+2	+38	28
DXL	KNCS	∼50		0	∼32	28
DEC	LiNCS	51	−9.7	0	+33	28
DMC	LiNCS	8.0	−5.2	+10	+51	27
BuOAc	LiNCS	3.7	−3.2	+9	+4	27
LiNCS Tetramers						
BuOEt	LiNCS			+29	+130	27
i-PrOPr	LiNCS			+41	+165	[27]

ΔG term. Hence the energy gain which derives from the process must be due to entropy changes. There must therefore be a favourable restructuring of the solvent molecules in the vicinity of the associating ions and the resultant ion pair. Also the component of the entropy term due to restructuring must be substantial because, not only should the translational entropy change for the process $M^+ + X^- \rightarrow [M^+ .. {}^-X]$ be expected to be comparatively large, it would normally oppose contact ion pair formation.

Good supporting evidence for the thesis that contact ion pair formation is opposed enthalpically is also available from the earlier work of Chabanel and coworkers. Table 2 lists some results of their infrared measurements; it should be noted that the value of K_{ass} for LiNCS in *DMF* is reasonably close to ours.

It is useful also to look at the corresponding ΔH and ΔS values for the formation of LiNCS dimers and tetramers in the relatively low donor solvents also listed in Table 2. ΔH is +ve in all cases, except that of KNCS in *THF* and, even here, ΔS must be +ve for dimer formation.

Replacement of a solvating solvent molecule in the cation's inner solvation sphere by NCS$^-$ is therefore associated with a positive enthalpy term. The more important conclusion, however, is that these processes all involve positive changes in the entropy term. There seems little doubt that the most important factor in the formation of these ion pairs is the reorganization of the bulk solvent structure in the immediate vicinity of the "free" solvated ions and the resultant ion pair. The

local environment of bulk solvent around the ionic structures in the solution is therefore all-important in determining the degree of ion association.

In the light of the conclusions drawn from vibrational spectroscopic results it is interesting to reconsider the results of the [205]Tl- and ^{14}N-NMR studies reported by Hinton et al. [40−41] for the formation of contact ion pairs between Tl^+ and NO_3^- ions in liquid NH_3. From the variation of chemical shifts with concentration at 273 K, 293 K, and 303 K, they suggested that $\Delta H_{ass} \sim +26\,kJ\,mol^{-1}$ and $\Delta S_{ass} \sim +150\,J\,K^{-1}\,mol^{-1}$. Over this relatively small temperature interval the dielectric constant of liquid NH_3 changes from $\varepsilon = 16.5$ to $\varepsilon = 19.0$ [43]. If we were to use the reasonable, but crude, assumption that $\Delta G_{ass} \propto 1/\varepsilon$ we would expect the magnitude of ΔG_{ass} to increase by a factor of only 1.15 over this temperature interval. The much larger change observed in ΔG_{ass} from $-8.9\,kJ\,mol^{-1}$ to $-12.8\,kJ\,mol^{-1}$ signifies that another factor is important in the process, namely the restructuring which leads to the accompanying positive change in the entropy term.

It is pertinent to point out that the K_{ass} values show that contact ion pairing is a much more favourable process in $TlNO_3$ solutions than in other nitrate solutions of monocharged cations in liquid NH_3 where, from Raman spectra, we estimate $K_{ass} < 4\,dm^3\,mol^{-1}$ for alkali nitrate solutions. The larger value of K_{ass} for $TlNO_3/NH_3$ should most likely be attributed to a specific bonding characteristic of the Tl^+ cation with the NO_3-anion. An anomaly appears in the Raman spectra of $TlNO_3/NH_3$ solutions. We have observed that the normally Raman-forbidden $v_2(NO_3)$ mode at ca. $830\,cm^{-1}$ (the through-the-plane vibration) is observed at concentrations $> 0.2\,mol\,dm^{-3}$; the vibrational spectra of $TlNO_3$ in NH_3 were first reported by Straughan et al. [44]. The only reasonable explanation is that in the $[Tl^+ .. \,^-NO_3]°$ contact ion pair the NO_3^- anion lies plane-on to the Tl^+ cation effectively producing a $Tl-N$ bond; probably structured tetrahedrally as $[(NH_3)_3Tl^+ .. \,^-NO_3]°$. In this structure the symmetry of the planar NO_3^- is destroyed allowing the forbidden v_2 vibration mode to be observed in the Raman spectrum.

Acknowledgements

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