Temperature-dependence of Ion-pair Formation of Simple Thiocyanate Salts in Liquid Ammonia

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Abstract

The concentration-dependences of the electrical conductances of NH_4SCN, $(CH_3)_4NSCN$, KSCN and NaSCN solutions in liquid ammonia were recorded in the temperature interval between 213 and 238 K. Computer evaluation of the data via the Lee–Wheaton equation led to the ion-pair formation constants (K), the ion–ion distance parameters (R) of the species and the limiting equivalent ionic conductances (Λ_o) of their solutions. With increasing temperature, the K values were found to increase while the R values decrease, indicating that a temperature increase facilitates the desolvation of solvated species, promoting ion–ion interactions, *i.e.* ion-pair formation.

Introduction

Having a high permanent dipole moment (μ = 1.49 D [1]), liquid ammonia is a good solvent for electrolytes. The ions dissolved in ammonia tend to associate and form ion-pairs because of the medium relative permittivity (ϵ = 24.3 at 223 K [2]) of the solution. The latter process depends on the electrolyte concentration, the solvation of the ions (determined by their charge, size and nature) and the temperature. A change in temperature results in changes not only in the physical properties (viscosity, relative permittivity, etc.) of the solvent, but also in the solvation of the ions in solution. The change in ion solvation influences the interaction between the dissolved ions, *i.e.* the ion-pair formation process.

Ion-pair formation in electrolyte solutions in non-aqueous solvents is usually studied by conductometry [3–5]. The Onsager equation [6], which characterizes the electrical conductance of electrolyte solutions, has been improved by several research groups [7–10]. The Lee–Wheaton equation [10] proved suitable for determination of the ion-pair formation constant ($K = [AB][A^+]^{-1}[B^-]^{-1}$), the ion–ion distance parameter (R) and the limiting equivalent ionic conductance at infinite dilution (Λ_o) from the concentration-dependence of the electrical conductance of simple salts in liquid ammonia [11].

A considerable amount of research has been devoted to the study of electrolytes in liquid ammonia through electrical conductance measurements [4, 11, 12]. The concentration-dependence of the electrical conductance of a simple salt dissolved in liquid ammonia is qualitatively similar to that measured for its aqueous solutions. However the lower relative permittivity of ammonia favours association reactions, e.g. ion-pair formation, in contrast to the situation in water, which usually contains dissolved electrolytes in dissociated form. Data characterizing ion-pair formation in liquid ammonia (formation constants, ion–ion distances etc.), and especially their temperature-dependence, could contribute towards a better understanding of solvation and other association–dissociation equilibria in this solvent. Unfortunately, the literature data are restricted mostly to measurements at one or only a few temperatures. No systematic study in a broad temperature range has been reported. Our aim was therefore to study the ion-pair formation in equilibria in liquid ammonia in the temperature interval from 213 to 238 K. The thiocyanate salts NaSCN, KSCN, NH_4SCN and $(CH_3)_4NSCN$ served as our first model systems. The results derived from electrical conductance measurements are reported in this paper.

Experimental

Apparatus

The conductance cell and apparatus were constructed in our laboratory, the equipment presented in the literature, [4, 13, 14] being modified to suit our needs. The measurements were made under a nitrogen atmosphere. Dried nitrogen was likewise used to mix the solutions. The volume change during the dilution of the solution was measured in the conductance cell, which bore a volumetric scale. The conductance was measured with two plane parallel bright platinum electrodes con-

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nected to an OK-102/1 Radelkis conductometer. The cell constant was determined with potassium chloride solutions and proved to be 0.2007 ± 0.0005 cm^{-1}. The temperatures of the solutions were recorded with a semiconductor thermistor connected to a D 1216 Digital Multimeter (Norma Messtechnik. Optik. Elektronik Gesellschaft MBH).

Procedure

In all measurements, air was excluded with a dry nitrogen flow system at atmospheric pressure. Before each measurement, the apparatus was dried at 423 K. An accurately measured amount of the salt to be investigated was dissolved in ammonia by condensing the solvent in the conductance cell. For measurement of the concentration-dependence of the conductance, this solution was diluted with known amounts of ammonia in a similar way. The volume change was measured directly in the conductance cell. The salt concentrations were varied in this way between 3.3×10^{-3} and 4.0×10^{-4} mol dm^{-3}. The upper limit of the concentration range was determined as the point at which the evaluation process indicated the presence of triple ions. Because of the small frequency-dependence of the electrolyte conductances, these were measured at the fixed frequency of 10 kHz. The measurements were repeated in 5 degree temperature intervals between 213 and 238 K.

The experimental concentration–conductance data pairs were analysed with the computer program HUNTER, written by Pethybridge on the basis of the Lee–Wheaton equation [10]. The relative permittivity and viscosity values for the evaluation were taken from the literature [2, 11, 15].

From the experimental data, the computer calculated the ion-pair formation constants (K), the ion–ion distances (R) in the ion-pairs, and the limiting equivalent ionic conductances at infinite dilution (Λ_o) (see Tables I and II). The standard deviations of the K values, reflecting the accuracy of the measurements, are also given. As a check on the evaluation, the experimental conductance *versus* concentration curves were simulated with the computer. The good fit of the experimental data to the simulated curves proves the reliability of the evaluation procedure. Figures 1 and 2 present examples of such calculated curves (full line), together with the experimental data (circles and dots).

Materials

The sodium, potassium and ammonium thiocyanates used were Merck products of analytical purity. Tetramethylammonium thiocyanate was prep-

TABLE I. The Limiting Equivalent Ionic Conductances (Λ_o), the Ion-pair Formation Constants (K) and the Ion-Ion Distances (R) Determined for Ammonium and Tetramethylammonium Thiocyanate Solutions in Liquid Ammonia

Temperature (K)	NH_4SCN (a_o = 3.7 Å[a])			$(CH_3)_4NSCN$ (a_o = 6 Å[a])		
	Λ_o (Ω^{-1} cm^2 mol^{-1})	K (dm^3 mol^{-1})	R (Å)	Λ_o (Ω^{-1} cm^2 mol^{-1})	K (dm^3 mol^{-1})	R (Å)
213	238.51	162 ± 15	11.8	236.04	471 ± 35	10.9
218	256.21	159 ± 19	9.5	256.04	471 ± 37	10.6
223	280.30	196 ± 33	7.2	275.21	500 ± 39	10.2
228	304.83	236 ± 33	5.3	297.54	525 ± 45	9.3
233	324.57	235 ± 28	4.5	315.47	510 ± 40	8.5
238	349.57	288 ± 27	3.5	337.78	545 ± 41	7.1

[a] The ion–ion distance calculated for the contact ion-pair.

TABLE II. The Limiting Equivalent Ionic Conductances (Λ_o), the Ion-pair Formation Constants (K) and the Ion–Ion Distances (R) Determined for Potassium and Sodium Thiocyanate Solutions in Liquid Ammonia

Temperature (K)	KSCN (a_o = 3.6 Å[a])			NaSCN (a_o = 3.2 Å[a])		
	Λ_o (Ω^{-1} cm^2 mol^{-1})	K (dm^3 mol^{-1})	R (Å)	Λ_o (Ω^{-1} cm^2 mol^{-1})	K (dm^3 mol^{-1})	R (Å)
213	290.88	284 ± 25	10.8	257.80	240 ± 32	10.5
218	307.73	268 ± 14	8.0	273.01	219 ± 57	9.1
223	330.29	292 ± 21	6.2	291.42	217 ± 61	7.9
228	359.79	341 ± 25	6.0	328.14	323 ± 53	4.3
233	382.49	364 ± 28	5.0	351.26	354 ± 45	3.4
238	403.43	384 ± 29	3.8	377.30	383 ± 16	2.7

[a] The ion–ion distance calculated for the contact ion-pair.

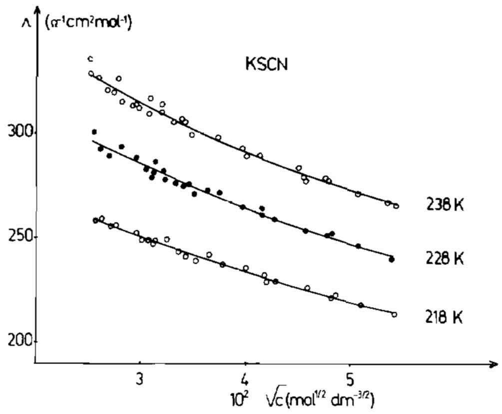

Fig. 1. The equivalent conductance (Λ) data *vs.* the square route of salt concentration ($\sqrt{c}$) curves of potassium thiocyanate at different temperatures.

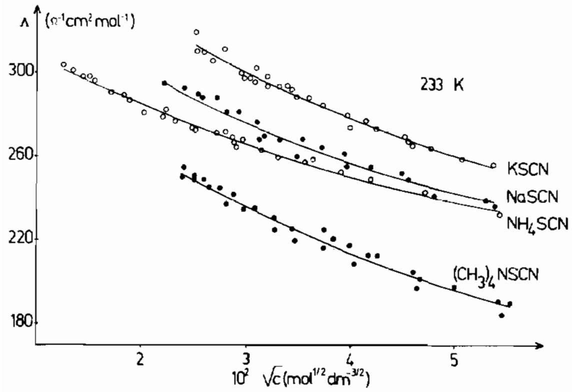

Fig. 2. The equivalent conductance (Λ) data *vs.* the square route of salt concentration ($\sqrt{c}$) curves of thiocyanate salts at 233 K.

ared by the neutralization of thiocyanic acid with tetramethylammonium hydroxide in aqueous solution. This acid was prepared in an ion-exchange process, using Varion KS cation-exchange resin. The aqueous solution of the tetramethylammonium salt was evaporated under vacuum at room temperature. All salts were dried at 378 K and stored above phosphorus pentoxide until use.

Liquid ammonia was purified by distillation from metallic potassium. The conductance of the purified ammonia proved to be below 2.10^{-6} Ω^{-1} cm^{-1}.

Results and Discussion

In spite of the great differences between the ion–ion distances (*R*) and ion-pair formation constants (*K*), the data in Table I show that the limiting equivalent ionic conductances (Λ_0) for the ammonium and tetramethylammonium salts are equal within experimental error. This may be due to the structure-breaking property of the $(CH_3)_4N^+$ ion, which therefore increases the electrical conductance of the solution so that it compensates the effect of ion-pair formation. The Λ_o values for the potassium salt (Table II) are significantly higher than those for the other salts, reflecting the weak solvation of the potassium cation. The Λ_o values for the sodium salt are close to those for the ammonium and tetramethylammonium salts, but they exhibit a steeper temperature-dependence, indicating the different types of solvation of these cations. The temperature-dependences of Λ_o reflect the viscosity changes in the solutions, and not the effects of ion-pair formation.

The sequence of the *K* values ($(CH_3)_4NSCN > KSCN > NaSCN > NH_4SCN$) seems to depend on the strength of the solvation of the ions. Decreasing solvation of the cation results in increased ion-pair formation, *i.e.* in a greater *K*. This may be the reason for the low *K* values for ammonium thiocyanate and for the outstanding *K* value for the tetramethylammonium salt. In liquid ammonia, the H-bonding interactions between ammonium ions and solvent molecules may be stronger than the coordinate bonds connecting the alkali metal ions with ammonia through the free electron-pair of the nitrogen of the latter. The tetramethylammonium ions are involved only in electrostatic (ion-dipole) interaction with the solvent of lower strength than the H-bonded or coordinated adducts.

The *K* values reveal an unexpected temperature-dependence. With increasing temperature, the ion-pair formation constants *K* increase. This anomalous behaviour can be explained in terms of the temperature-dependence of the ion–ion distances (*R*). With increasing temperature the *R* values decrease, indicating the decreased solvation of the species in the system, which favours ion-pair formation. Solvation and ion-pair formation seem to have different temperature-dependences in liquid ammonia. A temperature increase facilitates the desolvation of the solvated species, which promotes the ion–ion interaction, leading to ion-pair formation. This is why the *K* values increase and the *R* values decrease with increasing temperature. The different *R* values at different temperatures in the same system reflect the different compositions of the ion-pairs in solutions.

Consequently, the temperature-dependence of the data in the Tables show that species (solvated ions and ion-pairs) with different compositions, *i.e.* with different degrees of solvation, are formed in thiocyanate solutions of different temperatures, but containing the salt in identical concentrations. The temperature-dependence of the *K* values cannot, therefore, be used to calculate the thermodynamic data relating to the processes.

The ion–ion distances calculated for the contact ion-pairs given in the headings to the Tables indicate that the latter species are formed in the studied systems only near the boiling point of ammonia. Ion-pairs formed at temperatures lower than 233 K all contain bound solvent molecules. A temperature decrease results in increased solvation of the ion-pairs (larger R values) and lower ion-pair formation constants.

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