Permittivity and Dielectric Relaxations in Liquid-Ammonia Solutions

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Dielectric constant and loss in liquid-ammonia solutions of alkali halides have been measured in the frequency range 0.7 – 70 GHz. At least one relaxation process exists in this frequency range in addition to the relaxation of the solvent molecules. The additional relaxation is ascribed to the orientational polarisation of ion pairs. The concentration of the ion pairs, calculated with a special model, is 30 – 50% of the total concentration. The interaction between ions and solvent molecules is discussed.

Introduction

The dielectric behavior of ionic solutions at microwave frequencies has been investigated by a number of workers[1–5]. The experimental results provide information concerning the structure of the liquid and the dynamic properties of solvent molecules in the bulk and in the neighborhood of the ions. If more than one dispersion region exists, the shortest relaxation time may be assigned to the dipole orientation of the solvent molecules and the longer relaxation times to the orientational polarisation of ion aggregates[6].

With the exception of dissolved metals[7–9], the permittivity of liquid-ammonia solutions has been reported only briefly in the literature[10] so far.

In the present work the dielectric properties of liquid-ammonia solutions of alkali halides with relatively high solubility, i. e., LiBr, NaBr, and KI, have been measured in the frequency range 0.7 to 70 GHz at temperatures between – 75 and – 40 °C. The analysis of the experimental data yields values for the relaxation times and relaxation strengths of the orientational processes in the solutions. From these data information can be obtained about the formation of ion pairs, the solvation effects of the different ions in liquid ammonia, and the molecular motions of solvent molecules and ion pairs.

Experimental

The complex dielectric constant of the solution was measured[11] with five waveguide sets at 6, 10, 23, 35, and 70 GHz and a coaxial apparatus in the frequency range 0.7 – 2.5 GHz using bridge methods with null detection[12, 13] (Fig. 1). The liquid ammonia solutions

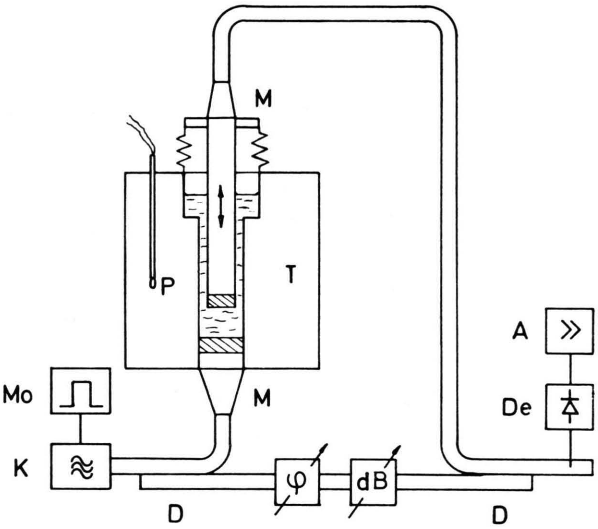

Fig. 1. Schematic of the microwave sets. Mo modulation, K klystron, D directional coupler, M mode transition, P platinum resistor for temperature measurement, T thermostat jacket, De demodulation, and A amplifier.

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were filled in cylindrical waveguides which could be thermostated between −75 and −40 °C. The circular waveguides were fed from the end of a rectangular waveguide. A second circular waveguide was moved through the liquid to pick up the response at different distances. From this probe the circular mode was transformed back into the rectangular mode and compensated to null using a calibrated phaseshifter and a calibrated attenuator (Fig. 1).

Real and imaginary part of the complex dielectric constant

$$\varepsilon = \varepsilon' - i\,\varepsilon'' \tag{1}$$

were calculated from the absorption coefficient α and the phase constant β using the following relations:

$$\varepsilon' = \left(\frac{\lambda_0}{2\,\pi}\right)^2 (\beta^2 - \alpha^2) + \left(\frac{\lambda_0}{\lambda_c}\right)^2, \tag{2}$$

$$\varepsilon'' = 2\left(\frac{\lambda_0}{2\,\pi}\right)^2 \alpha\,\beta - \frac{\sigma}{\omega\,\varepsilon_V}, \tag{3}$$

where λ_0 is the free-space wavelength, λ_c the cutoff wavelength of the empty circular waveguide, σ the conductivity, ε_V the permittivity of free space and ω the angular frequency of the microwave signal.

In order to obtain the dc conductivity of the solutions, the conductivity values measured in the frequency range 4−20 kHz were extrapolated to infinitely high frequencies to eliminate polarisation effects at the electrodes. The results of these measurements are given in Table 1.

The liquid ammonia was purified by means of vacuum distillation in the usual way. The final distillation was made into a calibrated glass vessel. Prior to distillation a measured amount of waterfree LiBr, NaBr, or KI of p. a. degree (E. Merck, Darmstadt) was given into the glass vessel. With this method the concentration of the solution could be determined to about ±0.1%.

Experimental Results

The Cole-Cole arc plot of the complex dielectric constant of pure liquid ammonia as shown in Fig. 2 indicates that essentially only a single relaxation process is present in the frequency range covered. The high-frequency intercept ε_∞ of the semicircles was found to be about 3.8 which is in reasonable agreement with the value reported in the literature[14]. The relaxation time τ_s of the solvent molecules as a function of temperature is shown in Fig. 3.

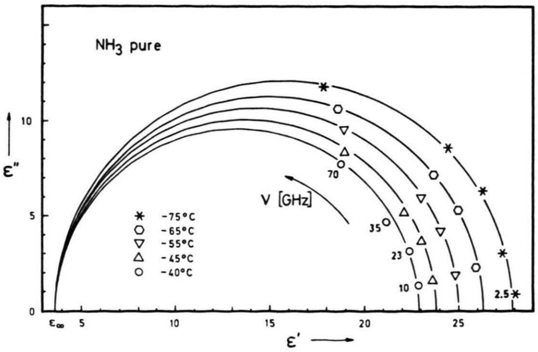

Fig. 2. Cole-Cole arc plot for pure liquid ammonia.

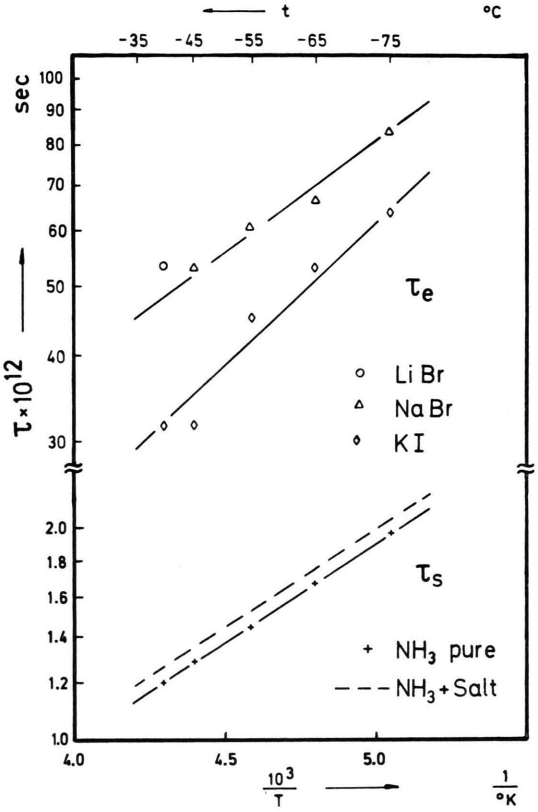

Fig. 3. Arrhenius plot of the relaxation times τ_s and τ_e of the principal and the additional relaxation process, respectively.

The Arrhenius plot yields an activation energy for the dielectric relaxation process of about 1.4 kcal/mole. This value is in approximate agreement with the activation energy for the viscose process[15]. The extrapolated static dielectric constant of pure liquid ammonia as a function of temperature is presented in Table 1. Our experimental results for pure liquid ammonia are in good agreement with those of Fish et al.[14]. We did not find, however, an indication for the distribution of relaxation frequencies suggested by Hasted and Tirmazi[9].

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T °C	ε_0	σ [$(\Omega\ \text{cm})^{-1}$]				
	NH_3	LiBr	NaBr		KI	
	pure	0.1 m	0.1 m	0.1 m	0.5 m	1.0 m
−35	—	0.00890	—	0.01514	0.0696	0.1307
−40	23.0	0.00842	0.01018	0.01433	0.0660	0.1230
−45	23.9	—	0.00961	0.01359	0.0619	0.1152
−55	25.0	—	0.00831	0.01205	0.0541	0.1009
−65	26.2	—	0.00708	0.01032	0.0463	0.0851
−75	27.8	—	0.00576	0.00862	0.0385	0.0698

Table 1. Static dielectric constant ε_0 and conductivity σ of liquid-ammonia solutions.

LiBr, NaBr, and KI have sufficient solubility in liquid ammonia for the present investigations. The Cole-Cole arc plots of the dielectric constants of these solutions deviate from the simple semicircle form in a characteristic way in the frequency range below 23 GHz as shown in Fig. 4 for 0.1 m KI.

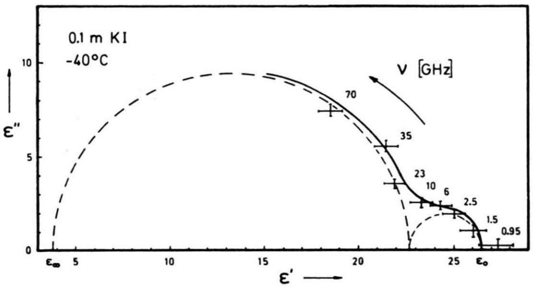

Fig. 4. Cole-Cole arc plot for a 0.1 m KL solution at −40 °C.

Taking into account the inaccuracy of the experimental results a separation into two relaxation processes with relaxation times τ_s and τ_e and relaxational strengths $\Delta\varepsilon_s$ and $\Delta\varepsilon_e$, respectively, appears to be reasonable, where the relaxation at higher frequencies (τ_s, $\Delta\varepsilon_s$) is ascribed to the orientation of the solvent molecules and the relaxation at lower frequencies to an additional effect due to the ions.

	c Mol/l	$\Delta\varepsilon_s$	$\Delta\varepsilon_e$	a Å	b Å	a' Å	μ D	c_I Mol/l	c_F Mol/l
NH_3 pure		19.0							
LiBr	0.1	18.7	4.0	6.3	3.3	6.7	28.3	0.050	0.030
NaBr	0.1	18.7	4.4	6.3	3.1	6.7	30.2	0.048	0.033
KI	0.1	18.7	3.8	6.1	2.7	6.4	33.2	0.034	0.044
	0.5	17.2	9						
	1.0	16.0	11						

Table 2. Relaxation strengths, model parameters, and concentrations of ion pairs and free ions at −40 °C.

The results of the analysis are given in Table 2. The relaxation strength $\Delta\varepsilon_s$ decreases while $\Delta\varepsilon_e$ increases with increasing concentration of KI. The relaxation strength $\Delta\varepsilon_e$ and the decrease of $\Delta\varepsilon_s$ are independent of temperature within the accuracy of our measurement. Figure 3 shows that the relaxation times τ_s of the 0.1 m solutions are slightly above the values for pure ammonia at all temperatures. This behavior is, however, not completely outside the error limits.

The relaxation times τ_e for the individual salts are also shown in Fig. 3. The activation energy is roughly the same as for the relaxation of the solvent molecules. At a given temperature, the relaxation time τ_e increases with decreasing ion size.

Discussion

In principle, a number of polarisation effects could cause the additional relaxation at lower frequencies, e. g., relaxation of the ion atmosphere [16], orientational relaxation of bound ammonia molecules in the solvation shells, or orientational relaxation of ion pairs or other aggregates with electric dipole moment. If one assumes that the theory of Debye and Falkenhagen holds qualitatively for solutions of higher concentrations, the relaxation strength of the ion atmosphere relaxation decreases with increasing temperature. The experimental results do not show such a temperature dependence. An estimation shows that, if the effect were caused by ammonia molecules in the solvation shell, approximately 80 ammonia molecules per ion would be affected. This number is in disagreement with the Stokes' radii in liquid-ammonia solutions (see below) and other data concerning the solvation shells.

As in aqueous solutions of 2 − 2 electrolytes, the orientation of ion pairs is most likely the process which causes the additional relaxation. Diebler and Eigen [17] proposed a multistep dissociation of 2 − 2 electrolytes in aqueous solution which may be modified for the solution of alkali halides in liquid ammonia as follows:

$$\underset{(1)}{[\mathrm{MeA}]_s} \rightleftarrows \underset{(2)}{[\mathrm{Me}^+(\mathrm{NH_3})\mathrm{A}^-]_s} \rightleftarrows \underset{(3)}{[\mathrm{Me}^+]_s} + [\mathrm{A}^-]_s\,, \qquad (4)$$

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[16] H. Falkenhagen, Elektrolyte, S. Hirzel-Verlag, Leipzig 1953.

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where Me^+ is the alkali metal ion and A^- the halide ion. The subscript s indicates the solvation of the individual species. The contact pair (1) is assumed to be not distinguishable in the dielectric measurement because of its small dipole moment. Only the ion pairs (2) in which the ions are separated by a solvent molecule contribute to the dielectric polarisation.

In order to estimate the dimensions of the ion pairs the Stokes' radii of the ions are determined using the formula

$$R = e\,F/6\,\pi\,\eta\,l\,f_t\,, \qquad (5)$$

where e is the electronic charge, F Faraday's number, η the viscosity, l the mobility of the ion, and f_t the translational micro friction factor [18] which is a function of the ion radius and the radius of the solvent molecules. The accuracy of the micro friction correction as stated by the authors is about ±20%. With the values for the ion mobility l in liquid ammonia [19] at −40 °C one obtains the ion radii R given in Table 3. Radii obtained from the empirically corrected Stokes' formula [20] agree with the calculated radii within the error limits mentioned above. The crystal radii [21] r are also shown in Table 3. It can be seen that the degree of solvation decreases with increasing crystal radius.

	Li^+	Na^+	K^+	Br^-	I^-
$l\left[\dfrac{cm^2}{\Omega\ equiv}\right]$	112	131	165	160	171
r [Å]	0.60	0.95	1.33	1.95	2.16
R [Å]	3.7	3.3	2.7	2.8	2.6

Table 3. Mobility, crystal radii, and Stokes' radii at −40 °C.

As a model for the ion pairs a solvated alkali ion and a solvated halide ion according to species (3) of Eq. (4) is taken with the respective Stokes' radii (Fig. 5). If one approximates the ion pair by a rotational ellipsoid the following estimations hold for the longer semiaxis a and the shorter semiaxis b:

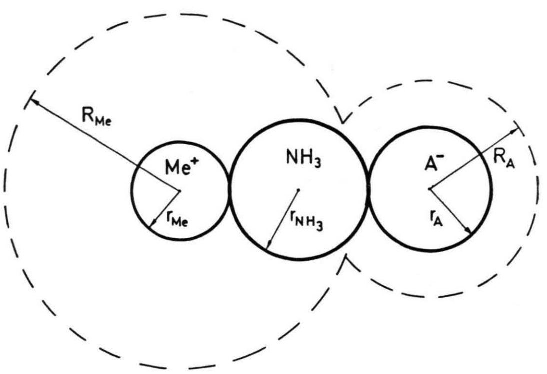

Fig. 5. Model of the ion pair.

$$a = \tfrac{1}{2}\,(R_{Me} + r_{Me} + 2\,r_{NH_3} + r_A + R_A)\,, \qquad (6)$$

$$b = \tfrac{1}{2}\,(R_{Me} + R_A)\,. \qquad (7)$$

Taking $r_{NH_3} = 1.7$ Å from X-ray diffraction data [22] one obtains for the semiaxes a and b the values given in Table 2. Although in KI solutions the crystal radii of the ions are largest, the dimensions of the ion pairs are smallest because of the low degree of solvation.

Additional information concerning the dimensions of the ion pairs may be obtained from the electrolyte circle of the Cole-Cole arc plot using Debye's formula

$$\tau_e = \frac{4\,\pi\,a\,b^2}{k\,T}\,f_l\,f_r \qquad (8)$$

where f_r is the rotational micro viscosity factor [18] and f_l the correction for applying the formula to ellipsoidal particles [23] in which the dipole moment has the direction of the longer semiaxis. Taking the ratio of the semiaxes from the model and the relaxation times of the ion pair orientation from the measurements at −40 °C (Fig. 3), one can calculate the values of the longer semiaxes from Eq. (8). With the notation a' these values are given in Table 2. A comparison with the values a obtained from the model calculation shows good agreement.

The ion pairs discussed here may be identical with the structural form of an aggregate postulated by Catterall et al. [24] and O'Reilly [25] in order to

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explain the ESR and knight shift data in liquid-ammonia solutions of alkali metal and KI.

The relaxation strength $\Delta\varepsilon_{\mathrm{i}}$ of a relaxation process is a function of the number N_i of dipoles per unit volume. With the assumption that the static dielectric constant is much larger than unity, which is certainly fulfilled in the present case, one can derive the following relationship from a generalized form of the Onsager-Böttcher relation [26]:

$$\Delta\varepsilon_{\mathrm{i}} = 4\,\pi\,\frac{N_{\mathrm{i}}\,\mu_{\mathrm{i}}^2}{(1-A_{\mathrm{i}})\;3\,k\,T} \tag{9}$$

where μ_{i} is the dipole moment of species i, and A_{i} takes into account the special ellipsoidal form of the species i.

With the relaxation strengths $\Delta\varepsilon_{\mathrm{e}}$ (Table 2) and the dipole moment μ taken from the model of the ion pair one obtains for the concentration c_{I} of the ion pairs in 0.1 m solutions at -40 °C the values given in Table 2. With this model the concentration of the ion pairs increases with decreasing crystal radii of the ions from 30 to 50% of the total concentrations.

In agreement with these results, the concentration c_{F} of free ions estimated from

$$\Lambda_{\mathrm{c}}/\Lambda_{\infty} = f_{\lambda}\,\alpha \tag{10}$$

(Λ_{c} the equivalent conductivity of a 0.1 m solution, Λ_{∞} that of an infinitely diluted solution, $f_{\lambda} \leqq 1$ the conductivity coefficient, and α the degree of dissociation), decreases with decreasing crystal radii of anion and cation. The values of c_{F} in Table 2 have been calculated with $f_{\lambda} = 1$, therefore they represent the lower limit of the free ion concentration. The sum of the concentration c_{I} and c_{F} is smaller than the total salt concentration so that contact pairs or other aggregates may exist in finite concentration. The concentrations c_{F} of free ions in 0.1 m solutions can also be calculated with dissociation constants given in the literature [27]. The values thus obtained for c_{F} agree roughly with those of Table 2.

The decrease of $\Delta\varepsilon_{\mathrm{s}}$ with increasing ion concentration may be explained [1, 5] on the basis that ammonia molecules in the vicinity of the ions are irrotationally bound, i. e., their contribution to the dielectric polarisation is reduced because of the strong electric field of the ion.

From the gradient of the plot $\Delta\varepsilon_{\mathrm{s}}$ versus concentration one obtains that about 6 moles ammonia per mole KI are irrotationally bound at -40 °C.

The solvent relaxation time τ_{s} increases slightly with concentration in liquid-ammonia solutions of LiBr, NaBr, and KI while it decreases in the corresponding aqueous solutions. Viscosity and ultrasonic absorption behavior differ also: in liquid-ammonia solution of NaBr and KI viscosity [19] and ultrasonic absorption [28] increase with concentration, they decrease in the corresponding aqueous solutions [20, 29] due to strong structure breaking effects. Liquid-ammonia solutions of alkali halides appear to be similar to aqueous solutions of polyvalent electrolytes [6, 30]. In both types of systems ion pairs exist due to the stronger ion-ion interaction and the dielectric relaxation time of the solvent molecules increases with increasing ion concentration.

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