

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/231429834>

Dielectric properties and molecular structure of amide solutions. 2. 2-Azacyclotridecanone in carbon tetrachloride

ARTICLE *in* THE JOURNAL OF PHYSICAL CHEMISTRY · APRIL 1984

Impact Factor: 2.78 · DOI: 10.1021/j150656a036

CITATIONS

9

READS

16

3 AUTHORS, INCLUDING:



[Przemysław Kędziora](#)

Institute of Molecular Physics, Polish Acade...

49 PUBLICATIONS 297 CITATIONS

[SEE PROFILE](#)



[Jan Jadżyn](#)

Institute of Molecular Physics, Polish Acade...

215 PUBLICATIONS 1,563 CITATIONS

[SEE PROFILE](#)

with stoichiometries corresponding to ethidium to ordered octamer ratios of 2:1 and 1:1.¹¹ One should expect only one mode of ethidium binding (intercalation) for stacked dimer units in which the extent of stacking is large. Moreover, the normalized intensities of the N(1)H and N(2)H lines found in the present work are incompatible with the stacking of dimers. The dimer model predicts 0.5 N(1)H and 0.5 N(2)H per ordered 5'-GMP, whereas the tetramer model predicts 1.0 N(1)H and 1.0 N(2)H, as observed. Finally, the estimated size of the ordered aggregate giving rise to H_α and H_β is consistent with the stacking of two tetramers, provided anisotropic rotations and hydrated dimensions are taken into account.¹⁰

In considering the ¹³C NMR spectra of ordered Na₂(5'-GMP), Petersen et al.⁹ say that the downfield shifts observed for certain carbon centers (C(2), C(4), C(8)) are inconsistent with a model that exclusively involves tetramer stacking since this mode of association is expected to produce only upfield shifts on the basis of ring current effects. We have previously pointed out¹⁰ that other factors also are likely to contribute to the observed chemical shifts, including (i) H bonding and Na⁺ complexation, (ii) electric field gradients arising from the proximity to phosphate or Na⁺, and (iii) solvation differences resulting from removal of the 5'-GMP base from a primarily aqueous to a more hydrophobic environment. Since these effects cannot be accurately assessed, it is impossible to draw meaningful structural conclusions on the basis of chemical shift data alone.

Despite our disagreement with the interpretation offered by Petersen et al.,⁹ these workers have made important observations which bear significantly on the dynamics of ordered Na₂(5'-GMP) structures. On the basis of spin saturation transfer measurements, they estimated the rate constant for interchange of H_α and H_β environments in the ordered nucleotide (C₄ isomers) to be $k_{\alpha\beta} = 0.3 \text{ s}^{-1}$. By comparison, the rate constant for exchange of H_α or H_β with H_γ of the disordered nucleotide was significantly lower than $k_{\alpha\beta}$ ($k_{\beta\gamma} = k_{\gamma\alpha} = 0.1 \text{ s}^{-1}$). Also, the rate constant for exchange of H_β (D₄ isomers) with H_γ was larger than $k_{\alpha\beta}$ ($k_{\beta\gamma} = 1.2 \text{ s}^{-1}$). Thus it was concluded that $H_\alpha \rightleftharpoons H_\beta$ interchange was *direct* (most

likely, intramolecular). They also concluded that for octamers consisting of stacking tetramers there was no apparent mechanism which would permit direct exchange of H_α and H_β to be faster than the exchange of these proton environments with H_γ of the disordered nucleotide. This latter conclusion, however, is incorrect.

The direct interchange of H_α and H_β can be explained in terms of the tetramer model by $\pm 60^\circ$ rotations of one tetramer unit with respect to the other about the C₄ symmetry axis. However, we must revise our previous proposal¹¹ that the twisting rate is sufficiently rapid to time average the isomer pairs. Though isomers II and III are formally distinguishable by the presence of a D-ribose phosphate attached to the left- and right-handed forms of a chiral core of stacked guanine tetramers, it is now apparent that the H(8) protons are magnetically equivalent, or nearly so, in the two isomers. Thus both isomers give rise to resonances at H_α and H_β . Under these conditions isomers II and III would not be distinguishable by NMR, but the environments of the upper and lower tetramer units would be interchanged by twisting about the C₄ axis. An interchange mechanism of this type does not preclude extratetramer H bonding for a C₄ isomer. If the lifetime of the H bond is comparable to the lifetime before tetramer twisting ($\sim 3 \text{ s}$), the ribose OH resonance should remain sharp, as observed.

In summary, the stacked tetramer model for ordered Na₂(5'-GMP) is consistent with (i) the stoichiometry of nucleotide aggregation, (ii) the dependence of structural ordering on the nature of the alkali metal counterion, (iii) the bimodal binding of ethidium to the ordered forms, (iv) the estimates of aggregate size, (v) the number of exchangeable H-bonded protons per ordered nucleotide unit, (vi) the kinetics of H(8) environmental interchange, and (vii) the alkali metal ion dependence of ordering phenomena in related systems such as guanosine, poly-I, and Poly-X. The dimer model, however, is incompatible with these collective observations.

Acknowledgment. The partial support of this research through NIH Grant GM-23516 is gratefully acknowledged.

Registry No. Na₂(5'-GMP), 5550-12-9; TMA₂(5'-GMP), 89999-10-0.

Dielectric Properties and Molecular Structure of Amide Solutions. 2. 2-Azacyclotridecanone in Carbon Tetrachloride

Krzysztof Prałat, Przemysław Kędziora, and Jan Jadżyn*

*Institute of Molecular Physics, Polish Academy of Sciences, Smoluchowskiego 17/19, 60-179 Poznań, Poland
(Received: February 3, 1983; In Final Form: August 21, 1983)*

The thermodynamic theory of the nonlinear dielectric effect proposed by Rivail and Thiebaut for systems in which one chemical reaction takes place has been generalized for systems with many simultaneous reactions. Experimental results of the nonlinear dielectric effect and static dielectric polarization for 2-azacyclotridecanone (lauryl lactam) in CCl₄ solutions are presented. Conformations of hydrogen-bonded multimers of this lactam are discussed.

Introduction

In the first part of this paper¹ dielectric and spectroscopic studies of *N*-methylacetamide (NMA) solutions in CCl₄ were presented. Numerous studies devoted to this amide result from the fact that the compound can be regarded as a simple model of biological systems containing peptide groups. The trans configuration of this group leads to such a strong chain association of NMA molecules via NH...O=C hydrogen bonds that this amide in a pure state is one of the most polar liquids ($\epsilon \approx 180$).

Our studies showed that, when highly diluted, the chain NMA multimers take conformations intermediate between linear (as in the crystalline state) and statistically random (as in the case of free rotation around hydrogen bonds). This conclusion agrees with the results of Bass, Nathan, Meighan, and Cole² obtained for pure NMA. Thus, the concentration of amide is not a main factor, implying the conformation of chains. It may be, to some extent, a surprise since it seemed that the distances between chains, determining the possibility of their appropriate packing (partic-

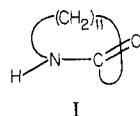
(1) K. Prałat, J. Jadżyn, and S. Balanicka, *J. Phys. Chem.*, **87**, 1385 (1983).

(2) S. J. Bass, W. J. Nathan, R. M. Meighan, and R. H. Cole, *J. Phys. Chem.*, **68**, 509 (1964).

ularly in pure liquid), should have an essential influence on conformations of multimers.

Thus, it seems that the conformation of secondary amide multimers depends mainly on the possibility of rotation of amide molecules or, more strictly, on the possibility of random relative orientation of neighbors about the O...HN bond lines. The occurrence of this rotation is connected with the size of substituents of the peptide group. The stereomodel of NMA multimer shows that the CH₃ groups permit a rotation of NMA molecules around the hydrogen bonds through a significant angle, but this is not a free rotation. Therefore, various conformations of the chain are not equally probable and the multimers are of elongated shape, which is not linear, as could be expected if the rotation were fully hampered. In this context, studies concerning the influence of the size of peptide-group substituents on the conformation of secondary amide multimers seem to be interesting.

In this paper we present the results of dielectric studies for 2-azacyclotridecanone (2-ACT) (I) in carbon tetrachloride so-



I

lutions. The peptide group of this lactam has a trans configuration,³⁻⁵ while its nitrogen and carbon atoms are linked in a large ring consisting of 11 methylene groups. The stereomodel of 2-ACT multimer shows that this substituent hampers to a significant extent the rotation around NH...O=C hydrogen bonds.

Considerably lower conductivity of 2-ACT solutions compared with those of NMA enabled us to measure the static dielectric polarization as well as the nonlinear dielectric effect, i.e., the effect caused by a strong electric field. Application of these two independent dielectric methods enabled us to determine two self-association equilibrium constants: K_2 (for dimerization) and K (for multimerization). The experimental values of these constants were then compared with those obtained with IR spectroscopy.

The interpretation of the nonlinear dielectric effect for associated systems in which, as in our case, many chemical equilibria coexist is not an easy task. Additionally, for secondary trans-amides, one must take into account a considerable symmetry of chain multimers.¹ A thermodynamic theory of the nonlinear dielectric effect for such systems is presented in this paper. The theory can be seen as a generalization of that proposed by Rivail and Thiebaut⁶ for mixtures of anisotropic molecules, where only one chemical reaction takes place.⁷

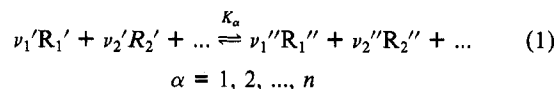
Nonlinear Dielectric Effects in Systems with Many Chemical Equilibria

A strong electric field applied to a molecular system produces its "nonlinear response", which contains much more information on the structure and intermolecular interactions than can be gained from static dielectric polarization. In a strong electric field the rotational motion of dipolar molecules is hampered, so the additional orientation by a measuring oscillatory field becomes less effective. This fact causes a decrease of electric permittivity of a system which is proportional to the square of the field strength. This nonlinear effect (Langevin saturation) depends on the concentration of the polar species and the fourth power of their permanent dipole moment.^{8,9}

When a high field is applied to a system in which chemical reactions take place, other nonlinear effects may arise. If the

polarity of the reagents and reaction products differ, the equilibrium position is displaced to favor the more polar reaction partners. This effect causes an increase of electric permittivity.

The theory of this positive nonlinear effect for systems containing anisotropic molecules has been worked out for the case when only one chemical equilibrium takes place.⁶ For solutions of trans amides the situation is more complicated. In this connection, let us consider the case in which the self-association of a studied substance can be described by n equilibria of the type



occurring simultaneously in solution. K_α denotes the equilibrium constant of the appropriate reaction defined as

$$\ln K_\alpha = \sum_i \nu_i \ln c_i \quad (2)$$

where c_i represents the molar concentration of the i -th component in the α -th reaction, while ν_i are the stoichiometric coefficients in eq 1 (positive for products R'' and negative for reactants R').

In a strong electric field the position of equilibrium for all these reactions shifts; i.e., concentrations of partners and thereby the equilibrium constants are subject to a change. Calculation of these changes is a main task in the analysis of the nonlinear dielectric effect for systems with chemical equilibria. Every change in molar concentration of partners in the α -th reaction can be expressed by the change of the extent of reaction ξ_α :

$$dc_1/\nu_1 = dc_2/\nu_2 = \dots = d\xi_\alpha \quad (3)$$

The change in values of equilibrium constants results directly from the change in Gibbs energy caused by applying a strong electric field E .¹⁰ For a system with electric permittivity ϵ this change is given by the following equation:

$$\ln K_\alpha(E) - \ln K_\alpha(0) = \frac{1}{RT} \frac{\epsilon_0 E^2}{2} \frac{d\epsilon}{d\xi_\alpha} \quad (4)$$

where $\epsilon_0 = 8.85 \times 10^{-12}$ F/m. To calculate the derivative $d\epsilon/d\xi_\alpha$ we use the Onsager equation¹¹ adapted to a mixture of anisotropic molecules by Thiebaut, Rivail, and Barriol:¹²

$$\frac{9\epsilon_0 kT}{N} \frac{(\epsilon - \epsilon_\infty)(2\epsilon + \epsilon_\infty)}{\epsilon(\epsilon_\infty + 2)^2} = \sum_i c_i \mu_i^2 (1 - \delta\eta_i) \left[\frac{1 + \eta_i}{1 - \lambda\eta_i} \right]^2 \quad (5)$$

where N is Avogadro's constant, c_i is the molar concentration of the species i , and

$$\eta_i = (\bar{\alpha}_i - \alpha_{ai})/\alpha_{ai}$$

$$\delta = (\epsilon - 1)(\epsilon_\infty + 2)/\{(2\epsilon + 1)(\epsilon_\infty - 1)\}$$

$$\lambda = (\epsilon - \epsilon_\infty)(\epsilon_\infty + 2)/\{(2\epsilon + \epsilon_\infty)(\epsilon_\infty - 1)\} \quad (6)$$

$\bar{\alpha}_i$ is an average polarizability, α_{ai} is the component of the tensor of polarizabilities of the species i along its dipole moment μ_i , and ϵ_∞ , often replaced by the square of the refractive index n^2 , is the permittivity measured at a frequency high enough to prevent orientational polarization.

In this formulation, the shape of molecules is characterized by an ellipsoid of revolution with semi-axes a and $b = c$, where the direction of the a axis is in line with the permanent dipole moment of the molecule in question. The anisotropy coefficient η_i is related to the shape coefficient A_{ai} by the equation¹²

$$A_{ai} = \frac{1}{3} + \frac{\epsilon_\infty + 2}{3(\epsilon_\infty - 1)} \eta_i \quad (7)$$

The calculation of $d\epsilon/d\xi_\alpha$ by differentiating eq 5 leads to the following form of eq 4

- (3) R. Huisgen and H. Walz, *Chem. Ber.*, **89**, 2616 (1956).
- (4) W. Luck, *Naturwissenschaften*, **52**, 25 (1965).
- (5) H. E. Hallam and C. M. Jones, *J. Mol. Struct.*, **1**, 413 (1967); *J. Chem. Soc.*, **5**, 1 (1970).
- (6) J. L. Rivail and J. M. Thiebaut, *J. Chem. Soc., Faraday Trans. 2*, **70**, 430 (1974).
- (7) For spherical molecules the statistic theory of the nonlinear dielectric effect has been given by J. Malecki, *J. Chem. Soc., Faraday Trans. 2*, **72**, 1214 (1976).
- (8) C. J. F. Böttcher, "Theory of Electric Polarization", Vol. I, Elsevier, Amsterdam, 1973, p. 289.
- (9) A. Chefkowsky, "Dielectric Physics", Elsevier, Amsterdam, 1980.

- (10) H. Fröhlich, "Theory of Dielectrics", Oxford University Press, London, 1958.
- (11) L. Onsager, *J. Am. Chem. Soc.*, **58**, 1486 (1936).
- (12) J. M. Thiebaut, J. L. Rivail, and J. Barriol, *J. Chem. Soc., Faraday Trans. 2*, **68**, 1253 (1972).

$$\ln K_\alpha(E) - \ln K_\alpha(0) = \frac{\epsilon^2(\epsilon_\infty + 2)^2}{2\epsilon^2 + \epsilon_\infty^2} \frac{E^2}{18k^2T^2} \sum_i \nu_i \mu_{pi}^2 \quad (8)$$

where summing over i contains all species of the α -th equilibrium, while μ_{pi} represents the expression

$$\mu_{pi}^2 = (1 - \delta\eta_i) \left[\frac{1 + \eta_i}{1 - \lambda\eta_i} \right]^2 \mu_i^2 \quad (9)$$

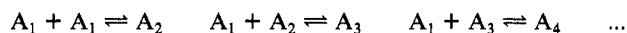
Differentiation of eq 2 and 8 with respect to E gives the following equation (for each of all n reactions of eq 1):

$$\sum_i \nu_i y_i = \sum_i \mu_{pi}^2 \quad (10)$$

where y_i denotes

$$y_i = \frac{9k^2T^2}{E} \frac{2\epsilon^2 + \epsilon_\infty^2}{\epsilon^2(\epsilon_\infty + 2)^2} \frac{dc_i}{c_i dE} \quad (11)$$

Equation 10 gives the relation between change in concentration of reaction partners and their dipole moments. $n + 1$ unknown values of y_i can be determined by solving the set of equations which consists of n equations of the type represented by eq 10 and one equation resulting from differentiation of the reagent mass balance equation with respect to E . The form of the equation of this balance depends on a given type of chemical reaction. In the case of multistep association, when reactions 1 are of the type



the mass balance equation has the form $\sum_i i c_i = c$. Its differentiation with respect to E gives the following equation:

$$\sum_i i c_i y_i = 0 \quad (12)$$

Equations 10 and 12 give the following expression describing y_i :

$$y_i = \mu_{pi}^2 - i \frac{\sum_j i c_j \mu_{pj}^2}{\sum_i i c_i^2} \quad i = 1, 2, 3, \dots$$

The values of dc_i/dE (calculated from y_i) enable one to calculate a macroscopic change in electric permittivity caused by applying a strong electric field. Taking into account the relation between $d\epsilon/dE$ and dc_i/dE ¹³ and the relation between $d\epsilon/dE$ and the measured value of the electric permittivity increment ($d\epsilon/dE = 2/3 \Delta\epsilon/E$)⁸ we obtain the following equation for the total nonlinear dielectric effect in a system with many chemical equilibria:

$$\frac{45\epsilon_0 k^3 T^3}{N} \frac{(2\epsilon^2 + \epsilon_\infty^2)(2\epsilon + \epsilon_\infty)^2}{\epsilon^4(\epsilon_\infty + 2)^4} \frac{\Delta\epsilon}{E^2} = \sum_i c_i \mu_{pi}^4 - \frac{5}{6} \frac{(2\epsilon + \epsilon_\infty)^2}{2\epsilon^2 + \epsilon_\infty^2} \sum_i c_i \mu_{pi}^2 y_i \quad (13)$$

where summing over i extends over all species present in solution, and μ_{si} denotes

$$\mu_{si}^4 = (1 - \delta\eta_i) \left[\frac{1 + \eta_i}{1 - \lambda\eta_i} \right]^4 \mu_i^4 \quad (14)$$

The first term on the right side of eq 13 describes the normal (negative) orientational effect (Langevin saturation), while the second one describes the chemical effect, i.e., shifting the equilibria caused by an electric field (positive effect).

Experimental Section

Materials. 2-Azacyclotridecanone (Aldrich) was purified by three crystallizations from chloroform (mp = 152 °C) and was stored over P₂O₅ in a vacuum desiccator. Carbon tetrachloride (POCH) was dried with P₂O₅, distilled twice (bp = 76.5 °C), and stored over 4A molecular sieves.

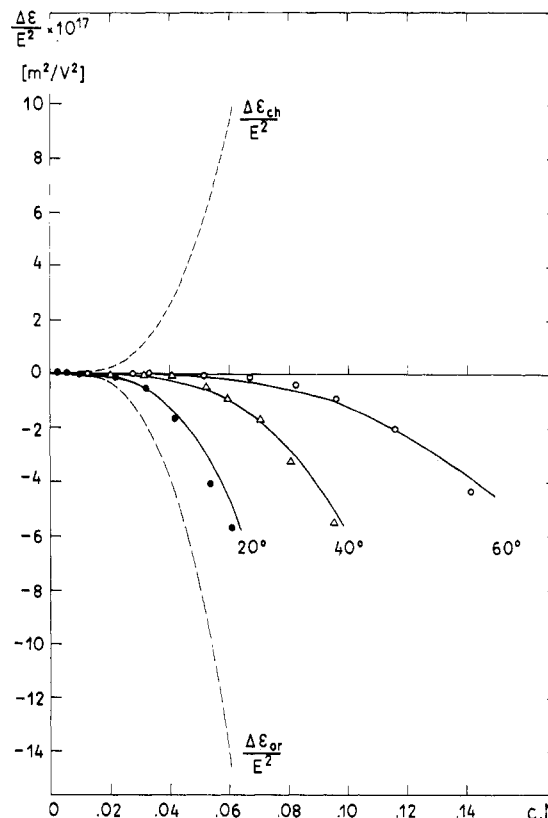


Figure 1. Nonlinear dielectric effect for the 2-azacyclotridecanone-CCl₄ system. Broken lines represent the orientational and chemical contributions (at 20 °C).

Apparatus. Electric permittivity was measured with a Wayne-Kerr B330 bridge at a frequency of 1.5 kHz and with an accuracy of $\pm 0.1\%$. Variations in electric permittivity $\Delta\epsilon/E^2$ were measured with an automatically recording pulse device^{14,15} at a frequency of ≈ 2 MHz, with an accuracy of $\pm 3\%$. The electric field E was applied in the form of rectangular pulses of 1-ms duration and $(0.5-5) \times 10^6$ V/m amplitude at a repetition rate of 1-100 Hz.

The density was measured by the hydrostatic method¹⁶ with an accuracy of $\pm 2 \times 10^{-4}$ g/cm³.

Spectroscopic investigations in the IR region were carried out on a Perkin-Elmer 577 spectrophotometer.

All measurements were performed at 20, 40, and 60 °C, over the whole range of solubility of 2-ACT in CCl₄.

Results and Discussion

The results of the nonlinear dielectric effect obtained for 2-ACT in CCl₄ solutions are shown in Figure 1. The negative effect, observed over the whole range of lactam concentration, means that the orientational part dominates over the chemical effect. Individual contributions of these two effects are indicated in the figure with broken lines (for 20 °C). Such a distribution results from the interpretation of dielectric results given in a later part of this paper.

The experimental results of polarization and nonlinear effect measurements can be conveniently expressed in terms of molar quantities μ_{app}^2 and $\mu_{app(s)}^4$, which in the case of nonpolar solvents have the following form:

$$c\mu_{app}^2 = \frac{9\epsilon_0 kT}{N} \frac{(\epsilon - \epsilon_\infty)(2\epsilon + \epsilon_\infty)}{\epsilon(\epsilon_\infty + 2)^2} \quad (15)$$

$$c\mu_{app(s)}^4 = -\frac{45\epsilon_0 k^3 T^3}{N} \frac{(2\epsilon^2 + \epsilon_\infty^2)(2\epsilon + \epsilon_\infty)^2}{\epsilon^4(\epsilon_\infty + 2)^4} \frac{\Delta\epsilon}{E^2} \quad (16)$$

(14) J. Mañeck, *Acta Phys. Pol.*, **21**, 13 (1962).

(15) J. Mañeck, *Faraday Trans. 2*, **72**, 104 (1976).

(16) J. Jadzyn and J. Mañeck, *Rocz. Chem.*, **48**, 531 (1974).

(13) Equation A5 in the work of Rivail and Thiebaut.⁶

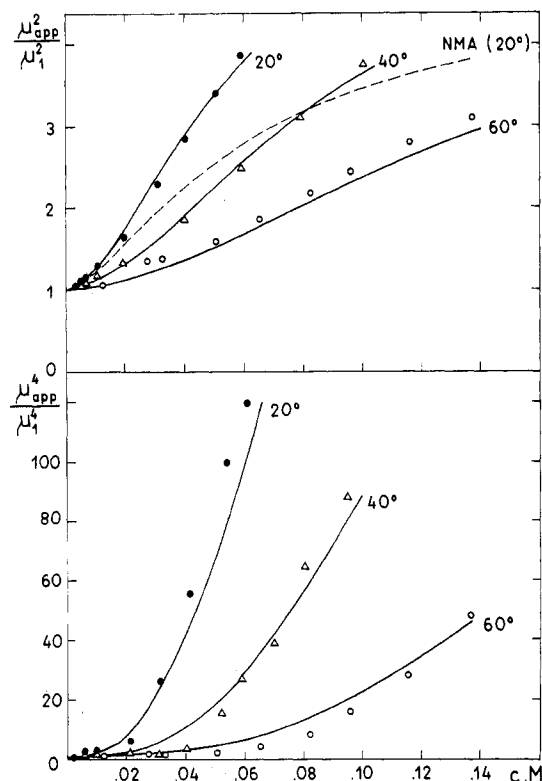


Figure 2. Experimental results of dielectric polarization and nonlinear effect (points) and the best fitting obtained in the proposed model (lines).

The dependence of these quantities on lactam concentration is shown in Figure 2.

The extrapolation of $\mu_{app}^2(c)$ to zero concentration of lactam gives the value of the monomer dipole moment. However, the very strong dependence of μ_{app}^2 on 2-ACT concentration in CCl_4 (stronger than in the case of analogous NMA solutions, Figure 2) makes this extrapolation rather a doubtful source of μ_1 value. Therefore, we performed additional precise measurements of polarization for very diluted solutions in benzene, where the dependence of μ_{app}^2 on c is considerably weaker. From these measurements we obtained $\mu_1 = 3.70 \pm 0.05$ D (at 20 °C).

According to eq 5 and 13 μ_{app}^2 and $\mu_{app(s)}^4$ are related to molecular quantities by

$$c\mu_{app}^2 = \sum_i c_i \mu_i^2 (1 - \delta\eta_i) \left[\frac{1 + \eta_i}{1 - \lambda\eta_i} \right]^2 \quad (17)$$

$$c\mu_{app(s)}^4 = \sum_i c_i \mu_i^4 (1 - \delta\eta_i) \left[\frac{1 + \eta_i}{1 - \lambda\eta_i} \right]^4 - \frac{5}{6} \frac{(2\epsilon + \epsilon_\infty)^2}{2\epsilon^2 + \epsilon_\infty^2} \sum_i c_i \mu_i^2 (1 - \delta\eta_i) \left[\frac{1 + \eta_i}{1 - \lambda\eta_i} \right]^2 \eta_i \quad (18)$$

To reconstruct theoretically the experimental dependences one must know concentrations of multimers (c_i), their dipole moments (μ_i), and anisotropy parameters (η_i).

In order to determine the concentrations of multimers one should assume a *thermodynamical model of association*. The model that we assume is analogous to that which was applied to the interpretation of results for NMA. Thus, we assume that all but the first equilibrium constant K_2 describing dimerization are the same

$$A_1 + A_1 \xrightleftharpoons{K_2} A_2 \quad A_1 + A_{i-1} \xrightleftharpoons{K_i} A_i \quad i = 3, 4, 5, \dots$$

$$K_2 \neq K_3 = K_4 = \dots = K$$

Thus, the equilibrium constants K_2 and K are connected with concentrations of successive multimers by the following equations:

$$K_2 = c_2/c_1^2 \quad K = c_i/(c_1 c_{i-1}) \quad i = 3, 4, 5, \dots \quad (19)$$

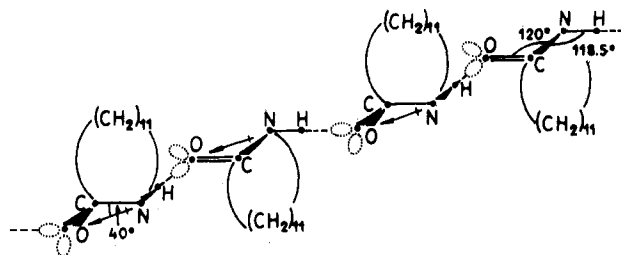


Figure 3. Model of 2-azacyclotridecanone linear multimer.

LaPlanche et al.¹⁷ showed that, for such a simplified model of self-association, the concentration of monomer (for a given nominal concentration (c) of the studied substance) can be calculated from the following equation:

$$c_1 + K_2 c_1^2 (2 - Kc_1) / (1 - Kc_1)^2 = c \quad (20)$$

Further, the concentrations of dimers and higher multimers can be easily calculated from eq 19.

So, in this model, the calculation of multimer concentrations resolves itself into determination of two equilibrium constants: K_2 and K .

To calculate dipole moments and the anisotropy of multimers one must assume their *geometry*. In the paper on NMA the following three geometric models of secondary trans amide multimers were discussed: linear, statistically random, and an intermediate model of elongated multimers. Fair agreement was achieved for the model of elongated multimers, which can be connected with the possibility of partial rotation of NMA molecules around hydrogen bonds.

In the presently investigated case of 2-ACT such a rotation is, from spatial reasons, much more restricted—this means that multimers should have a shape close to linear. Preliminary confirmation of such a shape was found in a considerably more rapid increase of μ_{app}^2 for 2-ACT than for NMA (Figure 2). For almost the same dipole moment of monomers of these two amides this indicates that multimers of the studied lactam are more polar.

Thus, we assumed that multimers of 2-ACT have a rigid linear structure as shown in Figure 3. In the model of the ellipsoidal cavity the shape of such an associate may be approximated by an ellipsoid of revolution in which the short semi-axis is equal to the monomer radius $b_i = a_1$, while the long one has a length of $a_i = i a_1$. Therefore, it is a chain in which balls with radii of a_1 are set side by side along a straight line.

In this model, the previously discussed¹ size coefficients A_{si} for successive multimers can be calculated with the following formula:

$$A_{si} = \frac{1}{i^2 - 1} \left(\frac{i}{(i^2 - 1)^{1/2}} \ln \frac{1}{i - (i^2 - 1)^{1/2}} - 1 \right) \quad (21)$$

Then, the anisotropy coefficients η_i can be calculated from formula 7.

The geometric parameters of the 2-ACT molecule necessary for the calculations of dipole moments of multimers (Figure 3) were taken from roentgenographic data.^{18,19} Further, we assumed that the angle between the dipole moment vector of the monomer and the C-N bond is 40°, i.e., is equal to that in formamide determined from the Stark effect.²⁰ The main reason for this assumption is that the values for the dipole moments of these molecules are the same, which is after all not by chance, since the reported data²¹ show that various hydrocarbon substituents

(17) L. LaPlanche, H. B. Thompson, and M. T. Rogers, *J. Phys. Chem.*, **69**, 1482 (1965).

(18) J. D. Dunitz and F. K. Winkler, *Acta Crystallogr., Sect. B*, **31**, 251 (1975).

(19) F. K. Winkler and J. D. Dunitz, *Acta Crystallogr., Sect. B*, **31**, 281 (1975).

(20) R. J. Kurland and E. B. Wilson, *J. Chem. Phys.*, **27**, 585 (1957).

(21) M. Meighan and R. H. Cole, *J. Phys. Chem.*, **68**, 503 (1960).

TABLE I: Self-Association Equilibrium Constants (in M^{-1}) of 2-Azacyclotridecanone in CCl_4 ^a

<i>t</i> , °C	dielectric		IR	
	<i>K</i> ₂	<i>K</i>	<i>K</i> ₂	<i>K</i>
20	7.3	47.9	7.5	48.1
40	4.0	27.0	5.1	22.1
60	2.2	14.9	2.7	14.3

^a $\Delta H_2 = -25 \pm 8$ kJ/mol, $\Delta H = -24.7 \pm 1$ kJ/mol, $\Delta S_2 = -51$ J/(mol·deg), $\Delta S = -33$ J/(mol·deg).

of the CONH group do not affect the dipole moment of trans amides. When calculating the dipole moments of multimers we assumed that the polarity of every hydrogen bond was 0.3 D.

The molecular quantities, i.e., anisotropy coefficients and dipole moments, necessary for testing our theory may be, within the scope of such a formulated model, calculated without introducing any variable parameters.

Eventually, the whole problem consists of finding such values of *K*₂ and *K* (at every temperature) to reproduce simultaneously the experimental results of polarization (eq 17) and nonlinear (eq 18) studies. The best obtained fitting (done by the least-squares method) is presented in Figure 2 (solid lines), and appropriate equilibrium constants are given in Table I.

A good theoretical simulation of experimental results obtained for the proposed model indicates its adequacy. However, since the values of equilibrium constants obtained from dielectric data strongly depend on the geometry of multimers, it is worth it to compare these constants with those obtained from IR spectroscopy, which are not affected by geometric assumptions. We determined *K*₂ and *K* (Table I) from the experimental dependence of molar extinction coefficients for the band of the free N-H group situated at 3454 cm^{-1} (monomers and end groups in multimers) on amide concentration, using the same method as in the case of NMA solutions.¹

The values of equilibrium constants obtained from IR spectroscopy agree, within the experimental accuracy, with those determined from dielectric data. This agreement provides strong support for the assumptions that we have made during the interpretation of the dielectric data.

Analysis of the temperature dependence of equilibrium constants shows that the significant differences between dimerization and multimerization constants are connected with the entropy factor. This agrees with theoretical predictions of Sarolea-Mathot,²² who showed that the change of entropy accompanying the formation of a dimer from two monomers is greater than in the case of *i*-mer formation from (*i*-1)-mer and monomer. The values of change in enthalpy and entropy shown in Table I were calculated by the van't Hoff method, using the equilibrium constants expressed in mole fraction units.

Conclusions

The volume of substituents on the peptide group, which determines the possibility of rotation of amide molecules around hydrogen bonds, is the main factor determining the geometry of chains. In the case of 2-ACT the ring consists of 11 methylene groups, which significantly reduce the possibility of this rotation. Consequently, the multimer structure should be very close to linear. Thus, the solution of 2-azacyclotridecanone in CCl_4 can be represented as a mixture of spherical solvent molecules and strongly anisotropic species of various lengths. The concentrations of these species depend on the nominal amide concentration, the temperature, and, after application of a strong electric field, also its strength.

This simple model describes quite well the properties of a real system placed in an electric field—both in a weak field, when dielectric phenomena are proportional to the field strength, and in a strong field, when the changes in component concentrations take place. The conclusions resulting from dielectric studies have full spectroscopic support.

These studies also give a positive test for the theory of Rivail et al. of nonlinear phenomena with its generalization for complex systems with many equilibria.

Acknowledgment. This work was supported by the Polish Academy of Sciences within the framework of Project MR-I.9.

Registry No. 2-Azacyclotridecanone, 947-04-6.

(22) L. Sarolea-Mathot, *Trans. Faraday Soc.*, **49**, 8 (1953).

Properties of 1,3-Dialkylimidazolium Chloride-Aluminum Chloride Ionic Liquids. 1. Ion Interactions by Nuclear Magnetic Resonance Spectroscopy

Armand A. Fannin, Jr., Lowell A. King, Joseph A. Levisky, and John S. Wilkes*

The Frank J. Seiler Research Laboratory, U.S. Air Force Academy, Colorado Springs, Colorado 80840

(Received: February 18, 1983; In Final Form: November 14, 1983)

Mixtures of 1-methyl-3-ethylimidazolium chloride with aluminum chloride are liquid at room temperature. The chemical shifts of protons on the cations of the melts are highly dependent on the proportions of aluminum chloride and organic chloride salt. The largest effect is in the basic melts, where there is an excess of organic chloride over aluminum chloride. The chemical shift behavior may be explained by assuming that the anions in the melt affect the chemical shift of the cation hydrogens and that the anions and cations interact in the fast-exchange regime on the NMR time scale. The model implies that the melts are relatively organized in the liquid state, especially basic compositions. The addition of LiCl or nonelectrolyte solvents to binary aluminum chloride-imidazolium chloride mixtures also affects chemical shifts of the cation protons.

Fused salts that are liquid at room temperature comprise an unconventional but interesting class of aprotic solvents for studying the chemistry of inorganic, organometallic, and organic solutes. In addition, these ionic liquids are potentially useful as electrolytes in batteries, photoelectrochemical cells, and electroplating. In recent years some mixtures of aluminum chloride and 1-alkylpyridinium halides^{1,2} or 1,3-dialkylimidazolium chlorides³ have

been found to be liquid below room temperature. An understanding of the physical and chemical properties of the ionic liquids is vital to establishing the usefulness of the new materials. Especially important are the transport properties such as electric

(2) Chum, H. L.; Osteryoung, R. A. In "Ionic Liquids"; Inman, D.; Lovering, D. G., Eds.; Plenum Press: New York, 1981; pp 407-23.

(3) Wilkes, J. S.; Levisky, J. A.; Wilson, R. A.; Hussey, C. L. *Inorg. Chem.* **1982**, *21*, 1263-4.

(1) Hurley, F. H.; Wier, T. P. *J. Electrochem. Soc.* **1951**, *98*, 203-6.