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Dielectric Properties and Molecular Structure of Amide Solutions. 3. N-Benzylformamide in Carbon Tetrachloride

Jan Jadżyn,* Krzysztof Prałat, and Przemysław Kędziora

Institute of Molecular Physics, Polish Academy of Sciences, Smoluchowskiego 17/19, 60-179 Poznań, Poland
(Received: March 5, 1985; In Final Form: January 22, 1986)

It was found that the prevailing amount of *N*-benzylformamide (NBF) monomers (~93%) occur in the trans configuration. The thermodynamic parameters of the NBF self-association in carbon tetrachloride were determined on the basis of IR spectroscopy studies. The results of dielectric studies showed that the hydrogen-bonded chains of NBF multimers have a statistically random conformation.

Introduction

In the previous papers of this series we have shown how decisively peptide group substituents affect the conformation of hydrogen-bonded multimers of the secondary *trans*-amides R_1CONHR_2.[1,2] The size of R_1 and R_2 determines the possibility of rotation of adjoining multimer elements around the axis of the NH···O=C hydrogen bond. In the previously studied systems this rotation was partly (*N*-methylacetamide[1]) or completely hindered (2-azacyclotridecanone[2]), which led respectively to elongated or linear shapes of the multimers. Therefore, if free rotation of *trans*-amide molecule around the NH···O=C hydrogen bond is possible, one should expect a statistically random conformation of multimers. The present paper is devoted to the discussion of this prediction. A compound appropriate for studies of this problem should be one of the *trans*-formamides ($R_1 = H$). Unfortunately, the results of all hitherto reported studies of formamides show a relatively high amount of cis conformers.[3] As shown below *N*-benzylformamide is an exception to this rule.

Experimental Section

Materials. *N*-Benzylformamide (Aldrich) was purified by three crystallizations from acetone and stored in a vacuum desiccator.

Apparatus. The experimental setup was described in the previous paper of this series.[2]

Configuration of the –NHCO– Group in N-Benzylformamide Molecules

The literature published hitherto lacks information on the peptide group configuration within the NBF molecule. To determine it we analyzed IR spectra of NBF solutions in CCl_4 within the region of N–H stretching vibrations (3100–3600 cm^{-1}, Figure 1). Two bands corresponding to the non-hydrogen-bonded N–H groups are located within this region: one situated at 3452 cm^{-1}, characteristic of secondary amides with a trans configuration, and another considerably weaker band at 3418 cm^{-1}, characteristic of cis configurations of the CONH group.[4] If the intrinsic intensity ϵ is assumed to be the same for the nonbonded ν_{NH} peaks of both isomers,[3,5] the intensity ratio of these bands allows us to estimate the percentage of trans and cis isomers. Since the studied bands and the band of the associated N–H groups overlap, the spectra had to be deconvoluted into components. The simple

graphical deconvolution was carried out at an amide concentration of about 0.02 M, i.e., for a relatively small intensity of the band at ~3300 cm^{-1} (solid line in Figure 1). This procedure revealed that at 30 °C only 7 ± 2% of the NBF monomers (I) have the cis configuration.

I, 7% cis　　　　II, 35% cis
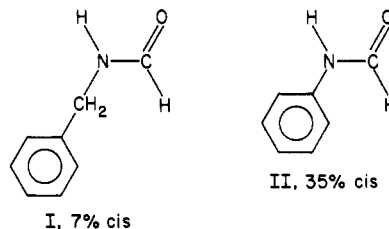
Our result agrees with some previous conclusions that the contribution of the cis configuration in the secondary amides essentially depends on repulsive interactions between the carbonyl oxygen of amide and the nitrogen substituent. For example, in formanilide (II), in which these interactions are considerable, the contribution of the cis form amounts to 35%.[6] In NBF, removing the benzene ring from the carbonyl oxygen by inserting a methylene group –CH_2– diminishes these interactions and causes the contribution of the cis form to be only about 7%.

Thermodynamic Model of NBF Self-Association

Though the trans–cis equilibrium of NBF monomers

$$A_1^{trans} \xrightleftharpoons{K_1} A_1^{cis}, \quad K_1 = c_1^{cis}/c_1^{trans} \ (= 0.08 \text{ at } 30 \text{ °C}) \quad (1)$$
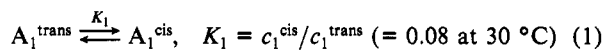
is strongly shifted to the trans form it must be taken into account as a whole in any thermodynamic description of NBF solutions, since even a relatively small amount of cis conformer significantly modifies the first step of association, i.e. the dimerization. Two monomers of any conformation can in principle form an open dimer

$$A_1 + A_1 \xrightleftharpoons{K_2} A_{2o} \quad (2)$$

However, as clearly demonstrated in a number of previous studies[7-10] an open dimer composed of two cis monomers will rapidly

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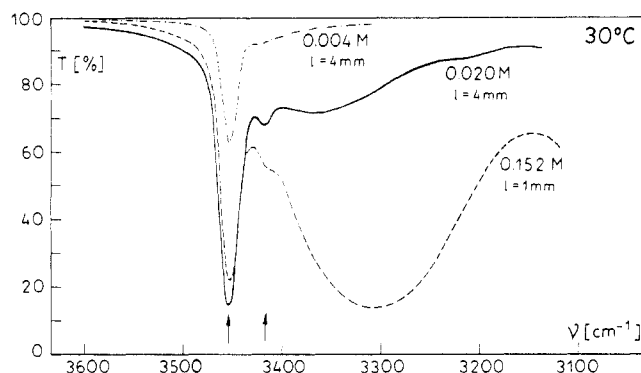
Figure 1. IR spectra of N-benzylformamide in CCl_4 solutions.

transform into a cyclic dimer. As shown below, despite the relatively small amount of cis monomers, the concentration ratio of cyclic to open dimers

$$z_2 = c_{2cy}/c_{2o}, \quad (c_{2o} + c_{2cy} = c_2) \tag{3}$$

amounts to about 0.5 and slightly decreases with increasing temperature. Cyclic dimers are the final product of association, whereas the open ones undergo further chain association:[11]

$$A_i + A_1 \xrightleftharpoons{K} A_{i+1}, \quad i = 2(o), 3, 4, ... \tag{4}$$
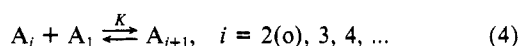
According to eq 2 and 4 the concentrations c_i of successive multimers are related to the equilibrium constants K_2, K and to the concentration c_1 of monomers in the following way:

$$c_{2o} = K_2 c_1^2, \quad c_i = K_2 K^{i-2} c_1^i, \quad i = 3, 4, 5, ... \tag{5}$$

Equations 5 substituted into the mass balance of amide ($\sum ic_i = c$) give the following relation between the concentration of monomers and the equilibrium constants:

$$c_1 + K_2 c_1^2 \left[2z_2 + \frac{2 - Kc_1}{(1 - Kc_1)^2} \right] = c \tag{6}$$

The three equilibrium constants occurring in this equation complicate the problem considerably. However, the z_2 constant can be eliminated if precise dielectric data for highly diluted amide solutions are available.

In case of spherical molecules and nonpolar solvents for both Onsager[12] and Barriol[13,14] models one obtains the following relation between the experimental value of the apparent dipole moment squared and the dipole moments of multimers μ_i and their concentrations c_i:

$$c\mu_{app}^2 = \sum_i c_i \mu_i^2 \tag{7}$$

Differentiating eq 7 in relation to the nominal amide concentration c and taking into account eq 3 and 5 one obtains

$$(\partial\mu_{app}^2/\partial c)_{c=0} = K_2[\mu_{2o}^2 + z_2 \mu_{2cy}^2 - 2\mu_1^2(1 + z_2)] \tag{8}$$

where μ_1, μ_{2o}, and μ_{2cy} denote the dipole moments of monomer, open dimer, and cyclic dimer, respectively. Due to the above relation, eq 6 can be converted into

$$c_1 + $$
$$K_2 c_1^2 \left[2\frac{K_2(\mu_{2o}^2 - 2\mu_1^2) - (\partial\mu_{app}^2/\partial c)_{c=0}}{K_2(2\mu_1^2 - \mu_{2cy}^2)} + \frac{2 - Kc_1}{(1 - Kc_1)^2} \right] = c \tag{9}$$

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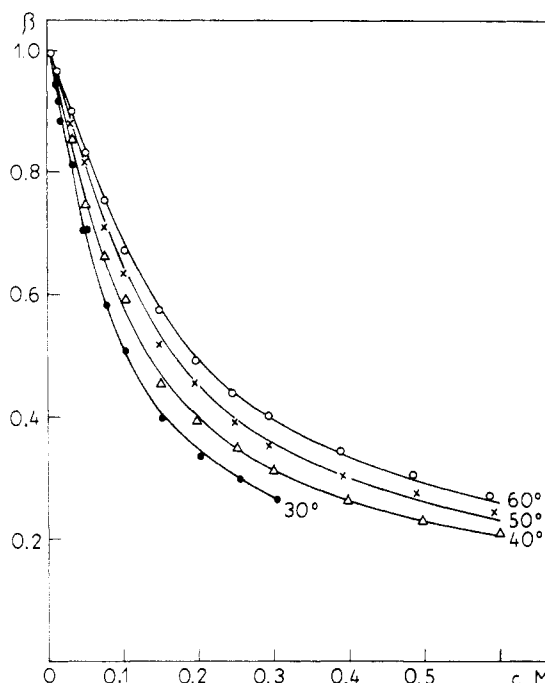

Figure 2. Dependence of $\beta = \epsilon^{max}/\epsilon_\infty^{max}$ (band at 3452 cm⁻¹) on N-benzylformamide concentration in CCl_4. Solid lines represent the theoretical dependences (eq 9 and 11).

where the z_2 equilibrium constant is eliminated.

The equilibrium constants K_2 and K were determined on the basis of IR studies. We analyzed the absorption band situated at 3452 cm⁻¹ corresponding to N–H groups of trans monomers and terminal trans groups of multimers. The extinction of this band

$$A = \epsilon^{NH\ trans}(c_1^{trans} + c_{2o}^{trans} + c_3^{trans} + ...)l$$

where c_i^{trans} ($i = 1, 2(o), 3, ...$) denotes the concentration of i-mers with the free terminal N–H group in the trans configuration. Therefore, the molar extinction coefficient $\epsilon^{max} = A/cl$ measured at the band maximum is related to concentrations of the successive multimers in the following way:

$$\epsilon^{max} = \epsilon^{NH\ trans}(c_1^{trans} + c_{2o}^{trans} + c_3^{trans} + ...)/c$$

For infinitely diluted solutions the value of the molar extinction coefficient is given by $\epsilon_\infty^{max} = \epsilon^{NH\ trans}/(1 + K_1)$ (since $c_1 = c_1^{trans} + c_1^{cis}$) and

$$\beta = \frac{\epsilon^{max}}{\epsilon_\infty^{max}} = \frac{c_1^{trans} + c_{2o}^{trans} + c_3^{trans} + ...}{c/(1 + K_1)} \tag{10}$$

From eq 1 the concentration c_1^{trans} can be expressed by $c_1^{trans} = c_1/(1 + K_1)$. If one assumes that the cis–trans distribution of the end molecules in the multimers is the same as in the monomers, the concentrations c_i^{trans} can be expressed as $c_i^{trans} = c_i/(1 + K_1)$, $i = 2(o), 3, 4, ...$. These relations together with eq 5 give

$$\beta = \frac{c_1}{c}\left(1 + \frac{K_2 c_1}{1 - Kc_1} \right) \tag{11}$$

While fitting the theoretical $\beta(c)$ dependence given by eq 11 and 9 to the experimental data only two parameters K_2 and K need to be varied. The values of K_2 and K obtained from the fitting procedure using the least-squares method (Figure 2) are presented in Table I. The table contains also the experimental values of the slope $(\partial\mu_{app}^2/\partial c)_{c=0}$. The value of the dipole moment of the NBF monomers, $\mu_1 = (\mu_{app})_{c=0}$, which we obtained is 3.87 ± 0.04 D, whereas for μ_{2o} we assumed the value obtained for N-methylacetamide dimer, i.e., 7.25 D.

For the cyclic dimers we assumed that the dipole moment equals zero. However, dielectric studies of cyclic dimer systems show that the apparent dipole moment of the cyclic dimer is approx-

TABLE I: Self-Association Equilibrium Constant of *N*-Benzylformamide in CCl$_4$

T, °C	$(\partial\mu_{app}^2/\partial c)_{c=0}$, D^2 M^{-1}	K_2, M^{-1}	K, M^{-1}	$z_2{}^a$
30	18	3.2 ± 0.4	18.8 ± 0.5	0.57 (0.65) ± 0.02
40	17	2.5	14.6	0.53 (0.60)
50	15	1.8	11.7	0.49 (0.54)
60	13	1.7	9.9	0.50 (0.57)

$-\Delta H_2{}^b = 20 \pm 3$ kJ/mol $\quad -\Delta S_2 = 37 \pm 9$ J/(deg mol)
$-\Delta H = 19 \pm 1$ kJ/mol $\quad -\Delta S = 20 \pm 2$ J/(deg mol)

^{a}Calculated from eq 8; values in brackets obtained for $\mu_{2cy} = 0.5\mu_1$. ^{b}The values of ΔH and ΔS were calculated by the van't Hoff method using the equilibrium constants expressed in molar fraction units.

imately equal to half of the monomer dipole moment.[15] These experimental results are often explained as caused by (i) the equilibrium between cyclic and open dimers[8,9] (in this case the dipole moment of cyclic dimers is assumed to be zero) or (ii) the increased atomic polarizability of cyclic dimers.[16] The latter effect cannot be verified on the basis of the dielectric polarization measurements without refraction measurements in the far-infrared region. To check how this effect influences our results we also fitted the $\beta(c)$ dependences for $\mu_{2cy} = 0.5\mu_1$. The values of K_2 and K obtained in this way practically do not differ from those obtained previously. The only significant change concerns the z_2 value (see Table I).

Conformation of *N*-Benzylformamide Multimers

The values of the apparent dipole moment squared, μ_{app}^2, were determined on the basis of experimental data (electric permittivity, density, and refractive index) by using the Onsager equation. μ_{app}^2 is related to the molecular quantities by eq 7, which for the assumed model of NBF self-association has the following form

$$\mu_{app}^2 = \frac{1}{c}\left(c_1\mu_1^2 + c_{2o}\mu_{2o}^2 + c_{2cy}\mu_{2cy}^2 + \sum_{i=3}c_i\mu_i^2\right) \quad (12)$$
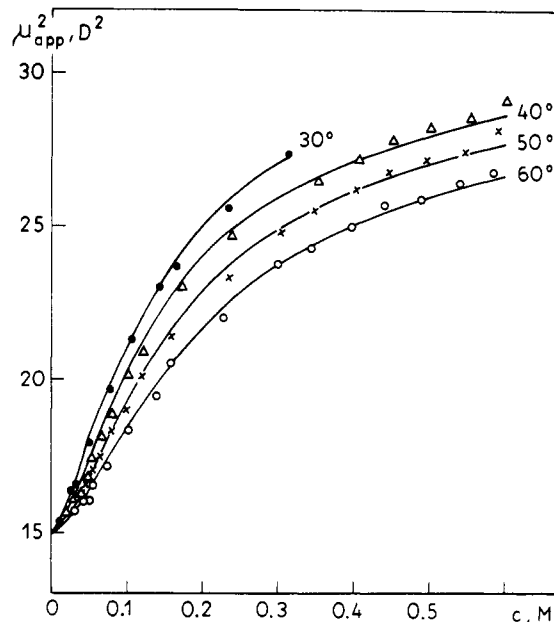
The problem resolves itself to such a fitting of parameters of eq 12 which reproduces the experimental function $\mu_{app}^2(c)$. Since the concentrations of multimers can be calculated from the values of K_2 and K (eq 3, 5, and 9) obtained from IR spectroscopy, the whole problem consists of finding the values of the dipole moments of multimers, i.e. selecting a proper geometrical model of multimers.

Because of the smallest possible size of the carbon substituent ($R_1 = H$), there are no spatial hindrances within NBF chains and free rotation of molecules around the axis of NH···O=C can take place. Therefore, one should assume that the NBF multimers occur in a statistically random conformation, i.e. all random relative orientations of neighbors in relation to the N–H···O=C bond have the same probability of existence. The dipole moments of such chains can be easily calculated with the formula given by Eyring:[17]

$$\mu_n^2 = \sum_{j=1}^n \mu_j^2 + 2\sum_{j=1}^n\sum_{s<j}\mu_j\mu_s\prod_{k=1}^{s+1}\cos\theta_k \quad (13)$$

where μ_j denotes the dipole moment of the jth element of the chain, and θ_k are the angles between the dipole moment vectors of neighboring elements.

In the case of NBF molecules the problem is slightly more complicated since a number of the molecules, however small, have the cis form. This can cause the nonlinearity and bending of chains as well as cyclization of their ends. This effect reduces the values of the dipole moments of multimers in relation to multimers built exclusively from trans molecules. Since obtaining a precise quantitative evaluation of this effect is a rather difficult task, we

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Figure 3. Dependence of μ_{app}^2 on *N*-benzylformamide concentration in CCl$_4$. Solid lines represent the theoretical dependences (eq 12).
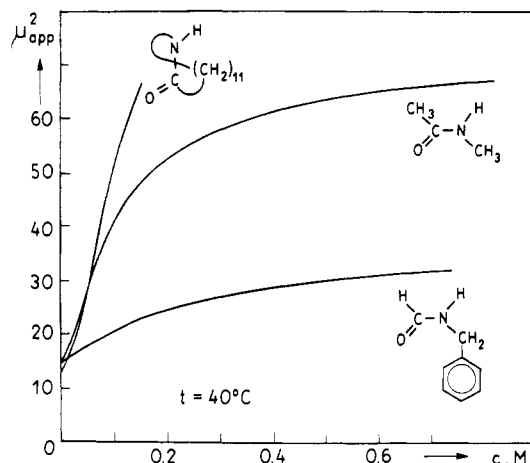
Figure 4. Comparison of $\mu_{app}^2(c)$ dependences for three *trans*-amides in CCl$_4$ solutions.

TABLE II: Thermodynamic Parameters for the Self-Association Processes of the Three *trans*-Amides *N*-Methylacetamide (NMA), 2-Azacyclotridecanone (2-ACT), and *N*-Benzylformamide (NBF) in CCl$_4$

T, °C	NMA[1] K_2, M^{-1}	NMA[1] K, M^{-1}	2-ACT[2] K_2, M^{-1}	2-ACT[2] K, M^{-1}	NBF K_2, M^{-1}	NBF K, M^{-1}
20	5.3	40	7.5	48.1		
30	4.0	31			3.2	18.8
40	3.1	25	5.1	22.1	2.5	14.6
50	2.9	20			1.8	11.7
60			2.7	14.3	1.7	9.9
$-\Delta H_2$, kJ/mol	18 ± 3		25		20	
$-\Delta S_2$, J/(mol deg)	25 ± 8		51		37	
$-\Delta H$, kJ/mol	19 ± 1		25		19	
$-\Delta S$, J/(mol deg)	15 ± 4		33		20	

have made some simplifying assumptions. We calculated the dipole moments of successive multimers (eq 13) assuming that all NBF molecules have a trans configuration (μ_i^{trans}). A comparison of the calculated $\mu_{app}^2(c)$ dependence with its experimental values shows that the latter are slightly smaller. A good fitting at all temperatures (solid lines in Figure 3) has been achieved for $\mu_i = 0.84\mu_i^{trans}$. This result reflects the presence of a few percent of the NBF cis conformers.

Fairly good reproduction of the experimental dependences of μ_{app}^2 and β on concentration and temperature obtained over the

whole studied range of NBF concentrations supports the pertinence of the chosen thermodynamic model of self-association and the assumed structure of NBF multimers.

Conclusions

In the present and two preceding papers we described the results of our extensive study of N-methylacetamide,[1] 2-azacyclotridecanone,[2] and N-benzylformamide in carbon tetrachloride solutions. The three amides manifest some strong similarities: (i) the peptide groups –NHCO– are in the trans configuration, (ii) the values of the dipole moments of their monomers are almost identical (3.8 ± 0.1 D), (iii) the equilibrium constants and the thermodynamic parameters (ΔH and ΔS) are close to each other (Table II). On the basis of spectroscopic (and calorimetric) studies one can conclude that in all three cases the self-association process proceeds in a quite similar way. No further information, beside the chain character of the association, can be gained from these methods.

In dielectric studies these three amides differ considerably (Figure 4). Because of the common features listed above, the observed differences in the μ_{app}^2 dependences on concentration must result exclusively from the various polarity of the formed multimers, i.e., from their different structure. We have shown how the size of the peptide group substituents is decisive for association as it determines the rotational freedom of some particular elements of the multimer chain. In multimers of 2-azacyclotridecanone large spatial hindrances practically inhibit the rotation around hydrogen bonds, and therefore their structure is "rigid" and linear. In the case of N-benzylformamide, due to free rotation, the multimers have a statistically random conformation, whereas N-methylacetamide makes an intermediate case in which the multimers have an elongated shape.

Direct Observation of Droplet Structure in a Vitrified Microemulsion

E. A. Hildebrand, I. R. McKinnon,* and D. R. MacFarlane

Department of Chemistry, Monash University, Clayton, Victoria, Australia 3168 (Received: May 20, 1985; In Final Form: January 8, 1986)

The recent development of glass forming microemulsions has opened the way to direct probing of their structure using electron microscopic techniques without the danger of the structure being modified by crystallization. In this work electron micrographs obtained after vitrification and fracturing of the sample are compared with those obtained by normal cold stage electron microscopy.

Introduction

Several years ago it was reported[1,2] that glass-forming microemulsions could be prepared by choosing a co-surfactant component of the microemulsion which would also act to inhibit the nucleation and growth of ice in the oil-in-water microemulsion when the temperature was lowered below 273 K. In the cases studied to date this co-surfactant component has always been propane-1,2-diol (propylene glycol, PG), although there is no reason to expect that other simple polyols would not act similarly. Propylene glycol is known[1] to render aqueous solutions glass forming at concentrations in excess of 12 mol % PG. As long as the dispersed oil phase is glass forming and provided that there is no lower temperature phase instability with respect to a two-phase mixture the microemulsion as a whole can be vitrified. No such phase separation has been observed in the PG-based systems studied to date. For example, a sample cooled quite slowly was obtained in vitrified form without any increase in turbidity,[2] and a H$_2$O/PG/Tween 80/CCl$_4$ (Tween 80 = polyoxyethylenesorbitan monooleate) microemulsion has been reported as stable to at least -90 °C for a number of hours.[3] However, at temperatures near the glass transition temperature, T_g, of the higher T_g component, kinetic slowing down of equilibration processes could inhibit any thermodynamically expected phase change.

The discovery of these microemulsion systems has opened up the important possibilities that the microemulsion structure can now be captured and studied by a variety of techniques including electron microscopy, small angle scattering, both neutron and X-ray, and NMR.

A recent article[4] in this Journal reported the vitrification in glassy microemulsion of three molecular liquids (CS$_2$, benzene, and CCl$_4$) which had not previously been vitrified and which, on the basis of bulk glass-forming trends, would not be expected to vitrify. The glass transition temperatures (an isostructural relaxation time point) for these liquids were as expected on the basis of extrapolations from binary solution T_g data, thus indicating that the microemulsion droplets exhibit largely unaltered relaxation properties with respect to their bulk liquids. Also reported were electron micrographs of the quenched microemulsions. These clearly indicated a simple droplet structure. At higher droplet concentrations there was an apparent hexagonal ordering of the droplets in the matrix phase. The electron micrographs just described were obtained by the quenching of a thin ($\sim$0.1 μm) film of the microemulsion on an electron microscope sample screen. It is possible that the ordering observed was the result of surface forces acting on the thin film. Also, because the samples were diluted with water before freezing the compositions studied were not those of the finger region of the pseudoternary phase diagram.

In this note we report a series of electron microscope experiments in the finger region of the pseudoternary phase diagram of the same system using two types of freeze fracture techniques (described below). These, we believe, have allowed us to obtain micrographs which are truly representative of the bulk microemulsion and avoid any artifacts associated with surface inter-

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