Dielectric Relaxation of Some N, N-Disubstituted Amides

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The dielectric spectrum has been measured between some MHz and 72 GHz for the following 14 pure liquids at 20°C: N, N–Di(methyl-, ethyl-, isopropyl-, butyl-, isobutyl) formamide, 1-formylpiperidine, N–methylformanilide, N, N–di(methyl-, ethyl-, isopropyl) acetamide, N-acetylcaprolactam, N, N–dimethyl-acrylamide, N, N–dimethylpropionamide, and N, N–diethyl-*m*-toluamide. Moreover, diisobutylformamide and diethyltoluamide have been studied in mixtures with n-hexane over the whole concentration range down to very dilute solutions. The relaxation parameters of all these systems are reported. Particular attention is given to the discussion of the two mixture systems since these exhibit a peculiar concentration dependence of the relaxation strengths of the Debye type spectral components used to describe their spectrum. This behaviour is likely to relate to a flexibility effect which is remarkably intensified on dilution.

1 INTRODUCTION

Dielectric studies of amides have contributed many details to the knowledge of this class of liquids which are of interest for both practical and theoretical reasons. The static as well as the dynamic dielectric properties yield in particular information on the different types of self-association in un-, mono- and disubstituted amides. It is agreed that pair of chainwise association via hydrogen bonds of amino hydrogen to carbonyl oxygen is essential for the dielectric behaviour of un- and monosubstituted amides. Disubstituted amides, on the other hand, are usually regarded as aprotic substances which are unable to form those associations. Nonetheless there are some indications from various experimental studies that in dialkylformamides specific interactions might be possible via the formyl proton as donor.

Concerning the dynamic dielectric properties of disubstituted amides, most work has considered substances consisting of relatively simple molecules, for instance dimethylformamide or dimethylacetamide, especially as these are widely used solvents. Those substances have extensively been studied in their pure liquid state[1-5] as well as diluted in nonpolar media[2,6,7]. Other investigations concern

mixtures of those diamides with water[8-13] or other polar components[14,15] The dynamic dielectric properties of higher members of the diamide family, on the other hand, have not drawn much attention. In the present work we have examined the dielectric relaxation of various diamides, in particular those consisting of larger molecules. Altogether, 14 substances as listed in Tab. 1 were studied as pure liquids. Since dilution with a nonpolar component is often a useful means to elucidate details of the relaxation behaviour, two of these substances, namely diisobutyl-formamide and diethyltoluamide, were additionally studied in mixture series with n-hexane down to very low concentrations.

2   EXPERIMENTAL

A number of different lumped circuit, coaxial and waveguide setups, particularly suited for higher loss liquids, was used for the determination of the complex permittivity, $\varepsilon(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega)$, covering the range between some 10 MHz and 72 GHz by 14 spot frequencies. Dilution series with the nonpolar component hexane could be studied with that intrumentation in the moderate and high concentration range. For very dilute solutions, on the other hand, a WTW dipolemeter for static measurements (ε_s) and a swept frequency apparatus was available which could be utilized for frequencies from 200 MHz to 15 GHz. The measured ε''_{tot} was corrected for the conductivity contribution ε''_c, if significant, to obtain the relaxational contribution $\varepsilon'' = \varepsilon''_{tot} - \varepsilon''_c$. Results have been regarded particularly in terms of that quantity. Errors are estimated to be a few percent in all cases. In addition, refractive index n_D, density ρ and viscosity η were determined. All measurements were performed at 20°C.

Chemicals from Aldrich, Fluka and Merck were used as obtained.

Table 1 Diamides studied in this work.

	$R' - (C=O) - NR''_2$	R'	R''	
1	N,N–Dimethylformamide	H	CH_3	DMFA
2	N,N–Diethylformamide	H	C_2H_5	DEFA
3	N,N–Diisopropylformamide	H	$CH(CH_3)_2$	DiPrFA
4	N,N–Dibutylformamide	H	C_4H_9	DBFA
5	N,N–Diisobutylformamide	H	$CH_2-CH(CH_3)_2$	DiBFA
6	1-Formylpiperidine	H	$(cy)-C_5H_{10}$	ForPi
7	N–Methylformanilide	H	R''(a): CH_3	MForA
			R''(b): ph	
8	N,N–Dimethylacetamide	CH_3	CH_3	DMAA
9	N,N–Diethylacetamide	CH_3	C_2H_5	DEAA
10	N,N–Diisopropylacetamide	CH_3	$CH(CH_3)_2$	DiPrAA
11	N–Acetylcaprolactam	CH_3	$(cy)-C_5H_{10}(C=O)$	ACapL
12	N,N–Dimethylacrylamide	$CH_2=CH_2$	CH_3	DMAcA
13	N,N–Dimethylpropionamide	CH_3CH_2	CH_3	DMPA
14	N,N–Diethyl-m-toluamide	$ph(CH_3)$	C_2H_5	DETA

3 RESULTS

For the amides studied in this work, the Debye function is not sufficient to describe the absorption $\varepsilon''(\omega)$ over the experimental frequency range. Generally a nonsymmetrical broadening (on the log ω scale) towards the high frequency side is observed. We have therefore formally fitted a sum of Debye type spectral components C_i to the data,

$$\varepsilon''(\omega) = \sum S_i \frac{\tau_i \omega}{1 + \tau_i^2 \omega^2} \tag{1}$$

using the minimum number of terms necessary in view of experimental uncertainties. In some cases, two adjacent terms could be replaced by one slightly (symmetrically) broadened term.

The parameters relaxation time τ_i and relaxation strength S_i obtained in that manner for the pure amides are recorded in Tab. 2. For the two substances studied in mixtures with hexane, i.e. DiBFA and DETA, the results are given graphically in Fig. 1. Here, S_i is depicted in normalized form as $S_i c^*/c$, where c is the (molar) amide concentration, the asterisk indicating the pure substance. The dilute solution data for these systems are obtained from concentration series ranging between amide mole fractions $x = 0.0005 \ldots 0.015$ (DiBFA) and $0.002 \ldots 0.025$ (DETA). Only spectral components C_1 and C_2 could be covered in these cases. However, since $S_1 + S_2$ amounts to about 92 (DiBFA) and 85% (DETA) of the static-optical dispersion step (decrement $\Delta(\varepsilon_s - n_D^2)$), it is obvious that higher frequency contributions are of only minor intensity. (With concentrations measured up to 72 GHz, there is $\sum S_i \approx 96$ and 94% of $\varepsilon_s - n_D^2$ for DiBFA and DETA, respectively.)

Table 2 Relaxation parameters τ_i and S_i of pure liquid diamides, 20 °C.

		τ_1 ps	τ_2 ps	τ_3 ps	S_1	S_2	S_3
1	DMFA	11.0	3.5	–	34.2	1.2_5	–
2	DEFA	26.5	3.5	–	24.9_5	0.8_5	–
3	DiPrFA[a]	49^b	3.0	–	17.9	0.8_0	–
4	DBFA	170^b	16.5	–	12.5_5	1.9_5	–
5	DiBFA	170	33.5	7.0	12.6_5	1.7_5	0.6_5
6	ForPi	40	7.0	–	19.9_5	2.1_5	–
7	MForA	210	55	10.5	8.7_5	3.1_0	0.7_0
8	DMAA	17.5	5.5	–	34.5	1.8_5	–
9	DEAA	60	13.5	–	24.4	3.5_5	–
10	DiPrAA	77^b	3.5	–	19.3	1.0_5	–
11	ACapL	195	12.0	–	8.6	1.1_5	–
12	DMAcA	28.5	5.0	–	29.0	0.8_5	–
13	DMPA	29.0	6.0	–	29.3	0.9_0	–
14	DETA	1065	115	10.5	13.8_5	1.0_0	0.6_5

[a] Additional low frequency contribution with $\tau \approx 1000$ ps, $S \approx 0.3$.
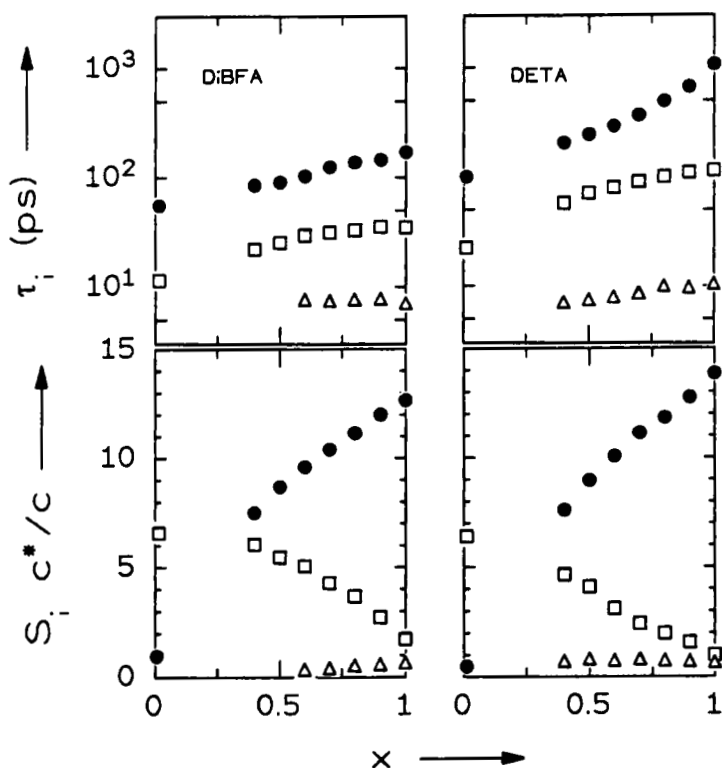[b] Slightly broadened term: Cole-Cole parameter $\alpha = 0.04$.

Figure 1 Relaxation parameters τ_i and S_i (normalized as $S_i c^*/c$) of DiBFA and DETA in n-hexane against mole fraction x of the amide. Symbols for spectral components: ● C_1, □ C_2, △ C_3.

4 DISCUSSION

4.1 *DiBFA and DETA Mixture Series with n-Hexane*

It seems worthwhile to regard these systems in the first place since the variation of parameters with amide concentration may lead to an interpretation of the relaxation behaviour which possibly is applicable to the other substances, too.

As a striking feature it may be mentioned at the beginning that the apparent dipole moment per molecule, μ_{app}, as calculated according to the Onsager relation from ε_s and $\varepsilon_\infty = n_D^2$, changes only little with concentration for both DiBFA and DETA. In the dilute solution limit, the moment is $\mu_{app} = 3.85$ D for both amides, while in the pure liquid limit it is 4.15 D and 4.05 D for DiBFA and DETA, respectively. Since the Onsager equation is approximate in character, an alteration of μ_{app} by only a few percent over the whole concentration range may be considered as nearly insignificant. The orientational correlation of molecular moments, if any, is thus weak enough to allow for the assumption that the relaxation behaviour is essentially governed by uncorrelated single molecule motion.

This conclusion is supported by the following consideration. From a wealth of experimental relaxation data on quasi-rigid polar molecules, which do not exhibit specific interactions but relax uncorrelated via their tumbling motion, it is known that there is a rough correlation of relaxation time, molecular size and viscosity [16]. This can be formulated as

$$\tau = \tau_0 \left(\frac{\eta}{\eta_0}\right)^{(r_{eff}/r_0)\ k_0} \tag{2}$$

The 'effective' radius r_{eff} characterizing the molecular size is the minimum radius of a sphere around the center of mass enclosing the most distant atomic sphere in a space filling model. The quantities indexed '0' are obtained empirically[16]. In order to check whether the relaxation times found with the present mixture series do obey that correlation, τ_1 and τ_2 are plotted against viscosity η in Fig. 2. Also, some lines corresponding to r_{eff} = const in Eq. (2) are included. As the figure shows, the relaxation times τ_1 for both DiBFA and DETA do not only qualitatively exhibit the 'normal' viscosity dependence as expected for single molecule tumbling motion, but agree well with those expectations in quantitative detail, since τ_1 corresponds to
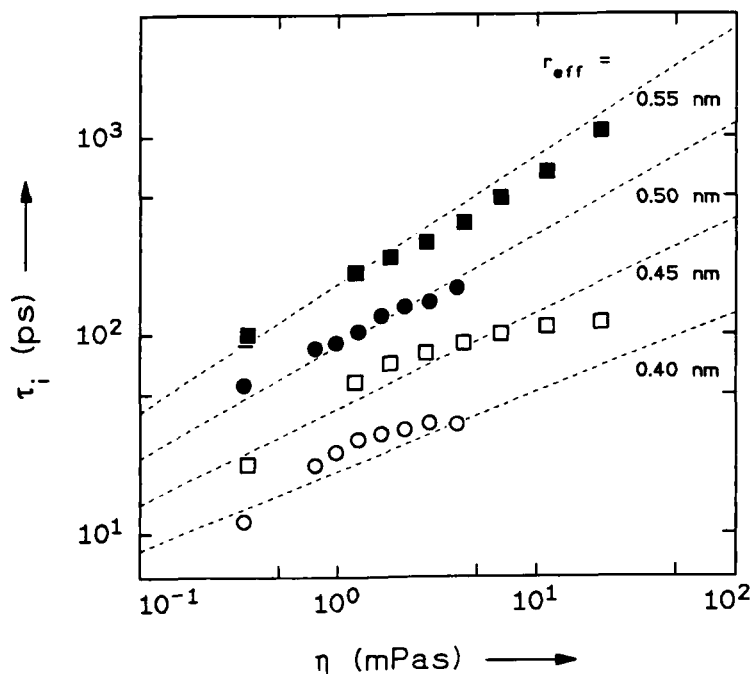

Figure 2 Relaxation times τ_1 and τ_2 of DiBFA and DETA in hexane mixtures against viscosity η. DiBFA: ● τ_1, ○ τ_2. DETA: ■ τ_1, □ τ_2. The straight lines represent Eq. (2).

reasonable r_{eff} values. The relaxation time τ_2, on the other hand, is inconsistent with Eq. (2) for two reasons. First, at higher concentrations (in Fig. 2, at higher viscosities) it is practically independent of viscosity. Second, even taking into account the scatter of data underlying the correlation Eq. (2), the effective radii corresponding to τ_2 are, on average, too small to be reconciled with models of the respective amide molecules.

At this point it should be emphasized that the normalized relaxation strength $S_2 c^*/c$ (Fig. 1) increases considerably on dilution, so that C_2 becomes the dominating spectral component in the dilute solution region. It is therefore desirable to get a physical assignment of that, so far only formally obtained, component.

Let us consider the possibility that not only C_1 but also C_2 (as, eventually, higher contributions) may be related to rotational tumbling of whole molecules, arising from the *anisotropy* of that motion. This seems conceivable in view of the non-symmetrical structure of the molecules DiBFA and DETA. For the classical semimicroscopic molecule-in-continuum model which regards tumbling entities of ellipsoidal shape, three different relaxation times are expected[17,18]. Also for more irregular shapes, as in the present cases, it seems reasonable to invoke three elementary processes according to the tumbling motion around the three principal axes of the moment of inertia tensor Θ. As a simplification, permissible for the frequency range of the present study, each of these processes may be assumed to lead to Debye type dielectric behaviour. Qualitatively, the relaxation time τ_i related to the reorientation of moment component μ_i (referring to the moment of inertia system) will vary as the two eigenvalues Θ_j, Θ_k with $j, k \neq i$. An even rough determination of Θ may therefore allow to estimate whether or not distinguishable relaxation times can be expected. If the tumbling steps around the different axes are uncorrelated, the relative weight of the relaxation strength S_i, associated with the motion of moment component μ_i, is u_i^2, where $\vec{u}$ is the unit vector indicating the moment direction.

Within that framework, one may tentatively regard the amide molecules as *rigid* entities, assuming moreover that the experimentally found concentration dependence of the ratio S_1/S_2 originates in *conformational changes*. We have therefore considered two somewhat arbitrarily chosen configurations of each molecule, one as compact (i) and the other as elongated (ii) as sterically possible, and using standard bond lengths and angles we have calculated their moment of inertia tensor Θ (for simplicity neglecting the hydrogen masses). These assumed conformations are shown in Fig. 3. The eigenvalues $\Theta_{a, b, c}$ are recorded in Tab. 3, where the principal axes a, b, c correspond, in that order, to decreasing Θ_i. The dipole moment of the amide group can be assumed to be approximately parallel to the O-N-direction. That direction is characterized by the unit vector $\vec{u}$ the squared components of which are also given in the table.

According to this model, the shortest relaxation time for DiBFA will be τ_a. The weight of this contribution varies between $u_a^2 = 0.030...0.167$ on changing conformation. This is insufficient to account for the observed variation of $S_2 c^*/c$. For DETA, one expects that roughly $\tau_a \approx \tau_b \ll \tau_c$. Here, the contribution with the *longest* relaxation time is that of minor intensity, $u_c^2 = 0.045 ... 0.133$ for the two conformations. Again this is inconsistent with the experimental concentration dependence of $S_1 c^*/c$ and $S_2 c^*/c$.
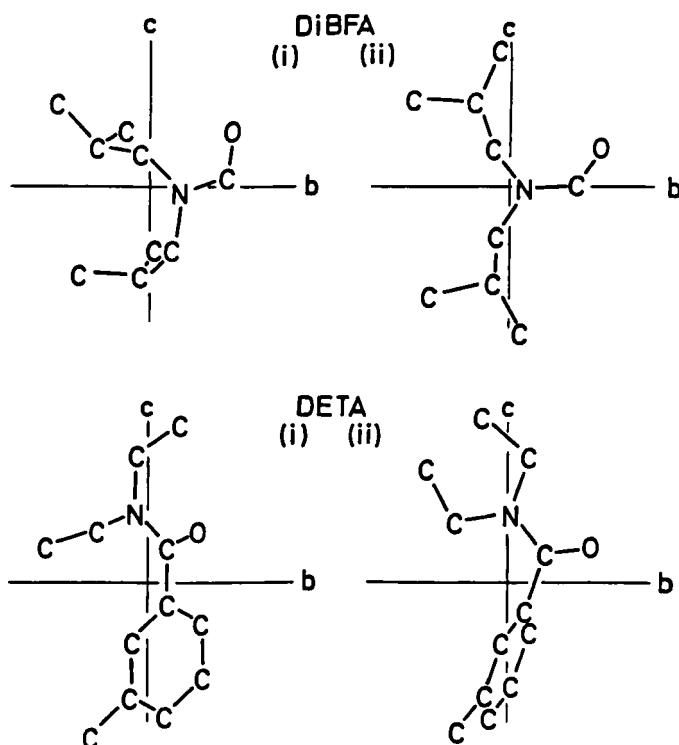
Figure 3 Conformations of DiBFA and DETA as considered in the text.

Table 3 Model parameters for different conformations of DiBFA and DETA. Eigenvalues Θ_i of the moment of inertia tensor (neglecting H atoms)[†], and squared components u_i^2 of a unit vector in dipole moment direction. Reference system: Moment of inertia principal axes a, b, c.

	Θ_a	Θ_b	Θ_c	u_a^2	u_b^2	u_c^2
DiBFA(i)	549	388	327	0.167	0.320	0.513
DiBFA(ii)	843	624	263	0.030	0.729	0.241
DETA(i)	1122	1030	321	0.465	0.490	0.045
DETA(ii)	1192	1133	308	0.052	0.815	0.133

[†]In units of $10^{-23}\,\mathrm{kgm^2}/N_A\,\mathrm{mol}$.

We conclude that the occurence of higher spectral components, and in particular their concentration dependence, can hardly be explained by the assumption of anisotropic motion of quasi-rigid molecules and conformational changes. This is in accord with the above-mentioned conjecture concerning τ_2 and the corresponding r_{eff}. Consequently one has to invoke *internal* mobility as contributing to C_2 (and eventually C_3). Fluctuation of the moment direction due to such a process is feasible in view of the flexibility of the alkyl substituents of both amides and, moreover, of

the possible rotational motion relative to the phenyl ring in DETA. The rotation around the C–N bond of the amide group, on the other hand, is rather unlikely to be effective because of the barrier height for that process[19]. An internal stochastic motion occuring in adition to the tumbling motion of the whole molecule, if sufficiently fast, will shorten the resulting relaxation time.

Accordingly, C_1 and C_2 may be ascribed to more rigid and more flexible molecular species, respectively, which are in a concentration dependent equilibrium. The r_{eff} values estimated from Fig. 2 for the tumbling entities causing C_1 indicate a more compact rather than elongated shape of DiBFA as well as DETA. Thus one may speculate as to whether on dilution by hexane more spacious, albeit ill-defined, conformations are developed which then facilitate more extensive internal motion, with the consequence that the faster relaxation contribution C_2 is intensified.

Lastly it should be stressed that a residual higher frequency contribution attributable to the stochastic tumbling of *whole* molecules cannot be ruled out, since also amides without flexible substituents show a slightly broadened absorption curve, e.g. DMFA (Tab. 2; also[3,11]). However, DMFA does not exhibit the peculiar interchange of relaxation strengths of two spectral components as found with the dilution series of DiBFA and DETA. This is seen from comparison of a dilute mesitylene solution of DMFA with the pure liquid, which both have practically the same viscosity ($\eta = 0.85$ mPas). The spectral component C_1 is found dominating for the dilute system as for the pure liquid, with $\tau_1 = 12$ ps[20], which nearly equals the pure liquid value. It follows that in this case there is no 'anomalous' behaviour on dilution.

4.2 Pure Amides

The relaxation behaviour of the pure liquids may sufficiently be discussed with respect to the interpretation of the dominating spectral component C_1.

Using the correlation Eq. (2), one estimates effective radii r_{eff} from the main relaxation time τ_1 which in all cases agree fairly well with model dimensions of the respective molecules. Just as for DiBFA and DETA, C_1 can therefore be attributed to the tumbling motion of single molecules for the other diamides studied, too. Consequently association effects need not be taken into consideration . Dimers have been discussed e.g. for pure DMFA[21]. If they should be long-lived on the time scale of the present experiments, they should contribute to dielectric absorption at *lower* frequencies than the single molecule contribution C_1. Nothing of that kind could be evidenced, except perhaps in the case of DiPrFA (Tab. 2) were a significant, though very weak, lower frequency contribution is found. This may point to specific interactions via the formyl proton as suggested by some workers[22] but considered questionable by others[23].

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