On the Assessment of Dielectric Relaxation Parameters of Liquids

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In an attempt to outline roughly the "normal" dielectric relaxation behaviour of polar liquids as a reference for the investigation of more complex (e.g. associating) systems, some theoretical considerations and experimental results (mainly on two component mixtures) are presented. They show that for a distinct spectral component a simple equation can be used which approximately relates the relaxation strength to the moment of the relaxing moiety. The rotational relaxation time is practically not affected by the static permittivity but is correlated to the molecular size and the macroscopic viscosity, thus allowing for conclusions on the effective radius of the tumbling moieties.

0. Introduction

Dielectric relaxation is a many particle phenomenon and as such a suitable tool to get insight into specific molecular interactions in polar liquids, as, for example, leading to the formation of "associates" or other molecular aggregates. Relaxation time, as dynamical parameter, and relaxation strength, as structural or geometrical parameter (since related to a mean squared moment) describe the behaviour of certain relaxing moieties or "relaxators", which generally will consist of a number of molecules correlated by short range interactions. It is just the nature of these relaxing moieties which one wants to elucidate. Their definition is, of course, somewhat arbitrary, since there is no sharp dividing line between general physical and specific interactions such as hydrogen bonding or charge transfer.

The assessment of the experimental relaxation parameters requires an at least vague knowledge of the "normal" dielectric behaviour of a polar liquid, as occurring when specific molecular interactions are absent and only "normal", including dipolar interactions are operative. In that case it might be reasonable to regard single molecules as relaxing moieties. Any assessment is thus connected to the question as to how parameters obtained from a macroscopic sample are to be related to the dynamical and structural circumstances on the microscopic scale. The work of two generations of theoreticians has shed light on the macro-micro relationships. For the experimentalist, however, the sometimes confusing variety of theoretical results can be an obstacle to a naive and straightforward interpretation of his results. The following may serve as an illustrative example for that. With a view to extract the microscopic relaxation time ${}^{\mathrm{RM}}\tau$ of a relaxating moiety from the experimentally obtained, macroscopic quantity τ, different expressions for the ratio $\theta = \tau / {}^{\mathrm{RM}}\tau$ can be found. Several widely accepted theories yield results of the type of the Fatuzzo-Mason equation [1, 2] and from that give [3]

$$\theta \gtrsim 1 . \tag{1}$$

Powles [4] and Glarum [5] introduced the relation

$$\theta = \frac{3\,\varepsilon_\mathrm{s}}{2\,\varepsilon_\mathrm{s} + \varepsilon_\infty} \tag{2}$$

(ε_s and ε_∞ are the static and extrapolated "optical" permittivity, respectively). Debye's original treatment [6] resulted in

$$\theta = \frac{\varepsilon_\mathrm{s} + 2}{\varepsilon_\infty + 2} , \tag{3}$$

and in some photophysical applications [7–9] a corrected dielectric relaxation time according to

$$\theta = \varepsilon_\mathrm{s} / \varepsilon_\infty \tag{4}$$

is used. Thus, for polar liquids, a wide variety of relaxation time macro-micro ratios is on hand. The situation concerning the relaxation strength is similar.

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It is the aim of the present work to give some arguments in favour of an elementary and rather simple (thus, of course, approximate) interpretation scheme for the "normal" dielectric behaviour of polar liquids, which then can practically serve as a reference in applications of the above mentioned kind. For that purpose, the following questions will be considered. Is there, especially for moderately and highly polar liquids, (i) a perhaps approximate yet practicable way to relate relaxation strength and dipole moment of the relaxing moieties; (ii) an explicite dependence of the macro-micro relaxation time ratio on the static permittivity; (iii) if not, then for the reorientational relaxation time a correlation with viscosity and molecular size as found with polar molecules in nonpolar solvents?

Concerning the first two problems, it seems appropriate to recapitulate briefly the theoretical background, in order to see which relationships are relevant even on a very simple model level, which uses mostly macroscopic pictures and scarcely statistical arguments. Some familiar relationships [10-13] occur in that first part of the work. In the second part, experimental results on a variety of liquid systems are presented which are hoped to get at "normal" behaviour. These examples will demonstrate the applicability of the theoretical results. Concerning the third question, they further will give evidence that a correlation of the supposed kind exists.

1. Some Theoretical Remarks

1.1. Macroscopic Relations

The macroscopic behaviour of a dielectric can be described either by its relaxation function or its susceptibility. The following notation will be used here. On switching off a constant field E_0 at $t=0$, the polarization P relaxes as $P = P_0 R(t)$, where $R(t)$ is the normalized relaxation function; $R(t) \to 0$ for $t \to \infty$. (For $t < 0$, where $P = P_0$, we set $R = 0$.) The Fourier transform of $R(t)$ is denoted by $u(\omega) = v(\omega) - i w(\omega)$. In an oscillating field, the complex amplitudes of field and polarization are related by $P = \chi E$, where instead of the susceptibility $\chi(\omega) = \chi'(\omega) - i\chi''(\omega)$ the permittivity $\varepsilon = 1 + 4\pi\chi$ can be used.

In describing the dielectric as continuum, χ is defined with respect to the field E_{int} inside the sample. On the other hand, considering the sample on the molecular level as an ensemble of discrete entities, one has to refer to the field E_{ext} as generated by true external charges. Then $P = {}^{\text{m}}\chi\, E_{\text{ext}}$, where ${}^{\text{m}}\chi$ is dependent on the sample shape. For a rotational ellipsoid polarized parallel to its axis, there is [14]

$${}^{\text{m}}\chi = \frac{\chi}{1 + 4\pi f \chi}\,. \tag{5}$$

The shape factor f varies between 0 and 1 and is $f = 1/3$ for a sphere.

We understand E_{int} to be the relevant reference field and χ the experimentally obtainable parameter. Since linear dielectric behaviour is presupposed, susceptibility and relaxation spectrum are related by

$$\chi(\omega) = \chi(0)\,[1 - i\,\omega\, u(\omega)]\,. \tag{6}$$

An equilibrium characteristic are the dipole moment fluctuations of the total sample. They may be characterized by the (extensive) autocorrelation function $\Psi(t) = \langle M_z(0)\, M_z(t)\rangle$ or its Fourier transform $z(\omega)$, which is the power spectral density of the moment fluctuations. It is related to the susceptibility by [15-17]

$$\chi''(\omega) = \frac{\omega\, z(\omega)}{2kTV}\,. \tag{7}$$

With the normalized spectrum $\zeta(\omega) = z(\omega)/2\langle M_z^2\rangle$, this may be written in factorized form as

$$\chi''(\omega) = \chi(0)\cdot\omega\,\zeta(\omega)\,, \tag{8}$$

where the first, structural factor

$$\chi(0) = \frac{\langle M_z^2\rangle}{kTV}\,, \tag{9}$$

depends only on spatial variables, while time appears only in the second, dynamical factor. By (8), the relaxation behaviour of an (isotropic) dielectric is definitively described in terms of macroscopic quantities.

1.2. Reduction of the Structural Factor to the Microscopic Scale

In order to discuss $\chi(0)$, or ε_s, on the microscopic level, we picture the sample as subdivided into smaller parts by taking several steps. First, regions are regarded which are still large enough to allow for statistically independent moment fluctuations. A representative one of spherical form is considered further. The microscopic level is entered by assuming that the total moment fluctuations of the spherical region originate in fluctuations of distinct relaxing moieties with moments $^{\mathrm{RM}}\boldsymbol{\mu}$. This change of the description mode means that χ is to be replaced by $^{\mathrm{m}}\chi$. Making use of ε_{s}, the result becomes

$$\frac{\varepsilon_{\mathrm{s}}-1}{\varepsilon_{\mathrm{s}}+2}=\frac{4\pi}{3}\,\frac{\langle(\Sigma\,{}^{\mathrm{RM}}\mu_z)^2\rangle_{\mathrm{SR}}}{kT\,V_{\mathrm{SR}}}\,, \tag{10}$$

where SR indicates the spherical region.

Note that the change of the description mode is accompanied by a *formal* alteration of the relaxation time just according to the Debye ratio (3). However, since we consider the spherical region in the usual manner [18, 19] as embedded in its own medium and adhere to E_{int} of the total sample as reference field, the altered relaxation time is physically meaningless, and a macro-micro discrimination of relaxation times is not yet needed.

In the second reduction step, one must take into account the mutual interactions between the relaxing moieties. Formally, they will be expressed by a factor F, which deviates from unity as a consequence of spatial correlations due to long-range interactions, in particular dipole-dipole interactions. With

$$S_0=\frac{4\pi N_{\mathrm{A}}}{3kT}\,{}^{\mathrm{RM}}c\,\langle{}^{\mathrm{RM}}\mu^2\rangle, \tag{11}$$

(10) gives thus the general [20] result

$$\frac{\varepsilon_{\mathrm{s}}-1}{\varepsilon_{\mathrm{s}}+2}=\frac{1}{3}\,F S_0\,. \tag{12}$$

In the special case of moieties with only permanent moments, that is only reorientational relaxation contributions, one obtains by singling out one representative moiety ($i=1$)

$$F=\frac{{}^{\mathrm{RM}}\boldsymbol{\mu}_1\cdot\langle\Sigma_j\,{}^{\mathrm{RM}}\boldsymbol{\mu}_j\rangle}{{}^{\mathrm{RM}}\mu^2}\,. \tag{13}$$

The distinct contribution ($j \neq 1$) is conventionally regarded in a semi-macroscopic approximation which pictures the influence of the neighbours by supposing a continuum shell with the bulk susceptibility around the chosen moiety. By this, the moment of the moiety appears to be screened, and the screening factor equals F. If the shell is assumed to be of spherical form with a concentric cavity (Onsager [21], Kirkwood [22], Fröhlich [10]), one obtains

$$F=\frac{9\,\varepsilon_{\mathrm{s}}}{(\varepsilon_{\mathrm{s}}+2)(2\,\varepsilon_{\mathrm{s}}+1)}\,. \tag{14}$$

The assumption of an abstract point dipole, on the other hand, allows to imagine the cavity as completely filled with the continuum dielectric. For this immersion model, one obtains

$$F=\frac{3}{\varepsilon_{\mathrm{s}}+2}\,. \tag{15}$$

Non-orientational contributions are to be treated with some modifications, since in (13) the first factor of the numerator will now be affected, too. This is adequately considered by the immersion model. Fast contributions, as in particular due to the polarizability, are usually assumed to be separable from the orientational ones and are comprised in ε_∞, and the quantity of interest is then $\varepsilon_{\mathrm{s}}-\varepsilon_\infty$. Since the screening factor F includes the ε_∞ effect, it is overestimated. Its correction results in the following equations. For the cavity model, one obtains the Onsager equation

$$\varepsilon_{\mathrm{s}}-\varepsilon_\infty=\frac{\varepsilon_{\mathrm{s}}(\varepsilon_\infty+2)^2}{3(2\,\varepsilon_{\mathrm{s}}+\varepsilon_\infty)}\,S_0\,. \tag{16}$$

For the immersion model, it is

$$\varepsilon_{\mathrm{s}}-\varepsilon_\infty=\left(\frac{\varepsilon_\infty+2}{3}\right)^2 S_0\,. \tag{17}$$

Generally, it may happen that already in the "classical" relaxation region a certain non-orientational contribution is observed. In calculating the factor F for that case, one may argue as for the ε_∞ consideration, which means in effect that the immersion model is reasonably applied. Thus (17) is advantageous in being employable for this relaxation type as well; a discrimination of the moment fluctuations according to the underlying mechanisms is not necessary.

1.3. Frequency Dependence of the Permittivity

Expressions for $\varepsilon(\omega)$ are now readily obtained. Referring to the *macroscopic* dynamical behaviour as characterized by $\zeta(\omega)$, (16) or (17) are simply to be combined with (8). For the consideration of the *microscopic* dynamical behaviour, one has to introduce a new frequency factor in order to describe the fluctuation spectrum of the relaxing moieties. Since the relaxation of the total sample is characterized by $\langle M_z^2 \rangle [1 - i\,\omega\, u(\omega)]$, we postulate analogously that $\langle {}^{\mathrm{RM}}\mu_z^2 \rangle [1 - i\,\omega\, {}^{\mathrm{RM}}u(\omega)]$ describes the moieties, where the microscopic relaxation spectrum ${}^{\mathrm{RM}}u(\omega)$ again refers only to the "slow" processes. Thus,

$$\gamma(\omega) = 1 - i\,\omega\, {}^{\mathrm{RM}}u(\omega) \tag{18}$$

is the appropriate frequency factor to be applied to $\langle {}^{\mathrm{RM}}\mu_z^2 \rangle$ or, according to (11), to S_0.

Application of that factor to the right hand side of (16) or (17) and substitution of ε_s by $\varepsilon(\omega)$ now leads to the following relationships. For the cavity model (16), one obtains

$$\varepsilon(\omega) - \varepsilon_\infty = \frac{3\,\varepsilon(\omega)}{2\,\varepsilon(\omega) + \varepsilon_\infty} \left(\frac{\varepsilon_\infty + 2}{3} \right)^2 S_0\, \gamma(\omega), \tag{19}$$

which is the Fatuzzo-Mason equation. It is not separable into equations for ε' and ε''. For the immersion model, on the other hand, separation is possible. Here we get

$$\varepsilon''(\omega) = \left(\frac{\varepsilon_\infty + 2}{3} \right)^2 S_0\, \omega\, {}^{\mathrm{RM}}v(\omega), \tag{20}$$

which differs from the result as obtained for the macroscopic behaviour only in the meaning of the frequency factor. It is

$$\zeta(\omega) = v(\omega) = {}^{\mathrm{RM}}v(\omega) \tag{21}$$

in this model, which means that macroscopic and microscopic relaxation behaviour need not be distinguished.

1.4. Provisional Conclusions

The result (19) of our elementary model considerations has been obtained from more rigorous macroscopic as well as microscopic theories [1, 18, 23–26] and is believed to describe correctly the reorientational relaxation behaviour of single molecules, which means a lower limiting case of relaxing moieties. On the other hand, an interpretation of these moieties as more extended regions shows that (20) becomes, in that sense, an upper limiting case of the employed model.

According to (19), a microscopic relaxation function of exponential form leads to nonexponential macroscopic relaxation. If τ is defined from the maximum of $\varepsilon''(\omega)$, only a weak dependence of τ on ε_s and ε_∞ is found, the ratio $\theta = \tau / {}^{\mathrm{RM}}\tau$ lying in the range of 1.0 to 1.1. Exponential microscopic relaxation, however, yields an $\varepsilon''(\omega)$ curve which is markedly narrowed in comparison to the Debye type even for realistic ε_s and ε_∞ values, and since this not yet has been observed, a nonexponential microscopic relaxation function (steeper at short times) is an inherent requirement in the application of (19). Though thereby the relaxation times become ill defined, the above given estimation may hold. From a practical point of view it is therefore justified to assume that the relaxation times τ and ${}^{\mathrm{RM}}\tau$ are nearly equal and experimentally undistinguishable. With respect to the macro-micro relaxation time ratio, it makes thus no difference whether the cavity or the immersion model is used.

Concerning the relaxation strength, (19) and (20) differ by the internal field factor, which lies between 1 and 3/2, depending on ε_s. An experimental discrimination seems to be difficult, since both equations contain ε_∞, an ill defined quantity which is obtainable only by extrapolation from the "classical" relaxation range. The 3/2 factor in (19) can easily be reproduced by an increased ε_∞ in (20), for instance $\varepsilon_\infty = 2.9$ instead of 2.0 ($\approx n^2$), which would be well within the range of experimental findings.

In view of the above mentioned implications of (19), the limiting equation (20) can thus be considered as a sufficient approximation for practical work.

2. Some Experimental Results on the Relaxation of "Normal" Liquids

2.1. Selection of Exemplary Systems

Candidates for a demonstration of "normal" dielectric behaviour should be looked for among non-associating liquids. Since such a choice does not guarantee the absence of specific effects, we have further made use of the experience that special intermolecular interactions mostly lead to increasing relaxation times, and have chosen those examples from our material which exhibit comparably fast relaxation. With respect to the permittivity effect in question, mixtures were investigated with both polar and nonpolar components. It was tried to have molecules with lower and higher dipole moments, and further to cover a broad viscosity range without changing the temperature.

Since we want to consider the "classical" relaxation region (where inertial effects, collision induced moments and so on can be disregarded), the molecules should not be too small. Rigid ones would of course be preferable, but quasi rigid ones should also be suitable provided hat the relaxation contribution from their inner flexibility is small enough. Several of the chosen molecules belong to that type.

Altogether 14 liquid systems have been examined, the composition of which may be seen from Table 1. Among them there is 2-pyrrolidinone, though it is known to associate [27]; it is, however, suspected to form distinct associates which may behave as additional, independent species. Benzophenone has often been used as example of a bigger rigid molecule [28–38]; a certain flexibility has been reported only recently [39]. The similar molecule diphenylsulfoxide is assumed to be strictly rigid [40].

2.2. *Experimental*

The substances were obtained from Aldrich, Fluka and Merck and were used without further purification. Measurements of the complex permittivity were made at 10 spot frequencies between 20 MHz and 36 GHz at 20 °C. The experimental error is a few percent at all frequencies.

2.3. *Results*

The absorption data (ε'', eventually corrected for the conductivity contribution) were fitted by a sum of Debye type spectral components according to

$$\varepsilon''(\omega) = \sum_i S_i \frac{\omega \tau_i}{1 + \omega^2 \tau_i^2} . \qquad (22)$$

The relaxation parameters τ_i and S_i are presented in Table 1. With one exception, two or three terms are needed. This is in all cases reasonable from physical grounds, according to which Table 1 has been arranged. Apart from the relaxation by overall reorientational motion of single solute molecules, indexed by A2, faster internal motions are observed in some cases (A3 term). The self associates of pyrrolidinone lead to the slow spectral component A1. On the other hand, the second mixture (solvent) components (B), both nitriles, give rise to only one spectral component.

Since the deviations from Debye behaviour are not so pronounced as to resolve the spectral components, the relaxation parameters are uncertain to some extent. Their variability range may best be shown for an extreme example which reveals comparably serious uncertainties since one spectral component is only partly covered by the experimental frequency range, an acetonitrile solution, Table 1, sys. 11, $c = 2.0$ mol/l. Doubtless two spectral components are needed, but within a given uncertainty range of the permittivity data, say 5 percent, *coupled* variations of the parameters are possible within the following utmost limits: $\tau_1 = 18 \rightarrow 35$ ps, $\tau_2 = 4 \rightarrow 7$ ps, $S_1 = 10 \rightarrow 3$, $S_2 = 16 \rightarrow 23$, whereby always $S_1 + S_2 \approx$ const. In a smaller parameter intervall, the resulting curves are practically indistinguishable from each other within the experimental frequency range. Thus the meaning of the parameter sets as formal shorthand description of the results is not affected.

The values in Table 1 represent generally a mean fit. In some cases, however, the results of those fitting runs were preferred which, for a given system, tended to reduce the variations of both S_A/c_A *and* S_B/c_B on changing the mixture ratio. With the present values (except for sys. 11), these ratios are constant within 10 percent.

2.4. *Discussion*

From the foregoing it raises hope that the various liquid systems under consideration should be suitable examples with respect to the problems mentioned in the introduction. They closely meet the requirement to exhibit distinguishable, not merging relaxation contributions from each mixture component. This as well as the approximate S_A/c_A and S_B/c_B constancy (with values as for the respective neat liquids) are indications that specific mutual interactions, if any, do not play a predominant role. We can therefore discuss the relaxation parameters of a given molecule in different environments, the properties of which are substantially determined by

Table 1. Viscosity η, relaxation parameters τ_i and S_i, according to (22), and static permittivity ε_s.

Sys.	Liquid components (A and B)	c_A (mol/l)	η (mPas)	Spectral components ascribed to A						... to B		ε_s
				τ_{A1} (ps)	τ_{A2}	τ_{A3}	S_{A1}	S_{A2}	S_{A3}	τ_B (ps)	S_B	
1	A: N-methylmorpholine (MMo), neat	9.10	0.90		13.2	1.2		1.7_6	0.2			4.1
2	A: N-ethylmorpholine (EMo), neat	7.86	1.07		27.6	6.2		1.6_8	0.4			4.1_5
3	A: N-cyanomorpholine (CMo), neat	9.89	6.14		123	8.5		11.0	1.1			14.3
4	A: N-cyanomorpholine	5.26	1.95		60	11.0		5.7	0.8_5			8.8
	B: benzene (Bz)	6.23	2.54		72	9.2		6.7	0.9			9.8
		7.18	3.16		82	10.0		7.5	1.1			10.8
		8.11	4.14		97	8.6		8.7	1.1			12.0
		9.01	5.38		115	8.4		9.8	1.0_5			13.1
5	A: N-methyl-2-pyrrolidinone (MPy)	5.19	1.12		18.0			13.5				16.3
	B: benzene	7.24	1.35		20.0			19.8				22.3
		8.33	1.49		20.0			23.6				26.2
		9.31	1.62		21.2			26.8				29.6
6	A: N-cyclohexyl-2-pyrrolidinone (CPy)	3.26	1.92		69.0	8.0		8.1	0.6			11.3
	B: benzene	4.44	3.53		95.0	8.0		11.8	0.7			15.3
		4.96	5.18		115.0	8.0		14.0	0.8			17.5
		5.51	7.67		145.0	8.0		15.3	1.0			20.1
7	A: 2-pyrrolidinone (Py)	6.46	2.57	84	11.8		5.3	2.4				10.2
	B: benzene	9.19	5.24	109	15.0		10.5	3.0				16.8
		10.48	7.51	138.5	15.9		13.7	3.9				20.8
		11.79	10.9	177.5	18.5		16.3	4.8				24.7
8	A: N-methylpyrrolidinone	1.97	1.53		18.2			6.9		48.0	16.5	27.0
	B: benzonitrile (BN)	3.99	1.73		19.9			12.5		56.5	11.6	28.3
		6.07	1.85		21.0			18.1		62.0	7.8	29.7
		8.19	1.87		20.6			23.6		82.0	4.0	30.8
9	A: N-cyclohexylpyrrolidinone	1.67	2.22		90.0	8.5		6.5	0.8	45.0	13.5	24.9
	B: benzonitrile	3.05	3.72		105	8.5		10.5	0.6	56.8	8.6	23.9
		4.20	6.01		141	8.5		13.7	0.9	70.3	4.7	23.4
		5.18	8.96		180	8.5		16.1	1.3	84.0	2.2	23.1
10	A: pyrrolidinone	2.05	1.82	66.5	10.0		2.2	2.3		48.0	17.5	25.7
	B: benzonitrile	4.34	2.71	80.0	12.5		5.0	2.9		62.5	13.6	25.4
		6.92	4.53	112	13.5		9.8	3.5		70.0	8.3	25.7
		9.83	8.39	155	15.0		14.3	4.8		95.0	3.8	26.9
11	A: benzophenone (BPh)	1.0	0.50		20.2			2.4		5.3	25.0	32.8
	B: acetonitrile (AN)	1.5	0.58		21.6			4.4		5.5	21.8	31.5
		2.0	0.70		23.5			6.1		5.8	19.0	31.5
12	A: benzophenone B: benzene	2.0	1.34		36			3.0				5.2
13	A: diphenylsulfoxide (DPSO)	1.0	0.53	140	27.3		0.4	3.1		5.4	27.6	34.4
	B: acetonitrile	1.5	0.66	140	30.0		0.6	4.8		5.7	25.1	32.3
		2.0	0.85	180	33.8		0.6	6.8		6.1	21.5	31.5
		2.5	1.11	220	42.0		0.8	7.9		7.7	18.75	30.1
14	A: diphenylsulfoxide B: benzene	2.0	1.73		71			5.1				7.8

the second mixture component. Taking up the introductory questions, we disregard irrelevant problems, e.g. the interpretation of minor additional relaxation contributions, but focus attention on the main spectral components which can be attributed to the rotational relaxation mechanism.

Table 2. Averaged dipole moments $\bar{\mu}$, obtained from (20) using the parameters from Table 1.

Molecule	Sys.	$\bar{\mu}$ (D*)	μ (lit.)
N-methylmorpholine	1	1.3 ± 0.2	(morpholine: 1.5–1.75 [45, 46])
N-ethylmorpholine	2	1.5 ± 0.2	
N-cyanomorpholine	3, 4	3.1 ± 0.3	
N-methyl-2-pyrrolidinone	5, 8	3.9 ± 0.3	3.75–4.1 [47, 48, 68, 69]
N-cyclohexyl-2-pyrrolidinone	6, 9	3.9 ± 0.3	
benzonitrile	8–10	2.9 ± 0.3	3.55–4.3 [48–50, 70]
benzophenone	11, 12	3.1 ± 0.4	2.9–3.2 [29, 31, 51–55]
diphenylsulfoxide	13, 14	4.3 ± 0.4	3.8–4.1 [56–58, 67]

* $1\,D = 3.336 \cdot 10^{-30}$ Cm.

Relaxation Strength

The S parameter of a certain molecule (A or B) is equivalent to $\varepsilon_s - \varepsilon_\infty$, and it remains to be seen how it is related to the molecular dipole moment. For that purpose, the S_{A2} parameter will be considered, eventually together with the small S_{A3} contribution which is due to internal motions. To define the concentration, only substances which are assumed to relax in form of single molecules are to be regarded, thus pyrrolidinone is excluded. Among the B components, only benzonitrile will be taken into consideration, since the relaxation region of acetonitrile is at so high frequencies that its parameters might be too uncertain (a relatively high extrapolated ε_∞ is indicative of the special acetonitrile properties, which have been extensively investigated over a broad frequency band including FIR [41–44]).

It was concluded before that (20) should be suitable to relate moment and relaxation strength. We use that equation to derive moment values from the experimental S, c and ε_∞ values, the latter being extrapolated as $\varepsilon_\infty = \varepsilon_s - \sum S_i$ (for better statistics, also $\sum S_i$ values from further fitting runs, not presented in Table 1, are considered). In view of the above mentioned uncertainties, this can only be a rough calculation. The resulting $\bar{\mu}$ values, as averaged over all mixture ratios, are given in Table 2 together with literature data.

A comparison shows that (20) is applicable at least on an estimation level. Application of (19) would result in smaller $\bar{\mu}$ values. The uncertainties, however, are such that any decision in favour of one or the other equation is impossible. By the way, the results of Table 2 corroborate the assessment of the spectral components and the assumption of independently relaxing components, since the $\bar{\mu}$ values for a certain molecule in different mixtures are found to be roughly the same.

Benzonitrile is the only molecule which exhibits an apparent moment $\bar{\mu}$ which is singnificantly lower than the referecne values. This holds for neat benzonitrile, too. The difference cannot be ascribed to the use of (20). Possibly the extrapolated ε_∞ is still too high, which would mean that a further high frequency relaxation contribution should be taken into account. On the other hand, the benzonitrile concentrations are relatively high, so that the lowering of $\bar{\mu}$ may be indicative of a special structural effect resembling that in acetonitrile.

Relaxation Time

It is common experience from various research methods, e.g. NMR or light scattering, that rotational time constants of single molecules are correlated with the macroscopic shear viscosity. In the field of dielectrics, this corresponds to Debye's early estimation and has been confirmed by numerous experimental results, in particular on dilute solutions of polar substances in nonpolar solvents. Obviously, the viscosity reflects, on the macroscopic level, to a certain degree those molecular interactions which govern the rotational fluctuations. For the present examples, Fig. 1 therefore depicts the relaxation times against viscosity of the liquids.

Let us first recall the question as to whether there is a dependence of the macroscopic relaxation time on the static permittivity. An experimental answer requires the comparison of systems with identical

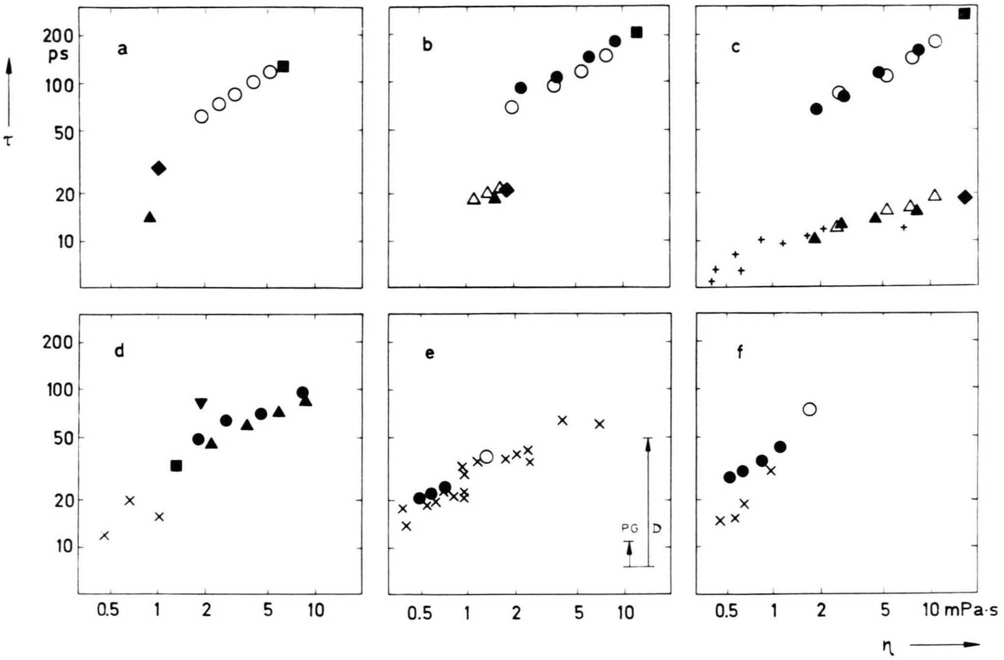

Fig. 1. Log-log plots of relaxation times τ against viscosity η:

a) MMo (▲, sys. 1); EMo (◆, sys. 2); CMo (■ neat, sys. 3; ○ in Bz, sys. 4).
b) MPy (◆ neat [27]; △ in Bz, sys. 5; ▲ in BN, sys. 8); CPy (■ neat [27]; ○ in Bz, sys. 6; ● in BN, sys. 9).
c) Py, spectral components 1 and 2 (■◆ neat [27]; ○△ in Bz, sys. 7; ●▲ in BN, sys. 10). – For comparison: + chlorobenzene, dilute, nonpolar solvents (lit.).
d) BN (■ neat; ▼ in MPy, sys. 8; ▲ in CPy, sys. 9; ● in Py, sys. 10; × dilute, nonpolar solvents, lit.).
e) BPh (● in AN, sys. 11; ○ in Bz, sys. 12; × dilute, nonpolar solvents, lit.).
f) DPSO (● in AN, sys. 13; ○ in Bz, sys. 14; × dilute, nonpolar solvents, lit.).

microscopic relaxation times. We shall presuppose that this case is given for a certain molecule in different environments which, however, yield the same macroscopic viscosity. Then the question remains as to whether, beyond the viscosity effect, an explicite permittivity dependence can be observed.

From our measurements, it is possible to compare the behaviour of pyrrolidinone and its derivatives in the presence of either a polar (benzonitrile) or nonpolar (benzene) mixture component. For benzophenone, which has been studied in many nonpolar solvents, results from the literature [28–38] are taken for comparison with our acetonitrile solutions. Let this example be regarded first (Figure 1 e). The uncertainty range of the relaxation times in acetonitrile is in the same order as the scatter of the reference values, which have been obtained with a wide variety of nonpolar solvents, so that the scatter may reflect special solvent dependent interactions. Nevertheless the overall behaviour is characterized by a good correlation between τ and η. The acetonitrile solution data now fit in the bandwidth of the reference points. Similarly there is no significant difference between the relaxation times of pyrrolidinone type molecules (Fig. 1 b, c) in either benzene or benzonitrile mixtures. It is remarkable that this even holds for the first spectral component of pyrrolidinone, which is due to self associates. These obviously behave as independently relaxing, quasi rigid probe species.

For diphenylsulfoxide (Fig. 1 f), the comparison with the scarce results reported for nonpolar solvents [28, 67] is less satisfactory. The discrepancy may be related to the occurrence of a slow spectral component (A.1) in that case. A discussion of that special feature is, however, beyond the present scope.

Altogether these comparisons allow to state that τ is mainly influenced by microscopic properties which express themselves in the macroscopic viscosity, but that beyond this there is no general

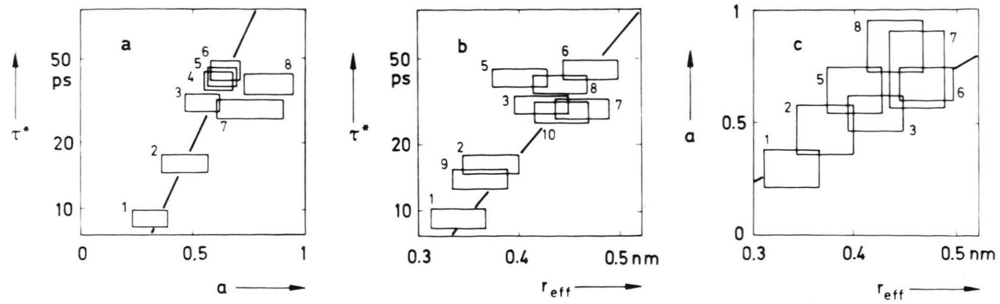

Fig. 2. Correlation between the parameters τ^* and a and the effective molecular radius r_{eff} (1: Py, comp. 2; 2: MPy; 3: BPh; 4: Py, comp. 1; 5: CMo; 6: CPy; 7: BN; 8: DPSO; 9: MMo; 10: EMo).

permittivity dependence of significance. If ε_s should enter according to the Debye ratio (3), this should clearly be observable, and even the Powles-Glarum ratio (2) is unlikely to be realistic, as seen from the expected enhancement of τ, which, for illustration, is shown in Figure 1e. This, at the most, weak dependence of τ on ε_s is in agreement with the theoretical considerations.

The relaxation time depends on the viscosity η approximately as

$$\tau = \tau^* \left(\frac{\eta}{\eta^*}\right)^a , \tag{23}$$

where τ^*, η^* and a are parameters. As reported for various other systems [59–64, 66], we find $a < 1$ (Fig. 1 shows, for the different examples, values of a between 0.25 and nearly 1). Both parameters, τ^* and a, vary parallel; their correlation is shown in Fig. 2a (τ^* is taken for $\eta^* = 1$ mPa s by extrapolation). As a consequence, quite different systems may exhibit the same $\tau - \eta$ dependence. As an additional example for that, the relaxation times of chlorobenzene in various nonpolar solvents are depicted in Fig. 1c, too [30, 36–38, 65, 66]. This molecule is larger indeed but still similar in size to (monomeric) pyrrolidinone, and it happens that both groups of results fit together.

It is plausible that the parameter τ^* reflects qualitatively the molecular size. For a rough comparison, we have estimated the molecular dimensions from Stuart-Briegleb models and, following Hufnagel [63, 64], have regarded the effective molecular radius r_{eff}. Figures 2b, c show that τ^* and a are clearly correlated with r_{eff}. The straight lines which are shown in Fig. 2 merely to indicate the mean correlation behaviour can be put together to a relation of the form

$$\tau = \tau_0 \left(\frac{\eta}{\eta_0}\right)^{(r_{\mathrm{eff}}/r_0 - k_0)} , \tag{24}$$

with the numerical values $\tau_0 = 1.65$ ps, $\eta_0 = 7.17 \cdot 10^{-3}$ mPa · s, $r_0 = 0.40$ nm and $k_0 = 0.50$. This equation describes, within the covered τ and η range, the interrelation between τ, η and r_{eff} fairly well, which means that for given η and r_{eff} it predicts the relaxation time within an octave (factor 2) bandwidth, or allows to estimate r_{eff} with an uncertainty of about 0.05 nm from the experimental τ and η. These findings are in good agreement with Hufnagel's results on dipolar molecules in nonpolar solvents [37, 38, 63, 64]. Thus we get evidence that, regardless whether we consider solutions or mixtures or neat liquids, the viscosity and the molecular size are the predominant parameters which determine by a general rule the relaxation time of distinct moieties in "normal" liquids.

It should be emphasized that there are some exceptions from those consistent results even among the systems of Table 1. With methylpyrrolidinone, benzonitrile (sys. 8) shows a dependence of τ on η which is markedly steeper than in the other cases and thus deviates significantly from the estimation rule (24). Also the deviating dilute solution results [71, 72] indicate that one should reckon with specific effects in the benzonitrile systems. Another exception in some manner, diphenylsulfoxide, has already been mentioned. The cyanomorpholine relaxation times appear to be comparably long in view of its r_{eff}, though beyond this the parameters fit into the scheme very well. These examples may be illustrative in pointing at the increase of relaxation times by special effects. In that sense, the "normal" dielectric behaviour seems to be a limiting case.

2.5. *Conclusions*

We have found that examples exist where a liquid in neat form as well as in mixtures with polar or nonpolar components exhibits a distinct dielectric relaxation behaviour, which can be described (i) concerning the relaxation strength, at least approximately by the relationship (20) between moment and dispersion step; (ii) concerning the relaxation time, by a strong correlation of τ with viscosity and molecular size which equals that found for nonpolar solvents, so that in particular there is no significant dependence on the static permittivity. Such general behaviour may be termed the "normal" one. As seen from the accidental examples, deviations from that behaviour might be considered an indication of specific interactions which then must be clarified for any individual system.

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