On the Occurance of Stereoisomeric Effects in the Dielectric Relaxation Behaviour of Pure Liquids

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In order to find out whether liquids consisting of pure enantiomers of a chiral molecule differ in their dielectric relaxation behaviour from that of corresponding racemic mixtures, the complex permittivity of the following pure substances was measured over a broad frequency range (3 MHz to 72 GHz) at 20 °C: Phenylethylisocyanate, carvone, fenchone, 2-octanol, 2-amino-l-butanol, diethyltartrate and diisopropyltartrate. With the achieved experimental resolution, no stereoisomeric effect could be observed with the exception of the tartrates, where there are clear differences in the low frequency features of the enantiomers as compared to the racemic mixture, which very probably are an association effect.

Key words: Association, dielectric relaxation, liquids, stereoisomers.
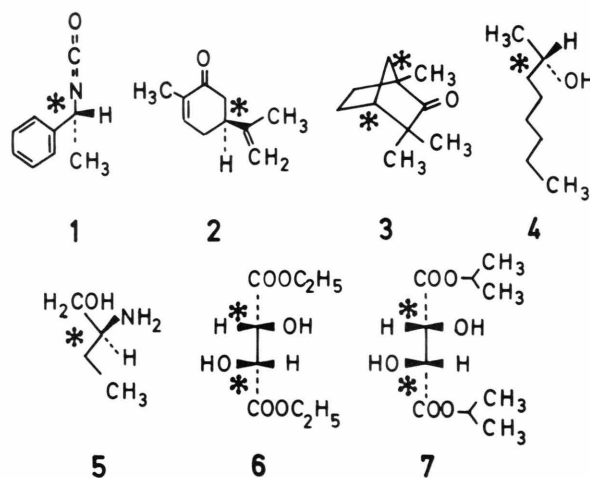
Introduction

Considering a pure liquid consisting of chiral molecules, the structural and dynamic properties should depend to some extent on the mixing ratio of the stereoisomeric forms. In molecular dynamics simulations of liquids consisting of rigid molecules, Evans [1] has found that the autocorrelation functions of several fluctuating physical properties differ for pure left- or right-handed stereoisomers from those of their racemic mixtures. This was ascribed to rotational-translational coupling. Until now, however, there exists only little experimental material concerning that effect [2–4]. It might be illuminating to regard spectroscopic properties which are affected by the rotational tumbling motion of the molecules in the liquid state. Evans and Evans, for that purpose, carried out some FIR measurements [2]. Another related method which may be employed is dielectric relaxation spectroscopy, since in simple cases the "classical" dielectric relaxation spectrum directly reflects the rotational tumbling motion of the molecules.

In a previous paper we reported on results obtained on the chiral molecules cyclohexanone and menthone [4], where in fact a difference in the dielectric relaxation behaviour of one of the stereoisomers and a racemic mixture could be evidenced. The present paper is a continuation of that work. In order to avoid possible errors due to differing purity of the compared liquids, it is advisable to measure both enantiomers and a racemic mixture prepared from just these samples. This could be done since a number of polar, chiral molecules are now commercially available in both enantiomeric forms.

The current paper contains dielectric relaxation results on pure enantiomers and racemic mixtures of seven liquids which differ in their chemical character. These are:

1 R(+)- and S(−)-1-Phenylethylisocyanate,

2 (+)- and (−)-Carvone,

3 (+)- and (−)-Fenchone,

4 S(+)- and R(−)-2-Octanol,

5 S(+)- and R(−)-2-Amino-1-butanol,

6 (2R,3R)(+)- and (2S,3S)(−)-Diethyltartrate,

7 (2R,3R)(+)- and (2S,3S)(−)-Diisopropyltartrate.

The structural formulae represent the (+)-form in any case.

Experimental

Chemicals from Fluka were used as obtained. Phenylethylisocyanate **1** was handled and measured under nitrogen.

For each substance, the complex permittivity of both enantiomers and of their racemic mixture was measured at a number of fixed frequencies in the 3 MHz to 72 GHz range, sufficient to cover the whole absorption region. The temperature was 20 °C.

The experimental uncertainty of the permittivity values is generally a few percent at all frequencies. It is partly due to systematic errors, while the reproducibility is better. Relative permittivity differences in the quoted order can therefore clearly be discriminated by alternating runs under constant conditions.

Results

For a shorthand description of the relaxation behaviour, a sum of Debye type spectral components C_i was fitted to the permittivity results, primarily the

imaginary part ε''. Thus the absorption curve $\varepsilon''(\omega)$, where ε'' is already corrected for the conductivity contribution, is described by

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

The parameters τ_i and S_i, obtained by using the minimum possible number of terms, are given in Table 1. (The table is arranged according to the physical interpretation of the spectral components as regarded in the following, so that the overall relaxational motion of single molecules is always indexed by $i = 3$). Two typical absorption curves, one with negligible and another with noticeable differences between enantiomers and racemic mixture, are shown in Figure 1.

In the case that no significant differences are observed between the results on the enantiomers and on their racemic mixture, the parameter set is given only once in Table 1. Some additional results are included in that table, which will be helpful in discussing the ester behaviour. They concern first mixtures of (racemic) diethyltartrate **6** and diisopropyltartrate **7** with a nonpolar component (mesitylene) and second a nonchiral molecule comparable to **6**, which is similar to the latter but with hydroxyl replaced by hydrogen, namely diethylsuccinate.

Table 1. Relaxation parameters τ_i and S_i of the studied liquids.

Substance	Relaxation time τ_i (ps)					Relaxation strength S_i				
	1	2	3	4	5	1	2	3	4	5
A) Pure liquids, chiral molecules										
1			58		1.7			6.93		1.05
2			80		1.6			10.5		1.00
3			44		2.4			10.0		1.18
4	1127		94	10.5		3.40		1.21	0.17	
5	1520	373	33.3		2.6	6.47	6.62	1.91		0.50
6 (+)		3482	449	28	2.6		8.73	2.19	0.80	0.50
(−)		3482	449	28	2.6		8.73	2.19	0.80	0.50
rac		2964	449	28	2.6		8.34	2.05	0.80	0.50
7 (+)		5647	591	46	2.6		6.18	1.26	0.59	0.28
(−)		5647	591	46	2.6		6.18	1.26	0.59	0.28
rac		5393	591	46	2.6		5.90	1.26	0.59	0.28
B) Liquids for comparison: Pure diethylsuccinate (**S**) and mixtures with mesitylene *										
S			33.3		3.3			2.83		0.50
S (0.87)			29.0		3.3			2.83		0.48
S (0.77)			25.8		3.3			2.35		0.28
6 (0.87)		1827	303	28	2.6		6.47	2.30	0.89	0.29
6 (0.77)		1180	183	21	2.6		4.91	2.14	0.63	0.32
7 (0.87)		2050	210	25	2.6		4.80	1.52	0.32	0.17
7 (0.77)		1324	183	21	2.6		3.81	1.35	0.40	0.20

* Concentration of the (racemic) polar mixture component given as volume fraction in parentheses.
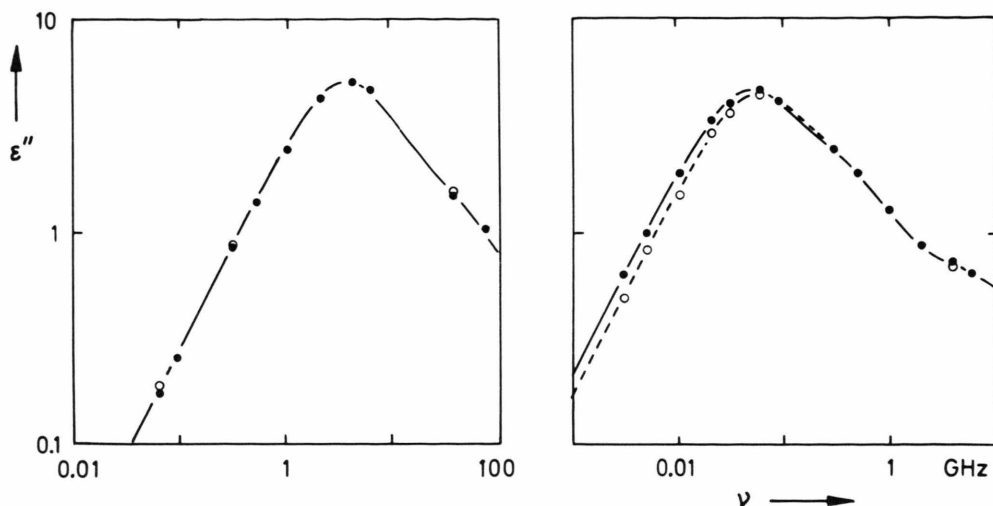
Fig. 1. Log-log plot of two exemplary absorption curves, ε'' versus ν. Left: fenchone **3**; right: diethyltartrate **6**. ●: (+)- and (−)-enantiomer; ○: racemic mixture. Lines represent fits according to Table 1.

Discussion

A main conclusion can readily be drawn from the above results: In the frame of our experimental resolution, significant differences between pure enantiomers and their racemic mixtures are observed only with the two esters (**6** and **7**), thus with molecules which are expected to have a relatively complex relaxation behaviour due to their internal flexibility and their ability to undergo hydrogen bonding. For substances which closer correspond to the model of rigid molecules the differences are obviously too small to be detected in our experiments.

In the following, we shall attempt to further eluci- date that qualitative ascertainment by briefly discus- sing the relaxation behaviour of the various sub- stances with respect to the underlying molecular processes, as far as these are deducible from the relax- ation spectrum. There is a large amount of experimen- tal material which, by comparison, allows a qualita- tive assessment of spectral components, which are often found to be due to distinguishable relaxation mechanisms. Quasi-rigid molecules without specific interactions generally exhibit a "normal" relaxation behaviour in the liquid state, characterized by empiri- cal correlations between the parameters τ_i and S_i of the corresponding spectral component and some mo- lecular and macroscopic properties, in particular the viscosity [5]. Additional spectral components on the high frequency side of the "normal" region can then be

ascribed to faster motions, while additional compo- nents on the low frequency side usually indicate spe- cial effects such as formation of local clusters, general- ly to be regarded as associates.

As seen from Fig. 1, the stereoisomeric effect, if any, concerns only the low frequency side of the absorption curve. Therefore we shall restrict the discussion to that region.

The substances **1** to **3** exhibit an essentially "nor- mal" relaxation behaviour. Their lowest spectral com- ponent, which also is the principal one, can be ascribed to the rotational tumbling motion of single molecules. This is not so for the alcohols (**4, 5**). As is well known, their principal (low frequency) spectral component is due to ill defined associates, and the observed relaxation time is representative of the mean lifetime of a molecule in the associated state rather than a reorientational tumbling time [6]. The prin- cipal spectral component resulting from those fluctua- tions is usually of Debye type, as observed here with 2-octanol (**4**).

For aminobutanol (**5**), however, our analysis yields two Debye type spectral components below the single molecule relaxation region (C_3), which alternatively can be combined and considered as one broadened region, decribable by a relaxation time distribution e.g. after Fröhlich ($\tau_F = 738$ ps, $p = 2.4$). Nevertheless an assessment as for other alcohols is most likely. Contrary to these, a variety of H-bonds is possible with aminobutanol. Like comparable aminoalcohols

[7], already the isolated molecule may probably form an intramolecular H-bond $N \cdots H - O$. In the pure liquid, additional intermolecular bonds of the $N \cdots H - O$ as well as of the $O \cdots H - O$ type are feasible. Those different competing H-bonds may by their fluctuation generate a broadened absorption curve, as observed.

Some more detailed considerations are required for the remaining substances, the esters **6** and **7**, since to our knowledge dielectric relaxation measurements on those and related substances are scarce. As mentioned above, the relaxation time for "normal" relaxation by rotational tumbling of quasi-rigid moieties is, for a given moiety size, correlated to the viscosity of the liquid. In order to use that experience for the assignment of the spectral components, the relaxation times of the lower components obtained for the pure esters and some of their mixtures with the non-polar solvent mesitylene (which are less viscous) are represented in Fig. 2 as a function of viscosity. This figure shows some informative features.

(i) Diethyltartrate and diisopropyltartrate, which only slightly differ in size, show groups of points lying accordingly close to a straight line, the slope of which is consistent with the empirical correlation [5, 8] (dashed lines). This is indicative of rotational tumbling processes as governing the relaxation of all the depicted components.

(ii) Taking into consideration the results on diethylsuccinate, it becomes evident from Fig. 2 that the lowest spectral component of that molecule (C_3) meets the second (again C_3) of the two other esters. Specific interactions of succinate molecules are not to be expected. This assumption is substantiated by the relaxation behaviour of diethylsuccinate in dilute benzene solution [9], which certainly is due to only single molecule motion. There a broadened absorption curve is observed with an unresolved relaxation time of 12 ps or, in terms of (1), a maximum relaxation time of about 20 ps. By extrapolating along the general viscosity dependence, these values are found to be consistent with the succinate results depicted in Figure 2. It follows that C_3 very probably represents a "normal" tumbling motion of single succinate as well as tartrate molecules. Consequently the spectral component C_2 of the tartrates should result from specific interactions which are only operative with these hydroxyl containing molecules, thus probably from hydrogen bonding.

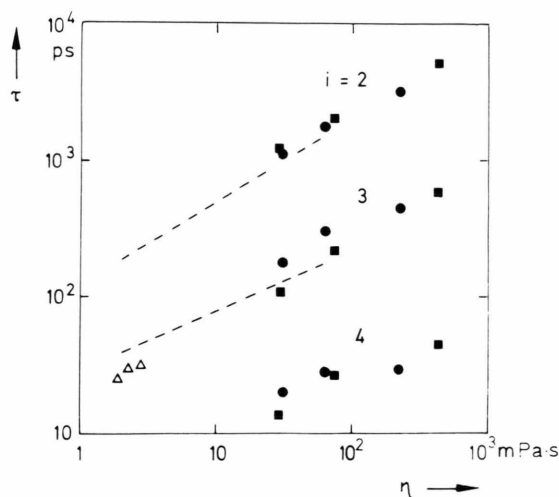(iii) The occurance of a further spectral component C_4, which again behaves "normally", is possibly

Fig. 2. Comparison of results on some (racemic) esters (pure and in mesitylene mixtures) by displaying the relaxation times τ_i of their lower spectral components versus viscosity η (log-log plot). ●: Diethyltartrate **6**, ■: diisopropyltartrate **7**, △: diethylsuccinate. – The dashed lines indicate the "normal" correlation between τ and η for two different sizes of relaxing moieties (above: $r_{eff} = 0.53$ nm, below: $r_{eff} = 0.43$ nm).

caused by the non-spherical shape of the ester molecules. In that case any non-vanishing moment component along an axis of the moment of inertia tensor leads to a corresponding relaxation contribution.

We infer from (i) and (ii) that C_2 of the tartrates is likely to be caused by a long-lived, quasi-rigid associated species. For further comparison, effective radii are given in the legend of Fig. 2 (according to the estimation rule used in [8]). These values, which should serve as estimates only, are consistent not only with the already given assignment of C_3, but also with the assumption that the tumbling moieties causing C_2 are compact tartrate dimers. Thus the low frequency component of the tartrates is very probably a consequence of association, which moreover, in contrast to the alcohols, can roughly be pictured by distinct, long-lived rather than ill defined, elusive associates. We cannot exclude that higher associates occur, too; but these, if any, could only be of the ill defined, short-lived type (lifetime in the order of τ_2).

The spectral component C_2 of the tartrates, as ascribed in this way to their associates, exhibits nearly the same relaxation strength S_2 for the pure enantiomers and for the respective racemic mixtures. Thus one has to reckon with associates built up from equal as well as from antipodal stereoisomers. Conclusions

on the preference of either of these types, however, might be drawn only with caution. The individual S_i values of a four term analysis can be varied to some extent, while their sum, $\sum S_i$, stays constant, so that the latter quantity should be regarded primarily. According to Tab. 1, one finds for the tartrates that $\sum S_i(+) = \sum S_i(-) > \sum S_i (\text{rac})$. The individual S_2 values, though less certain, show a corresponding relation which is likely to be significant as well. Thus it is obvious that associates built up from equal isomers contribute somewhat more strongly to the overall dielectric absorption than those from antipodal ones, as already to be seen from Figure 1. Further conclusions, however, in particular on the ratio of both types of associates, cannot be drawn from merely dielectric results, since S_i does not only depend on the concentration c_i of the respective species but is proportional to $c_i \mu_i^2$, where the apparent moment μ_i is unknown.

Since the only stereoisomeric effect which we were able to detect concerns just the C_2 component of the tartrates, one can now resume that it results from differences in the relaxation behaviour of different associates. In terms of the tumbling motion of the suspected dimers, this means differences in size and shape, depending on the combination of either two equal or two antipodal stereoisomers.

Conclusions

It follows from our results that dynamic stereoisomeric effects in the rotational tumbling motion of molecules in a liquid are too small to be revealed by our dielectric measurements. On the other hand, clear structural effects were detected and may be caused by specific interactions, e. g. in those special liquids where distinct associates occur.

Acknowledgement

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