Dielectric Spectroscopy of Solutions of Some Alkylammonium Salts in Chloroform and 1-Octanol

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Dielectric loss spectra between 1 MHz and 36 GHz have been measured at 20°C for solutions of hexadecyl trimethylammonium bromide and chloride, tetrahexylammonium bromide and tetrabutylammonium bromide in chloroform and 1-octanol (three solutes per solvent) at moderate and high concentrations. The discussion is aimed at identifying relaxation processes involving ions. Describing the relaxational part of the spectra (after subtraction of the conductivity contribution) by a sum of spectral components, the lowest frequency component can be attributed to the solute in all cases. Its concentration dependence is indicative of two ionic relaxation processes differing in physical nature. The solvent is partly involved in those processes; moreover a structure breaking effect is likely to occur in case of the alcoholic solvent. The results are also discussed in comparison with a molten alkylammonium salt and with solutions of this and of inorganic salts.

Key words: Dielectric Relaxation; Electrolyte Solutions; Ionic Aggregation.

1. Introduction

Dielectric spectroscopy is a means to obtain information about liquid electrolytes. Regardless of the physical nature of the underlying microscopic processes, this is contained in only one measurable quantity, that is either the complex conductivity $\kappa(\omega)$ or, equivalently, the complex permittivity $\varepsilon(\omega)$, which are generally related by

$$\varepsilon(\omega) = -\,\mathrm{i}\,\frac{\kappa(\omega)}{\varepsilon_0\,\omega}, \tag{1}$$

where $\omega = 2\pi\nu$ denotes the circular frequency and ε_0 the electric field constant. In the following, the permittivity point of view is adopted as it is common usage in the case of liquid systems.

As a consequence of the fluctuation-dissipation theorem, the negative imaginary part $\varepsilon''_{\text{tot}}(\omega)$ of the measured (total) permittivity spectrum is directly related to the spectral density of polarization fluctuations of the sample. These can result from the stochastic translational motion of ions (monopoles) as well as from the rotational tumbling motion of dipolar entities. If the conductivity relates merely to the classical long range diffusion of ions it keeps its static value κ_s for all frequencies, thus leading to a conductivity contribution to the imaginary part of permittivity,

$$\varepsilon''_c(\omega) = \frac{\kappa_s}{\varepsilon_0\,\omega}, \tag{2}$$

which could be determined by a dc experiment. Deeper insight into dynamic processes is gained by a spectroscopic experiment which measures the relaxational contribution

$$\varepsilon''(\omega) = \varepsilon''_{\text{tot}}(\omega) - \varepsilon''_c(\omega). \tag{3}$$

With regard to electrolyte solutions, that contribution reflects short range/short time motional modes of ions, for example the internal motion within ionic aggregates or clusters, the tumbling motion of polar aggregates and, often predominating if present, that of polar solvent molecules either unaffected or elese affected by the existence of ions.

The $\varepsilon''(\omega)$ spectra can often be deconvoluted into a sequence of two (or more) spectral components C_i, which then may be attributed to conceptually distinguishable processes, usually the lower frequency one to the motion of "ion-pairs", using that term in quite a broad sense for polar species involving ions, and the higher frequency component to the motion of solvent molecules. More detailed assignments are conceivable if model assumptions on ion-ion and ion-solvent interactions are taken into consideration. Concerning "ion-pairs", one may consider two limiting cases, that is on the one hand, long-lived "complexes" undergoing rotational motion, so that the relaxation time is determined by the tumbling time, and on the other hand, short-lived aggregates where the relaxation time is determined by dissociation-association kinetics. If these are competing, the observable relaxa-

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tion behaviour will be dominated by the more rapid of both processes. Owing to the multitude of conceivable processes, the assessment of dielectric spectra of electrolyte solutions is in general difficult. Aiming at an identification of relaxation processes it seems therefore advisable to *comparatively* regard the spectral features of different systems.

Quaternary ammonium salts are distinguished from typical inorganic salts by their bulky cations. By looking at differences and similarities of their solutions, further experimental information may be gained to aid the interpretation of relaxation processes in which ions are involved. Alkylammonium salts have received attention in dielectric spectroscopy over the last decades. Early studies were carried out using non-polar solvents [1] which have again attracted interest recently [2]; others dealt with polar solvents [3], in particular with aqueous systems [4] including those which exhibit micellization effects without additional salt [5]. Recently we have reported on a salt which is liquid at room temperature (trioctylammonium chloride) and have compared its dynamic dielectric properties in pure liquid form and with some non-polar diluents [6]. It turned out that the dielectric spectra of the molten salt and of the mixtures do not essentially differ from each other. The spectral shape resembles that of solid ionic conductors and melts of inorganic salts inasmuch as $\varepsilon''_{\mathrm{tot}}(\omega)$ shows at lower frequencies an ω^{-1} decrease according to (2), which at higher frequencies turns to an ω^{-a} tail with $a < 1$. As in some cases of short chain tetraalkylammonium salt solutions [1, 2], this cannot be described by addition of a Debye type relaxational contribution $\varepsilon''(\omega)$ to the conductivity contribution $\varepsilon''_{\mathrm{c}}(\omega)$ but requires (on the $\log\omega$ scale) an unsymmetrical, broadened "ion-pair" relaxation function such as the Cole-Davidson function.

In the present communication we have extended our previous work to examine some further alkylammonium salt solutions at moderate and high concentrations. The choice of salt/solvent combinations is a matter of sufficient solubility. Here we have used two moderately polar solvents which to our knowledge have not yet been considered in that context, on the one hand a solvent consisting of small molecules, thus exhibiting its relaxation region at clearly higher frequencies than "ion-pairs", and, on the other hand, another one which due to self-association *via* hydrogen bonds relaxes in roughly the "ion-pair" region. These are:

Chloroform, CF (relaxing around 30 GHz),
1-Octanol, OCT (relaxing around 0.1 GHz).

The following alkylammonium salts were used (in parentheses, the alkyl chain lengths of the cation are given):

Hexadecyl trimethylammonium bromide, HTMAB (16, 1, 1, 1),
Hexadecyl trimethylammonium chloride, HTMAC (16, 1, 1, 1),
Tetrahexylammonium bromide, THAB (6, 6, 6, 6)
Tetrabutylammonium bromide, TBAB (4, 4, 4, 4)

For comparison, the previously published results [6] on

Trioctylmethylammonium chloride, TOMAC (8, 8, 8, 1)

will also be regarded.

2. Experimental

The dielectric loss $\varepsilon''_{\mathrm{tot}}$ of the solutions was measured with the help of various setups developed in our laboratory for studying high loss liquids. The frequency range was between 1 MHz and 36 GHz. The use of different apparatus prevents us from failing to notice errors. The uncertainty of $\varepsilon''_{\mathrm{tot}}$ is a few percent at all frequencies. The dc conductivity κ_{s} was determined conventionally at 4 kHz.

Chemicals from Fluka were used as obtained. Three systems with CF and three with OCT as solvent have been studied at salt concentrations c_{s} ranging between 0.1 mol/l and the solubility limit. Measurements at 20 °C were carried out with all systems. Morevover, OCT solutions were studied at higher temperatures up to 50 °C. These results, however, will be referred to only a few times for comparison.

3. Results

To illustrate some typical features, Fig. 1 shows the $\varepsilon''_{\mathrm{tot}}$ and ε'' spectra of a THAB/CF solution. As in the TOMAC spectra mentioned above, the ω^{-1} decrease of $\varepsilon''_{\mathrm{tot}}$ is followed by a region which in the double logarithmic plot appears again nearly linear, corresponding to ω^{-a} with $a < 1$. Unlike TOMAC spectra, a local maximum appears at higher frequencies, doubtless owing to the polar solvent (CF) used here; pure CF exhibits a spec-

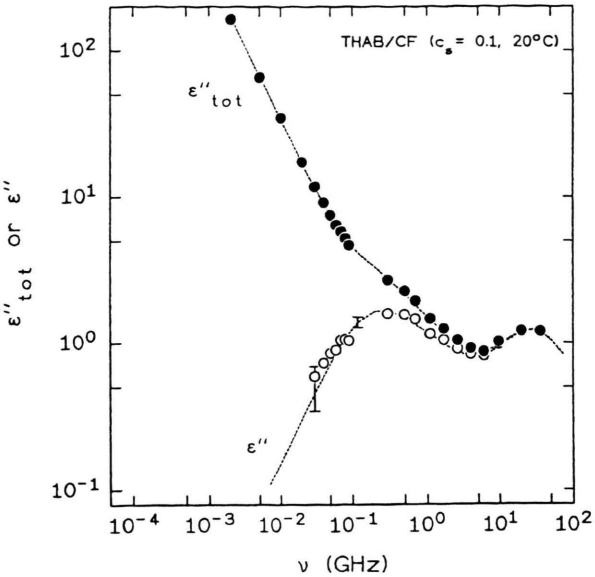

Fig. 1. A typical spectrum, ε''_{tot} and ε'' against frequency ν: THAB in chloroform, $c_s = 0.1$ mol/l, 20°C (double log plot). Full symbols: Total measured los ε''_{tot}, open symbols: Difference $\varepsilon'' = \varepsilon''_{tot} - \varepsilon''_c$. Lines are fits with the parameters given in Table 1.

trum of practically Debye type in just that region with, however, higher intensity. The overall spectral shape suggests a description by a conductivity contribution according to (2), a Cole-Davidson (CD) function, the high frequency side of which is suitable to fit the spectral range with reduced negative slope, and a Debye type component. In a number of cases, a more satisfactory fit is obtained by inserting an additional Debye type component on the low frequency side of the CD component.

For reasons of comparison discussed below, the relaxation time which characterizes the onset of deviations from the ω^{-1} decrease is of interest. Aiming at both a description of that onset and a fitting scheme applicable to all systems studied, we have therefore used the following sequential procedure. The low frequency ε''_{tot} values are fitted according to (2), which by the way yields a κ_s value in agreement with the static measurement to within experimental uncertainty. A first spectral component C_1 of Debye type is then introduced to describe the onset of deviations from ω^{-1}, and a subsequent component C_2 of CD type is added to describe the ω^{-a} range with $a < 1$. Finally a Debye type component C_3 is added to describe the high frequency (possibly solvent) contribution. Thus the fitting scheme reads (in the order of increasing frequency)

$$\varepsilon''_{tot} = \frac{\kappa_s}{\varepsilon_0\,\omega} - \mathrm{Im}\left(S_1 \frac{1}{1+\mathrm{i}\,\tau_1\,\omega} + S_2 \frac{1}{(1+\mathrm{i}\,\tau_2\,\omega)^{\beta_2}} + S_3 \frac{1}{1+\mathrm{i}\,\tau_3\,\omega} \right) \tag{4}$$

and the relaxational part of the spectrum is formally described by relaxation times τ_i, the CD skewness parameter β_2 ($\beta_2 = 1$ means Debye behaviour), and relaxation strengths S_i.

The relaxation parameters obtained in that way are compiled in (Table 1).

It should be emphasized that some parameters can be changed over a certain variability range without impairing the fit quality. With octanol (OCT) as solvent, the spectral components C_1 and C_2, which reflect not only ionic contributions but also the relaxation of the solvent itself, cannot unambiguously be distinguished from each other. For these systems, the constraint was introduced that the relaxation time τ_2 should not exceed the corresponding CD relaxation time τ_2^{OCT} of pure octanol. It is worth noting here that at higher temperatures the $\varepsilon''(\omega)$ spectra of OCT systems exhibit a shape such that, concerning components C_1 and C_2, a fit complying with that constraint becomes self-evident. For both chloroform (CF) and octanol (OCT) systems the relaxation strengths S_1 given in Table 1 tend to vanish for salt concentration $c_s \to 0$, indicating that the spectral component C_1 is ascribable to the solute. Thus τ_1 can serve the purpose to describe the onset of deviations from the conductivity contribution. Notwithstanding this, both S_1 and S_2 can be varied in, however, opposite sense such that $S_1 + S_2$ stays practically unchanged. Only that sum will therefore be regarded in the discussion. Concerning component C_2, it can be seen from Table 1 that $S_2 \to 0$ with $c_s \to 0$ in the case of CF solutions. This is not so for OCT solutions where, instead, $S_2 \to S_2^{OCT}$ and also $\tau_2 \to \tau_2^{OCT}$ in accordance with the assignment of that component. The spectral component C_3 covers the solvent relaxation in case of CF. For OCT, on the other hand, the main relaxation as governed by association dynamics is included in C_2. Here C_3 resembles the minor high frequency "shoulder" usually found in the spectra of alcohols due to the presence of temporarily unassociated molecules. From the only weak dependence of S_3 on concentration, as well as from findings in the absence of a polar solvent (e.g. TBAB [2], TOMAC [6] at higher temperatures) it appears very likely that also ionic effects contribute to C_3.

Table 1. Static conductivity κ_s and relaxation parameters τ_i, β_2, and S_i of tetraalkylammonium salt solutions (concentration c_s) in chloroform (CF) and 1-octanol (OCT), 20 °C.

System	c_s mol/l	κ_s S/cm	τ_1 ps	τ_2 ps	τ_3 ps	β_2	S_1	S_2	S_3
HTMAB/CF	0.10	$1.36 \cdot 10^{-5}$	3100	830	6.0	0.48	0.75	2.70	2.15
	0.30	$1.85 \cdot 10^{-4}$	2100	380	5.8	0.50	6.05	3.30	1.60
	0.50	$3.00 \cdot 10^{-4}$	1000	230	5.2	0.52	2.90	2.60	1.50
	1.30	$6.28 \cdot 10^{-4}$	720	125	5.0	0.55	2.80	2.20	1.20
HTMAC/CF	0.10	$1.15 \cdot 10^{-5}$	3200	850	6.1	0.49	0.65	2.75	2.20
	0.30	$2.01 \cdot 10^{-4}$	2100	400	5.7	0.50	6.10	3.40	1.70
	0.50	$2.82 \cdot 10^{-4}$	1000	230	5.1	0.50	3.10	2.50	1.60
	0.70	$6.74 \cdot 10^{-4}$	820	170	5.2	0.50	3.00	2.15	1.35
	1.00	$6.16 \cdot 10^{-4}$	800	150	5.1	0.54	2.65	2.35	1.15
THAB/CF	0.10	$1.85 \cdot 10^{-4}$	820	300	5.3	0.56	2.60	1.70	2.05
	0.25	$7.01 \cdot 10^{-4}$	620	240	5.3	0.57	3.15	2.05	1.80
	0.50	$1.25 \cdot 10^{-3}$	500	165	5.0	0.60	3.20	1.75	1.50
HTMAC/OCT	0.10	$5.33 \cdot 10^{-6}$	7000	2300	30	0.76	0.85	6.95	0.35
	0.25	$1.60 \cdot 10^{-5}$	5500	2000	30	0.69	2.55	5.35	0.35
THAB/OCT	0.10	$2.34 \cdot 10^{-5}$	6000	2200	30	0.70	3.20	5.60	0.35
	0.25	$5.99 \cdot 10^{-5}$	5000	1900	30	0.55	3.40	3.50	0.30
	0.39	$7.77 \cdot 10^{-5}$	4000	1400	30	0.53	2.25	2.55	0.30
TBAB/OCT	0.10	$2.89 \cdot 10^{-5}$	5000	2150	30	0.76	2.60	5.80	0.35
	0.25	$7.77 \cdot 10^{-5}$	4000	1900	30	0.61	3.35	3.75	0.35
	0.50	$1.33 \cdot 10^{-4}$	3500	1350	30	0.53	1.80	2.55	0.35

4. Discussion

4.1. The Ionic Relaxation Contributions

Longest detectable relaxation time of ionic contributions

For all systems studied here it can be supposed that the spectral component C_1 is related to ionic processes. This component shall be regarded first. An often tried starting assumption is that the ionic contribution be due to the tumbling motion of well-defined contact or solvent shared ion-pairs. Unfortunately, the respective relaxation strength cannot unequivocally be discussed since it depends on two unknowns, the concentration of those species and their dipole moment. Concerning the relaxation time, on the other hand, there is a wealth of comparative material from studies on polar quasi-rigid molecules which allows for an at least rough estimation of the effective radius of the tumbling entity from the relaxation time and viscosity. Note that experimental findings for not too large molecules have shown that the relation between the dielectric relaxation time, effective radius and viscosity differs considerably from the Debye-Stokes relation; so we use to refer to an empirical correlation between these quantities [7].

The relaxation times τ_1 of Table 1 are illustrated against viscosity η in Fig. 2, which additionally repre-

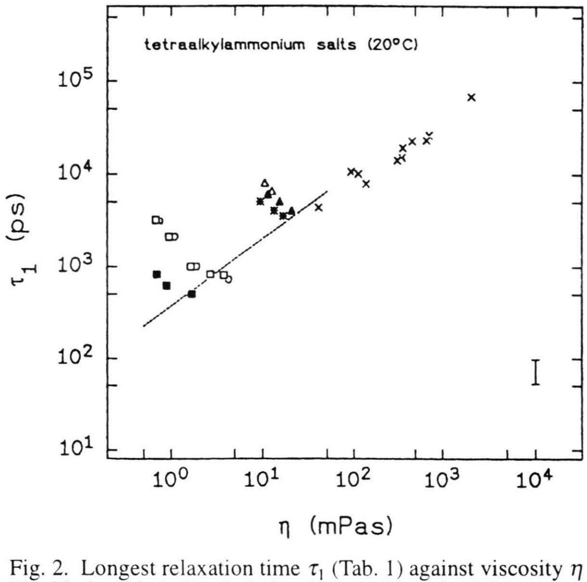

Fig. 2. Longest relaxation time τ_1 (Tab. 1) against viscosity η (double log plot). Symbols for the solutions: ○ HTMAB/CF, □ HTMAC/CF, ■ THAB/CF, △ HTMAC/OCT, ▲ THAB/OCT, ✱ TBAB/OCT. Added for comparison: × TOMAC in different non-polar solvents [6] (the point at the highest η value stands for pure TOMAC). The straight line indicates the "limiting" relaxation time τ_1 which (at 20 °C) was found to be not exceeded by solutions of inorganic salts, *viz.* those consisting of small ions. Note that for all systems the viscosity η is an increasing function of the salt concentration c_s.

sents data for TOMAC in pure from and in non-polar media [6]. Also shown is a line representing the empirical correlation between relaxation time and viscosity [7] for a certain effective radius, $r_{\text{eff}} = 0.6$ nm. As Fig. 2 shows, dilute solutions of the salts studied here lead to τ_1 values above that line, approaching the line gradually as the concentration is increased. In contrast, TOMAC systems following this line closely.

If τ_1 of diluted systems should relate to the tumbling motion of "ion-pairs", it follows from Fig. 2 that these should necessarily have an effective radius r_{eff} larger than about 0.6 nm. Radii of alkylammonium ions are not very well defined. In Table 2 we give, therefore, two estimations for radii of the smallest feasible "ion-pair" species, that is contaction-pairs. The two values mean lower [8] and upper limits [9]. Qualitatively, these values are in accordance with the requirement $r_{\text{eff}} > 0.6$ nm. Thus the conclusion is sufficient though not necessary that at *low* concentrations the slowest relaxation contribution consists in the tumbling motion of contact ion-pairs. It is worth mentioning that with inorganic salt solutions, *viz.* salts consisting of much smaller ions than the quaternary ammonium ions regarded here, the appearance of *contact* ion-pair relaxation contributions could not be ascertained so far, possibly since they lie at so high frequencies that they are obscured by the solvent relaxation.

The above conclusion is questionable for the *concentrated* solutions and for the TOMAC systems. At this point it is helpful to look at results on concentrated inorganic salt solutions. These exhibit often relaxation times τ_1 below the 0.6 nm line in Figure 2. Values around that line occur increasingly, but no examples above it have been found [10]. So the line shown in Fig. 2 has incidentally the secondary meaning of a "limiting" line which is not exceeded by relaxation times of inorganic salt solutions. This finding cannot generally be reconciled with the assumption that well-defined ionic species are acting as relaxators but leads to the conjecture that a relaxation mechanism of more general physical nature is operative [10]. Possibly this is a collective process of vague similarity to that found in the dynamics of chain association in liquids such as monohydric alcohols, a conjecture which is suggested by the longest relaxation times of these liquids which approach the same "limiting" line (Figure 3). If such a process should actually occur, it is likely to gradually replace the suspected ion-pair tumbling mechanism of the present systems when the salt concentration is increased, and it seems to be dominating in all TOMAC systems. Consequently two different relaxation processes have to be taken into account.

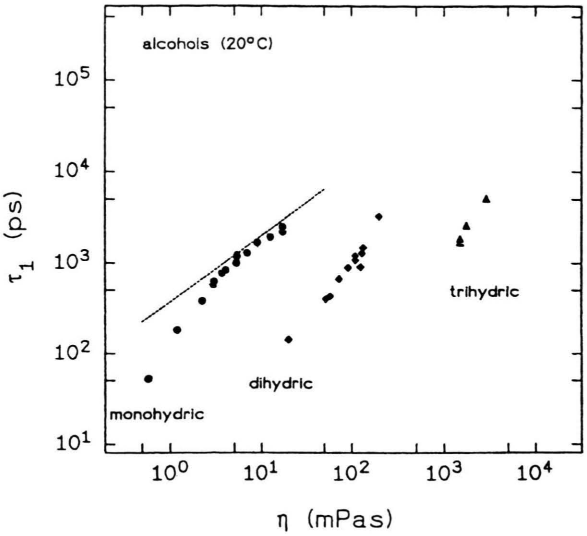

Fig. 3. As Fig. 2 showing, however, the longest relaxation time τ_1 of various pure alcohols at 20 °C [11].

Table 2. Radii r_{IP} of contact ion-pairs estimated after [8] and [9].

Ion-pair	r_{IP} [8] nm	r_{IP} [9] nm
HTMAB	0.72_7	0.79_4
HTMAC	0.71_1	0.77_8
THAB	0.60_5	0.75_4
TBAB	0.57_9	0.69_2

Relaxation strength of ionic contributions

Regarding OCT solutions, ionic relaxation processes give rise to the spectral component C_1, but it remains uncertain to what extent they contribute to C_2 (see Sect. 4.2). Mainly CF systems will therefore be considered here. In that case C_2 does certainly not reflect *unaffected* solvent relaxation, albeit ion-solvent interactions, thus it can be considered an ionic contribution as C_1. For reasons mentioned before we discuss the relaxation strengths of both components together, *viz.* $S_1 + S_2$.

If a certain relaxation mode of "ion-pairs" is presumed to cause both spectral components, the normalized relaxation strength $(S_1 + S_2)/c_s$ is a qualitative measure for the aggregated fraction of salt. Conductivity is due to charge carriers, in particular to "free" ions, thus the normalized conductivity (the Walden product) $\kappa_s \eta / c_s$ could serve as a crude measure for the complementary fraction of salt which is *not* involved in "ion-pairs". As a typical value for a completely dissociated alkylammonium salt, we

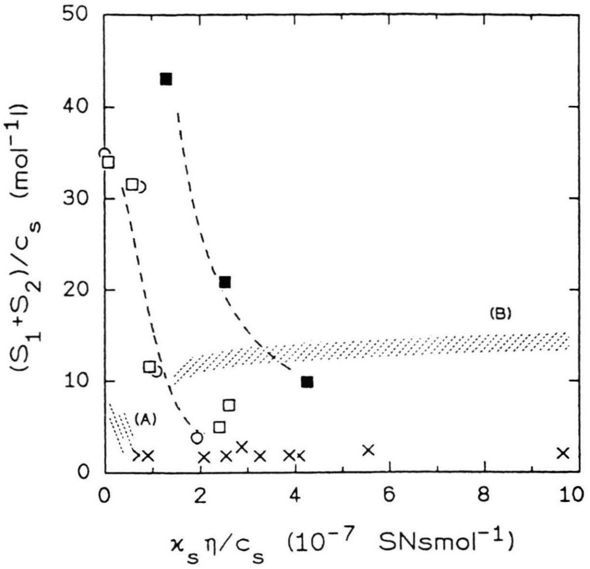

Fig. 4. Normalized relaxation strength $(S_1 + S_2)/c_s$ against normalized conductivity $\kappa_s\eta/c_s$ for the three CF solutions and the TOMAC systems [6], 20 °C. Symbols as in Figure 2. Dashed lines are guidelines to the eye only. The $\kappa_s\eta/c_s$ values increase with the salt concentration c_s. For comparison, two further systems are represented by hatching: (A) THAB in 1,4-dioxane, $c_s = 0.1 \ldots 0.5$ mol/l [6]. (B) LiCl in mixtures of N-methylpyrrolidone/1,4-dioxane, $c_s = 0.5 \ldots 1.0$ mol/l [14], dioxane content increasing from right to left, $c_{DX} = 1 \ldots 6$ mol/l.

quote that for tetraethylammonium chloride in different solvents at infinite dilution: $\kappa_s\eta/c_s \approx 60 \cdot 10^{-7}$ SNs mol^{-1} [12] (this is roughly half the value for standard aqueous KCl solutions). For all (CF and OCT) systems regarded here the $\kappa_s\eta/c_s$ values are more than an order of magnitude lower, indicating that uncharged "ion-pairs" are formed to a large extent.

For the present CF systems, $(S_1 + S_2)/c_s$ and $\kappa_s\eta/c_s$ are plotted against each other in Figure 4. Note that in all cases there is an increase in $\kappa_s\eta/c_s$ with increasing salt concentration c_s, while normally the situation (at least for lower concentrations) is found to be reverse. According to [13] the increase in $\kappa_s\eta/c_s$ may be considered a hint at weakened ion-solvent interactions and a re-dissociation of "ion-pairs".

In case of a salt/solvent combination where besides "free" ions only one kind of well-defined "ion-pairs" occurs one would expect that the quantities shown in Fig. 4 are inversely related on changing the salt concentration. In a qualitative fashion, this is actually found (dashed lines in Figure 4). An exception are TOMAC and its mixture with non-polar diluents (among them 1,4-dioxane, DX) [6] which exhibit rather low values $(S_1 + S_2)/c_s$ changing little as the concentration is varied. The figure shows also results for two other systems. One is THAB/DX [6], the other is an inorganic 1 : 1 salt, LiCl, in the mixed solvent N-methylpyrrolidone (NMP)/DX [14], which is chosen to demonstrate that on increasing the DX content also the data for a quite different electrolyte solution approach the THAB/DX data, as it is similarly the case for TOMAC/DX.

Figure 4 suggests to distinguish groups of data which are likely to represent physically differing relaxation mechanisms:

1. High $(S_1 + S_2)/c_s$ (values even higher than for LiCl/NMP) and low $\kappa_s\eta/c_s$, that are the present systems at low salt concentrations which in the previous section were characterized by τ_1 values above the "limiting" line.
2. Low $(S_1 + S_2)/c_s$, that are the present system at high salt concentrations, moreover the TOMAC systems and all DX rich solutions mentioned. On the whole, these follow the τ_1 "limiting" line in Figure 2.
3. Intermediate $(S_1 + S_2)/c_s$ at moderate $\kappa_s\eta/c_s$ as found with inorganic salt solutions such as the NMP rich solutions of LiCl (see Fig. 4; note that the $\kappa_s\eta/c_s$ values can only roughly be compared with those of alkylammonium salts because of the differing mobility of ions). These examples are mentioned here to complete the picture. They are characterized by τ_1 below the "limiting" line, and the relaxation mechanism is most likely to be different in a physical sense from that of group 2 [14].

It may be stressed that up to this point the discussion of both the relaxation times and the relaxation strengths lead concurrently to a distinction between different ionic relaxation processes, in so far achieving at least partly the aim of identifying ionic processes.

4.2. The Solvent Relaxation Contributions

Chloroform (CF) as solvent

With that solvent, it is the spectral component C_3 which can reasonably be ascribed to unaffected (bulk) CF. As generally for non-associating liquids, the relaxation strength S_3 can be assumed to be roughly proportional to the concentration of *unaffected* solvent. It may be compared to the relaxation strength ${}^eS_3$ as expected according to the *analytical* solvent concentration by regarding the ratio

$$\zeta_{CF} = \frac{S_3}{{}^eS_3}. \tag{5}$$

This becomes increasingly less than unity on increasing salt concentration, for example there is $\zeta_{CF} \approx 0.8_0 \ldots 0.7_0$ at $c_s = 0.25 \ldots 0.50$ mol/l for the salts studied in CF solutions. The complementary fraction of solvent which has "disappeared" from the spectral component C_3 must be considered as affected solvent. As a more illustrative quantity, the number z_{CF} of affected solvent molecules per salt unit may be estimated from ζ_{CF}. Also this number decreases the more, the larger c_s and comes to $z_{CF} \approx 10 \ldots 5$ for $c_s = 0.25 \ldots 0.50$ mol/l. This is within, or slightly above, the range found with inorganic 1 : 1 salts in aprotic solvents at corresponding concentrations [14, 15].

The "disappeared" fraction of solvent must be ascribed to ion-solvent interactions. It could be neutralized in the solvation shells of ions or could contribute as loosely affected solvent with longer relaxation time than in the bulk state to other spectal components, *viz.* C_1 and/or C_2. The former one should be excluded as far as it encompasses contact ion-pairs.

1-Octanol (OCT) as solvent

The discussion of the OCT relaxation contribution is rather uncertain in comparison to that of CF since solvent and solute relaxation regions are not resolved. Moreover the main relaxation strength of an associating liquid is determined by the mean structure and number density of temporary associates and is therefore not generally proportional to concentration.

According to the relaxation spectrum of pure OCT, the solvent is likely to contribute mainly to spectral component C_2, so it is tempting to regard the ratio

$$\zeta_{OCT} = \frac{S_2}{{}^{e}S_2} \tag{6}$$

as a measure for the fraction of unaffected solvent. Presupposing that ${}^{e}S_2$ relates to solvent with bulk properties, it is justified to estimate it as proportional to the OCT concentration. The numerator, however, will possibly be overestimated since it may also include solute relaxation contributions.

In addition to the data analysis summarized in Table 1 we have therefore carried out an alternative one for the OCT systems which is based on the model assumption that a bulk OCT contribution should exist which is characterized by the same τ_2, β_2 and also τ_3 as pure OCT. Among the other parameters, the fit yields the main relaxation strength S_2' of the presumed solvent contribution. Before regarding this quantity, some general results of the alternative fit procedure are worth mentioning here. A spectral component C_1 is required as before with, however, longer relaxation time τ_1. An additional component with a relaxation time of about 200 ps must be introduced between C_2 and C_3. It describes that part of the spectrum which in the original fit it covered by the more and more stretched CD tail of C_2 (note that β_2 is not constant but decreases with increasing c_s). According to the model assumption, the additional component may be due to solvent which is associated to a lesser degree, thus indirectly to ionic effects. Lastly, concerning S_2' it is found that this differs on average only little from S_2 (Table 1). (This is not so for higher temperatures, *e.g.* at 50 °C there is one average $S_2'/S_2 \approx 0.7$.)

At $c_s = 0.25$ mol/l and 20 °C we find with (6) that $\zeta_{OCT} \approx 0.8_0$ for HTMAC and 0.5_5 for both THAB and TBAB. Since there may still be a solute contribution remaining, the ζ_{OCT} ratios which actually relate to the solvent might be somewhat lower but not higher. Thus the ζ_{OCT} are clearly smaller than the corresponding ζ_{CF} values. Probably this is due to additional effects not feasible in case of CF, such as a structure breaking effect exerted by ions on the associated OCT chains.

4.3. *Remarks on Individual Cases*

Are there chain length effects with homologous salts?

In the case of long alkyl chains, internal relaxation modes due to the flexibility of the chains are feasible, which for aliphatic polar molecules are known to reduce the relaxation times and also to broaden the relaxation spectra. The data for the homologous salts THAB and TBAB are rather similar and do not indicate any influence of chain length. We have studied these salts and, additionally, tetraethylammonium bromide (TEAB) at 50 °C in OCT solution. Significant differences appear now in the relaxation times τ_2 but not in other parameters: For THAB, TBAB and TEAB we find at $c_s = 0.25$ mol/l that $\tau_2 \approx 100$, 230 and 280 ps, respectively, *viz.* shorter relaxation times for longer chains. Since C_2 may comprise ionic as well as solvent effects, it cannot be decided whether this finding might relate to internal motion in case of longer chains or to a more intense structure breaking effect.

Are there micellization effects?

Returning to Fig. 4 and the grouping suggested there it is interesting to note that group 1 examples (high

$(S_1+S_2)/c_s$ at low $\kappa_s\eta/c_s$) are in particular found with CF as solvent, while group 2 examples (low $(S_1+S_2)/c_s$) are typically found with dioxane, DX. Both solvents differ in some molecular properties which may be responsible for those differences. CF has an appreciable polarizability, while DX is known as a good electron donor, thus effective in solvating cations.

For group 1 examples it was conjectured above that the slowest relaxation contribution may consist in the tumbling motion of contact ion-pairs, which was a sufficient but not necessary conclusion. High normalized relaxation strengths have been reported for HTMAB in aqueous solution at concentrations where micellization is known to occur [5], that is below the concentration range studied here. These normalized relaxation strengths, corresponding to our $(S_1+S_2)/c_s$, are still higher than our findings. Common features are the decrease of τ_1 and $(S_1+S_2)/c_s$ with increasing salt concentration. Thus the question may be raised as to whether group 1 examples might represent micellization effects in CF which do not occur in DX.

In that context it seems noteworthy that in Fig. 4 there appears a decrease of $(S_1+S_2)/c_s$ which in case of HTMAB/CF and HTMAC/CF has the form of a particularly sharp decline. This occurs (expressed by corresponding concentrations) from $c_s = 0.3$ to 0.5 mol/l. In the same concentration range these solutions show an edge of the refractive index/concentration curve, which is not found with other systems studied.

Thus microheterogeneity as dependent on the solvent properties cannot be ruled out, which could play a role at low salt concentrations. Relevant details for HTMAB/CF and HTMAC/CF systems could not be noticed in the literature. If association in micelles should occur, the tangential motion of bound counterions around the micellar core, according to a model advanced by Pottel [5], could be the process causing spectral component C_1.

In any case, the results on the present systems make sure that a change of the dominating relaxation mechanism takes place from moderate to high concentrations.

[1] M. Davies and G. Johansson, Acta Chem. Scand. **18,** 1171 (1964); E. A. S. Cavell and M. A. Sheikh, J. Chem. Soc. Faraday Trans. II **69,** 315 (1973); H. Cachet, F. F. Hanna, and J. Pouget, J. Chim. Phys. **71,** 1546 (1974); J.-C. Lestrade, J.-P. Badiali, and H. Cachet, Spec. Per. Repts., Dielectr. Relat. Proc., Vol. 2, Chemical Soc. London 1975, p. 106.

[2] H. Weingärtner, H. G. Nadolny, and S. Käshammer, J. Phys. Chem. B **103,** 4738 (1999).

[3] H. Cachet, A. Cyrot, M. Fekir, and J.-C. Lestrade, J. Phys. Chem. **83,** 2419 (1979); J. Barthel, M. Kleebauer, and R. Buchner, J. Solution Chem. **24,** 1 (1995).

[4] R. Pottel and O. Lossen, Ber. Bunsenges. Phys. Chem. **71,** 135 (1967); P. S. Yastremskii, G. V. Kokovina, A. K. Lyashchenko, and Y. A. Mirgorod, Zh. Strukt. Khim. **16,** 1002 (1975); G. V. Kokovina, A. K. Lyashchenko, and P. S. Yastremskii, Zh. Strukt. Khim. **24,** 152 (1983); R. Pottel, E. Asselborn, R. Eck, and V. Tresp, Ber. Bunsenges. Phys. Chem. **93,** 676 (1989); J. Barthel, R. Buchner, and M. Münsterer, Electrolyte Data Collection Pt. 2 (Chem. Data Ser. Vol. XII/2), Dechema, Frankfurt/Main 1995.

[5] R. Barchini and R. Pottel, J. Phys. Chem. **98,** 7899 (1994).

[6] R. Elsebrock, M. Stockhausen, G. Czechowski, and J. Jadżyn, Polish J. Chem. **72,** 2463 (1998).

[7] G. Turky, G. Wilke, U. Witt, A. Ghoneim, and M. Stockhausen, Proc. 3rd Conf. Dielectr. Relat. Phenomena, Zakopane 1994, p. 146.

[8] W. L. Masterton, D. Bolocofsky, and T. P. Lee, J. Phys. Chem. **75,** 2809 (1971).

[9] R. A. Robinson and R. H. Stokes, Electrolyte Solutions, 2nd edt., Butterworth, London 1959, p. 125.

[10] M. Stockhausen, 4th Conf. Dielectr. Relat. Phenomena, Szczyrk 1996 (ed. A. Włochowicz), Proc. SPIE **3181,** 65 (1997).

[11] A. Lux and M. Stockhausen, Phys. Chem. Liq. **26,** 67 (1993); Further results of our laboratory.

[12] Landolt-Börnstein, Zahlenwerte und Funktionen, Vol. II/7, Springer-Verlag, Berlin 1960.

[13] L. C. Kenausis, E. C. Evers, and C. A. Kraus, Proc. Natl. Acad. Sci. U.S. **48,** 121 (1962); **49,** 141 (1963).

[14] R. Biedenkap and M. Stockhausen, Z. Phys. Chem. **211,** 29 (1999); R. Biedenkap, private communication.

[15] S. A. Markarian and M. Stockhausen, Z. Phys. Chem. **214,** 139 (2000).