The Dielectric Relaxation of Water on Addition of Ethylene Carbonate and some Related Substances

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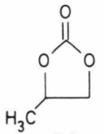
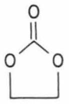
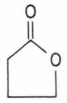
The dynamic dielectric properties of diluted aqueous solutions of propylene carbonate, ethylene carbonate (EC), 4-butyrolactone and cyclohexanone (CH) have been measured at 20 °C. On assuming normal solute relaxation, the water relaxation can be described by two superimposed Debye type contributions, which may be interpreted in terms of a hydration model. Qualitatively, the influence on the water relaxation increases from EC to CH.

Organic molecules dissolved in water usually induce a significant alteration of the dielectric relaxation behaviour even at low concentrations, which therefore must be attributed to water itself rather than to the (eventually polar) solute. Numerous aqueous systems [1–3] have been investigated in that respect, in particular by the Göttingen group. In the present note, we report some further results on such systems, namely on water rich solutions of propylene carbonate (PC), ethylene carbonate (EC), 4-butyrolactone (BL) or cyclohexanone (CH). They are termed A + B systems in the following, where A is water and B one of the cyclic compounds. These compounds have a quite similar influence on the water relaxation, which shall be considered briefly with a view to its possible molecular interpretation. Furthermore, some qualitative inferences can be drawn concerning the role of ring oxygen.


PC


EC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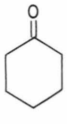
CH

Both PC and CH are only weakly soluble in water and have therefore been studied at only one concentration, while EC and BL were measured up to a mole fraction $x_B = 0.2$, though our main interest is in the relaxation behaviour at lower concentrations. The complex permittivity of the liquids was measured at 20 °C between 30 MHz and 72 GHz. Its imaginary part, ε'' (already corrected for the conductivity contribution), was fitted by a sum of Debye type spectral components C_i according to

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

Thus, the relaxation behaviour will be regarded in terms of the parameters τ_i and S_i.

Two spectral components are necessary to describe the overall absorption (Fig. 1 a), which exhibits the characteristic lengthening of the relaxation time with x_B as a common feature of all systems. To get rid of the contribution of the polar solute molecules, let us suppose that these behave as single entities relaxing in "normal" manner by rotational tumbling, so that their contribution can be roughly estimated [2, 4]. For that purpose, PC and BL were measured in the pure state and analyzed according to (1). Their relaxation times then were changed corresponding to the actual viscosity, following the empirical correlation as usually observed [4]. Further, their relaxation strengths were reduced proportional to their molar concentration. The EC and CH parameters were treated analogously, using literature values of dipole moments [5, 6]. The solute contribution estimated in that manner was subtracted from the total absorption, leaving the absorption to be attributed to water.

A description of this water contribution requires two spectral components. Because of the experimental uncertainties, their parameters can be varied over a certain range. Two possible sets of those "A" parameters are represented in Figures 1 b, c. (Here the relaxation strengths S_i^A are normalized with respect to the water volume fraction v_A, since this normalized quantity should stay constant if only dilution efffects should occur.) The similarity of Figs. 1 a and 1 b shows

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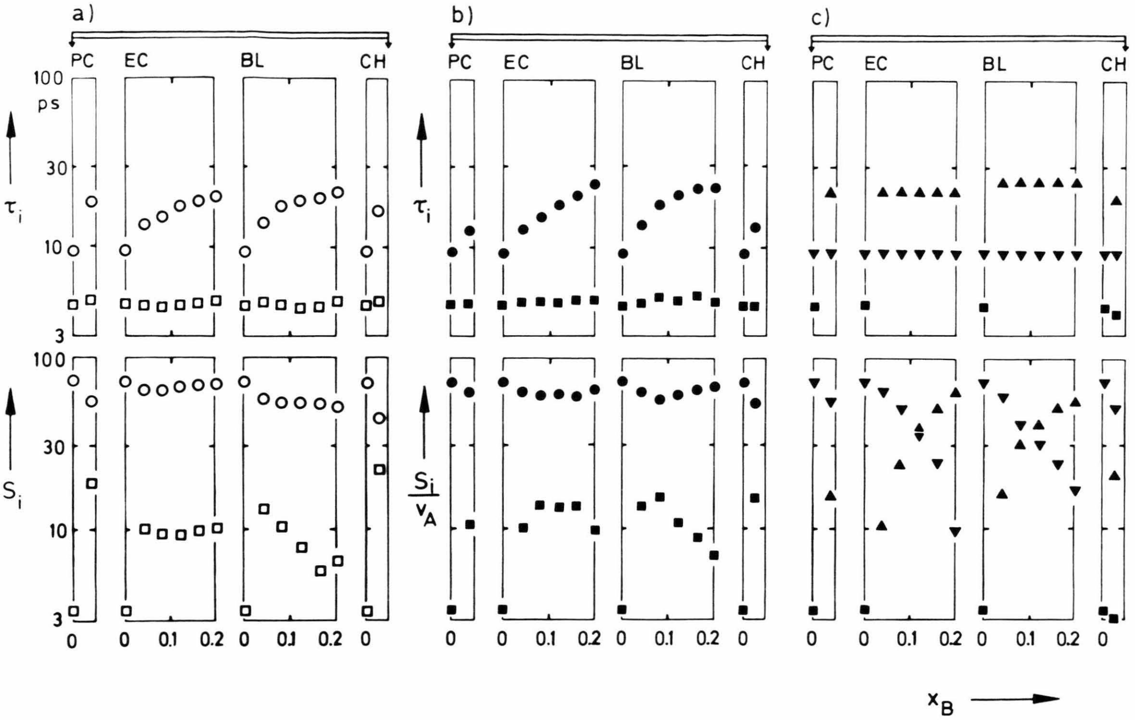

Fig. 1. Relaxation parameters τ_i and S_i versus mole fraction x_B of solute. (a) Overall absorption; (b) and (c) two possible analyses of the absorption contributions ascribed to water. – Notation of spectral components mentioned in the text: (b) ● C_1^A, ■ C_3^A; (c) ▲ C_1^A, ▼ C_2^A, ■ C_3^A.

that, as to be expected, the polar B solute does not *directly* generate the marked features.

In view of the formally different descriptions of the water relaxation depicted in Figs. 1 b, c, the question may be raised as to how these can be interpreted in terms of molecular motion.

The parameters of Fig. 1 b may be discussed in terms of a fluctuating hydrogen bonded network of water molecules. Large aggregates, which practically do not tumble as a whole, may be in dynamic equilibrium with smaller ones (possibly monomers). In that model [7], the mean residence time T_a of the latter determines the main relaxation time τ_1^A of Fig. 1 b, which increases on addition of B. We desist from discussing the normalized relaxation strengths, since, in that model, the fraction of associated water molecules and the weight factor of the resulting spectral component may be related nonlinearly if T_a is not very long in comparison to the "free" tumbling time of small aggregates, a condition which possibly does not hold for the present examples. The assessment of the two spectral components of water as resulting from still one uniform relaxation process means of course that cooperative effects should be involved.

Figure 1 c, however, suggests a concept of an only short ranged influence of the B molecules on water. Since S_1^A/v_A increases proportional to x_B for EC (somewhat weaker for BL), a hydratation model, as developed by Pottel and Kaatze [8], comes into mind. According to this, C_1^A may relate to water which is affected by the solute so that its motion is slowed down, though this "hydration" water is not firmly bound to the solute. Component C_2^A, on the other hand, may denote the unaffected portion of the solvent, which exhibits the relaxation time of pure water. It should be stressed that the sum of the normalized water relaxation strengths, $\Sigma = \Sigma S_i^A/v_A$, in any case (i.e. in Fig. 1 b as well as in Fig. 1 c) changes little as the B content is increased (whilst $\Sigma_0 = 75.5$, an average $d\Sigma/dx_B \approx 7$ is found for EC and BL over the concentration range studied; corresponding results are known from static dielectric measurements [6, 9]). This leads suggestively to the assumption that the relaxation process of "hydration" water is essentially of the same type as of unaffected water but modified on the time scale. A similar behaviour (yet with other solutes) has been observed for non-associating solvents such as methylpyrrolidone [10] or DMSO [11].

The present material does not allow to decide on the above interpretation schemes which both are feasible for the water relaxation. It is, however, sufficient to infer that the initial assumption of individually relaxing (i.e. non-associating) solute molecules is appropriate.

Regardless of the interpretation problem, the effect of the various B molecules on the water relaxation can be considered qualitatively, since the relative alterations of the relaxation parameters of all the analysis sets (Figs. 1 a–c) follow the same ranking order. As an illustrative quantity we introduce the "hydration" number Z_h, derived from S_1^A/v_A (Fig. 1 c) as number of affected water molecules per solute molecule. The following values (for $x_B \to 0$) are approximate ones, in particular for PC and CH:

	PC	EC	BL	CH
$Z_h \approx$	5.5	3.5	5.5	15

Obviously, the effect on water increases as the number of ring oxygen atoms decreases, provided that one of the PC ring oxygens is considered to be shielded by the CH_3 group. (Note the analogous relations of some other properties: the velocity constant for hydrolysis of EC is twice that of PC; the melting point of EC is about 100 K above that of PC which, on the other hand, is close to that of BL.)

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