Dielectric Relaxation of Three Ethanolamines

M. Wichmann and M. Stockhausen

Institut für Physikalische Chemie der Universität Münster,
D-48149 Münster

Reprint requests to Prof. M. St.; Fax: (+0251) 8323441

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Relaxation spectra have been measured at 20 °C for mono-, di- and triethanolamine in the pure liquid state and in a 0.6 mole fraction mixture with 1,4-dioxane. The general resemblance to the dielectric behaviour of alcohols and aminoalcohols shows that relaxation is governed by association effects. In this regard, several features point to significantly differing behaviour of the mono compound in comparison with both di- and triethanolamine.

Key words: Association; Dielectric Spectroscopy; Hydrogen Bonding; Liquids.

The dielectric properties of liquid ethanolamines, $(HO{-}CH_2{-}CH_2)_n{-}N{-}H_{3-n}$ (EA), have rarely been studied. For monoethanolamine (MEA, 2-amino-1-ethanol) static [1, 2] and dynamic parameters [2] have been reported (also for aqueous systems [3]). For diethanolamine (DEA) static parameters [1] and for triethanolamine (TEA) also dynamic parameters [4] can be found. With respect to information on microscopic motional processes and interactions in those associating liquids it seems worthwhile to directly compare their dynamic dielectric properties. In the present note we report some relevant results which were obtained in extension of our previous work on aminoalcohols [2]. As in [2], the substances have been studied in their pure liquid form and in concentrated ($x \gtrsim 0.6$) mixtures with 1,4-dioxane (Dx) over the whole frequency range of dielectric absorption (up to 72 GHz). The temperature was 20 °C. Although DEA is reported to have a higher melting point, it could be kept liquid at that temperature.

In the case of DEA and TEA, the dielectric spectrum can satisfactorily be represented by a Cole-Davidson (CD) function. This is not so far MEA. Since its absorption spectrum appears more flat around the maximum, a further spectral component on the low frequency side is required in addition to the CD term. Therefore we have formally fitted the spectra by two spectral components C_1 (Debye type) and C_2 (CD type), characterized by relaxation times τ_i, relaxation strengths S_i and the CD skewness parameter β_2 (where $\beta_2 = 1$ means Debye behaviour). These parameters are listed in Table 1, where data are given for the pure substances and, as typical example, for only one particular dioxane mixture with each ethanolamine.

Table 1. Relaxation parameters τ_i, β_2 and S_i according to a fit with two spectral components C_1 (Debye) and C_2 (Cole-Davidson) for pure EAs and for EA/Dx mixtures (EA mole fraction x, molar concentration c), 20 °C. The S_i values are given in normalized form, $S_i\, c^*/c$, where c^* refers to the pure substance.

	x	c mol/l	τ_1 ps	τ_2 ps	β_2	$S_1 c^*/c$	$S_2 c^*/c$
MEA	1.0	16.7	630	220	0.52	11.1	16.9
MEA/Dx	0.6	8.6	480	140	0.47	7.1	14.1
DEA	1.0	10.45	–	5800	0.55	–	22.5_5
DEA/Dx	0.6	6.5	5000	1300	0.49	1.3	20.5
TEA	1.0	7.5	–	7500	0.54	–	29.5
TEA/Dx	0.6	5.2	6000	2800	0.50	0.7	27.5_5

The longest relaxation times, that is τ_1 for MEA and τ_2 or better $\tau_2\beta_2$ (which refers to the absorption maximum of the CD component) for DEA and TEA, are much longer than to be expected from molecular size and viscosity under the assumption of single molecule rotational tumbling motion. The Onsager moments to be deduced from $\sum S_i$ are larger than to be expected, too (Kirkwood factor $g > 1$). Thus there is a general resemblance to the dielectric properties of alcoholic systems, which are well known to be controlled by association via hydrogen bonding.

However, closer examination of the spectra reveals striking differences between MEA on the one hand, and DEA and TEA on the other hand.

(i) As already noted, the spectral shapes differ for both groups, so that the formal fit scheme applied here requires two spectral components for MEA while one component is practically sufficient for DEA and TEA.

(ii) The normalized relaxation strenght $\sum S_i/c$, which agrees well with the normalized dispersion step $(\varepsilon_s - n^2)/c$, and, consequently, also the apparent dipole moment decreases noticeably on dilution with Dx in case of MEA, as usually found with alcohols and aminoalcohols [2]. In case of DEA and TEA, on the other hand, there is an only slight decrease of these quantities over the concentration range studied.

(iii) It is known [5] that in a plot of effective relaxation time $\tau\beta$ vs. viscosity η, mono-, di- and trihydric alcohols appear as 'families'. MEA fits into the dihydric 'family', while DEA and TEA (which are very similar in that respect) form a separate group close to the trihydric alcohols.

(iv) In that connection it is interesting to note that, within the EA/Dx mixture series, the excess viscosity, defined as

$$\eta^{E} = \eta - \exp\left[x \ln \eta_{EA} + (1-x) \ln \eta_{Dx}\right],$$

is negative for MEA as in the case of alcohols and other aminoalcohols [6], while it is positive for DEA and TEA.

In conclusion, the change of parameters on admixture of dioxane points to interactions which are stronger in DEA and TEA than in MEA, resulting in a preference for persistent, relatively long-lived aggregates or networks. Whether or not the formation of well-defined complexes and/or intramolecular hydrogen bonds might contribute to the special relaxation behaviour of DEA and TEA must remain a matter for conjecture.

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