Dynamic Dielectric Properties of Some Alkylamino Ethoxylates

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Nine ethoxylated (EO) alkyl amines, $(C_nH_{2n+1})N(EO)_xH(EO)_yH$, with $n=10$ to 16 and $\bar{p}=x+y=7.6$ to 14.5, were studied as pure liquids with respect to their dielectric relaxation behaviour over the frequency range 5 MHz to 36 GHz at 20 °C. The broad and structureless dielectric loss spectrum is similar for all samples. It can be described by a main lower frequency spectral component of Havriliak-Negami type plus two minor, higher frequency Debye type components. The relaxation parameters are reported.

Alkylamino ethoxylates $(C_nH_{2n+1})N(EO)_xH(EO)_yH$, where $EO=CH_2CH_2O$, belong to the class of polyethylene oxide condensates which act as surfactants if the ethoxylation degree is sufficiently high (that is, if $x+y\gtrsim 5$). Intending to study the dielectric behaviour of surfactant solutions also at concentrations where micellation occurs, it was noticed that comparative data on the dynamic dielectric properties of the bulk substances are not available in the literature. The aim of the present communication is to report those properties for some homologous alkylamino ethoxylates in their pure liquid state.

Substances were prepared with alkyl chain lengths $n=10$, 12 and 16 [1]. It was checked by NMR that two branches are ethoxylated with mean numbers x and y of EO units. The samples are distinguished by the total mean number $\bar{p}=x+y$. The broadest range of $\bar{p}$ was available for the $n=10$ samples, namely $\bar{p}=7.6$ to 14.5. Nine substances have been studied which are viscous liquids at room temperature.

The complex permittivity of the liquids was measured at 20 °C for a number of spot frequencies ranging between 5 MHz and 36 GHz, employing different lumped-circuit, coaxial and waveguide devices. In addition, the conductivity $\varkappa$ was determined in the kHz region.

The imaginary part of the permittivity, ε''_{tot}, which primarily will be regarded, contains a contribution $\varepsilon''_c=\varkappa/(\varepsilon_0\omega)$ due to the (weak) conductivity $\varkappa$ (here ε_0 is the permittivity of empty space), but only the relaxational contribution $\varepsilon''=\varepsilon''_{tot}-\varepsilon''_c$ is of interest.

The spectra $\varepsilon''(\omega)$ consist of a single, very broad and unstructured peak in all cases studied. A representative example is shown in Figure 1. The spectral shape can only roughly be reproduced by one of the widely used functions. A satisfactory fit, however, is possible by using a spectral component of the Havriliak-Negami (HN) type [2] for the lower frequency range (main absorption) plus two minor Debye type components for the high frequency region. Accordingly, the function

$$\varepsilon''(\omega)=S_1\left(-\mathrm{Im}\,\frac{1}{[1+(\mathrm{i}\,\tau_1\,\omega)^{\alpha}]^{\beta}}\right)+\sum_{i=2}^{3}S_i\,\frac{\tau_i\,\omega}{1+\tau_i^2\,\omega^2}$$

(apart from the conductivity contribution) was fitted to the experimental data. Since already visual comparison of the $\varepsilon''(\omega)$ data shows the close similarity of the spectra, it was tried to keep as many parameters as possible unchanged within the series of substances, reducing in this way the variability range of the remaining parameters.

The relaxation parameters τ_i and S_i obtained are graphically represented in Figure 2. The HN shape

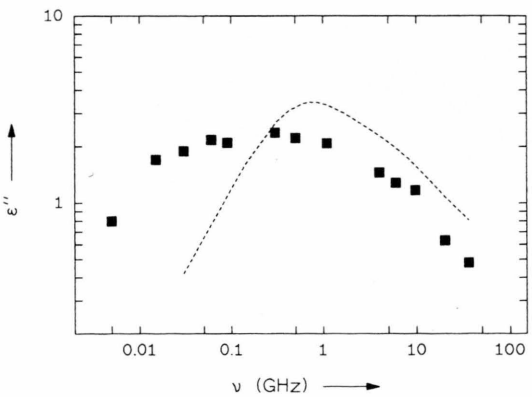

Fig. 1. Dielectric loss spectrum ε'' against frequency ν for an alkylamino ethoxylate with $n=10$, $\bar{p}=9.9$. The dashed curve indicates, for comparison, the spectrum of polyethylene glycol 400 [3].

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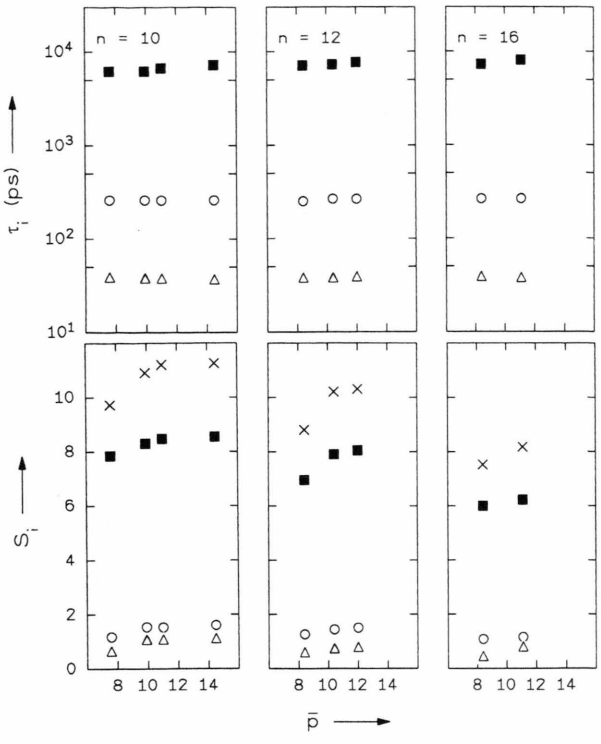

Fig. 2. Relaxation parameters τ_i and S_i of the alkylamino ethoxylates against composition, characterized by alkyl chain length n and mean ethoxylation degree $\bar{p}$. Symbols for the spectral components C_i: ■ C_1 (HN type with $\alpha = 0.78$ and $\beta = 0.45$ in all cases); ○ C_2; △ C_3. The symbol × (lower part) denotes the total relaxation strength $\sum S_i$.

parameters of the main spectral component (termed C_1) are the same for all spectra: $\alpha = 0.78$ and $\beta = 0.45$.

A significant dependence on alkyl and EO chain lengths is only found for the relaxation strengths S_i but not for the relaxation times τ_i. The S_i values clearly increase with increasing ethoxylation degree $\bar{p}$, according to the increased number density of polar groups. On the other hand, they decrease with increasing alkyl chain length n, which is a 'dilution effect' as to be expected.

It is worth noting that the spectra are considerably broader than those of liquid polyethylene glycols (PEG), although each EO branch of the present molecules corresponds to a PEG chain molecule. To illustrate this, a PEG spectrum is shown in Figure 1.

The analysis into several spectral components is formal and does not necessarily mean that these relate to separate physical processes. For both kinds of substances, however, the higher frequency region of the spectrum is likely to reflect the motion of polar chain units. The motional processes leading to the main absorption of the ethoxylated amines, which possibly are cooperative in character, are slowed down for these branched molecules in comparison to PEG (viz. linear molecules). Interactions due to the basicity of the amino nitrogen may, at least partly, contribute to the low frequency relaxation.

Acknowledgement

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[1] S. Abo-El-Fotouh, PhD thesis, Ain Shams University, Cairo 1993.
[2] S. Havriliak and S. Negami, J. Polym. Sci. C **14,** 99 (1966).
[3] E. Wessling, M. Stockhausen, and G. Schütz, J. Molec. Liq. **49,** 105 (1991).

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