

Dielectric Properties of Ethanolamines

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The dielectric constants and losses of three ethanolamines, monoethanolamine, $\text{H}_2\text{N}\cdot\text{C}_2\text{H}_4\cdot\text{OH}$, diethanolamine $(\text{C}_2\text{H}_4\cdot\text{OH})_2\text{NH}$, aminoethylethanolamine $\text{H}_2\text{N}\cdot\text{C}_2\text{H}_4\cdot\text{NH}\cdot\text{C}_2\text{H}_4\cdot\text{OH}$, were measured over the audio- and radio-frequency ranges at temperatures between -70 and 60°C in order to study the dielectric properties of these hydrogen-bonded liquids and to correlate the properties with molecular structures of these compounds. Kirkwood's correlation factors of these compounds are smaller than those of monohydroxyl compounds and the dielectric constants showed straight lines with respect to reciprocal of absolute temperature. Only aminoethylethanolamine supercooled, setting to a glassy state below -70°C and exhibited a dielectric dispersion at low frequencies. The dielectric relaxation observed could not be described simply by the Debye, Cole-Cole, or Davidson-Cole equations but was analyzed in terms of superposition of these relaxation equations. The results are discussed in comparison with those of glycols and polyethyleneimines.

INTRODUCTION

The dielectric properties of hydrogen-bonded compounds¹⁻³⁾ generally shows somewhat different behavior from that of normal polar molecules because of the particular molecular interaction due to hydrogen bonding. It is worthwhile to study the dielectric behavior of the molecules containing particular groups such as OH, NH_2 or NH groups which form the hydrogen bonding in order to explain the effect of these groups on dielectric polarization and relaxation. One⁴⁾ of the present authors has recently studied the dielectric properties of ethylenediamine oligomers $\text{H}_2\text{NC}_2\text{H}_4(\text{NHC}_2\text{H}_4\text{NH})_{n-1}\text{H}$, $n=1, 2, 3, 4$, and found that these oligomers exhibited considerably different dielectric properties from those in mono- and dihydroxyl compounds. The compounds in this investigation have OH groups which are substituted for some of the NH_2 groups in ethylenediamine oligomers. Examination of the effect of OH group substituted for NH_2 group on dielectric properties may provide new information concerning the nature of dielectric polarization and relaxation, since the hydrogen-bonding force of $\text{OH}\cdots\text{O}$ bonding is generally accepted to be stronger than that of $\text{NH}\cdots\text{N}$ bonding.

The present work was thus undertaken to investigate the dielectric constant and relaxation of the compounds that have hydroxyl and amino or imino groups in a molecule.

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EXPERIMENTAL

Materials and measurements

Commercial products of monoethanolamine (MEA) $\text{H}_2\text{N}\cdot\text{C}_2\text{H}_4\cdot\text{OH}$, diethanolamine (DEA) $\text{HN}(\text{C}_2\text{H}_4\cdot\text{OH})_2$ and aminoethylethanolamine (AEEA) $\text{HN}_2\cdot\text{C}_2\text{H}_4\cdot\text{NH}\cdot\text{C}_2\text{H}_4\cdot\text{OH}$ were stored over calcium hydride a few weeks for removal of residual water. Water free samples were fractionally distilled more than three times under reduced pressure.

Purified samples are handled carefully not to react with carbon dioxide. MEA: b.p., 52° (3.5 mm); m.p., 10.2° . DEA: b.p., 126° (5 mm); m.p., 28.0° . AEEA: b.p., 106° (4 mm). Refractive indices were measured by a Pulfrich refractometer and densities by a Lypkin type dilatometer. Physical constants of these samples observed are given in Table 1.

Table 1. Physical constants of ethanolamines.

Temp., $^\circ\text{C}$	Densities ρ , g/ml		
	MEA	DEA	AEEA
20	1.01633	1.09648	1.02907
30	1.00853	1.09040	1.02181
40	1.00056	1.08379	1.01407
Temp., $^\circ\text{C}$	Refractive indices n_D^{20}		
	MEA	DEA	AEEA
20	1.45396	1.47763	1.48579
30	1.45039	1.47481	1.48224
40	1.44661	1.47180	1.47847

The dielectric measurements were carried out over the frequency range of 7.5 Hz to 250 MHz at temperatures between -70 and 60°C . An Ando Electric Co. Type TR-IA transformer ratio arm admittance bridge was used between 7.5 Hz to 5 MHz. A Boonton Radio Corporation Type 250A RX meter was used at frequencies of 0.5 to 250 MHz. The dielectric cell was consisted of concentric platinum cylinder of which vacuum and stray capacities were determined by standard liquid⁵⁾. The dielectric cell was immersed in a well-stirred alcohol bath ($-70^\circ\sim 10^\circ\text{C}$) and a water bath ($10\sim 60^\circ\text{C}$). Temperature measurements were carried out by an Au-Co versus Cu thermocouple which was calibrated at sublimation temperature of carbon dioxide and boiling point of liquid nitrogen. Dipole moments were determined in dioxane solutions by use of the Halverstadt-Kumler relation with a heterodyne beat method⁶⁾.

RESULTS AND DISCUSSION

The equilibrium dielectric constant

The observed values of the equilibrium dielectric constant ϵ_0 of ethanolamines are tabulated, together with those of the dipole moment, in Table 2. These

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Table 2. Dielectric constants ϵ_0 and dipole moments μ of ethanolamines.

Temp., °C	ϵ_0		
	MEA	DEA	AEEA
-50	...	...	31.52
-40	...	...	29.68
-30	...	...	28.10
-20	40.18	...	26.61
-10	37.75	...	25.26
0	35.76	28.01	24.06
10	33.89	27.11	22.86
20	31.94	25.75	21.81
30	...	24.64	20.80
40	...	23.65	19.83
50	...	22.65	18.99
μ, D			
20	2.37	2.79	2.65

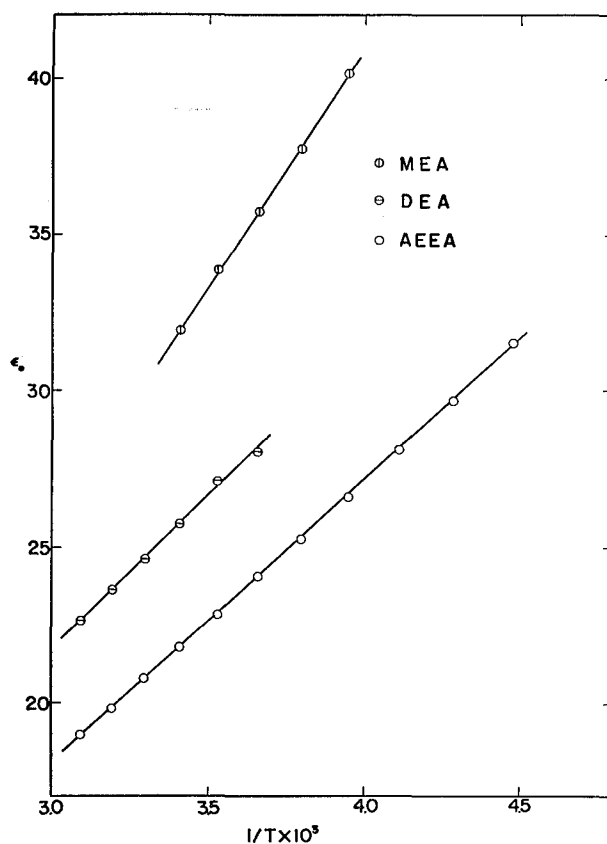


Fig. 1. Static dielectric constants ϵ_0 versus reciprocal absolute temperature for three ethanolamines.

ethanolamines showed larger values of ϵ_0 in comparison with ethylenediamine oligomers owing to hydrogen bonding of OH groups. Monoethanolamine froze at melting point and the dielectric constant dropped down to a small value corresponding to induced polarization. Diethanolamine supercooled for a short time, but froze abruptly to a crystalline solid.

Only aminoethylethanolamine supercooled becoming glassy at low temperature. Since no discontinuity of the equilibrium dielectric constant in this compound was seen between liquid and supercooled states, the rotational freedom remained in glassy state. As shown in Fig. 1, the variation of the dielectric constants observed with reciprocal of absolute temperature was represented by an empirical formula

$$\epsilon_0 = a + \frac{b}{T}$$

where ϵ_0 is the equilibrium dielectric constant, T absolute temperature, and a and b are numerical constants. Numerical values of a and b are given in Table 3.

Table 3. Numerical values for equation $\epsilon_0 = a + b/T$.

	a	b
MEA	-19.562	1.511×10^4
DEA	-7.196	9.658×10^3
AEAA	-8.924	9.007×10^3

The dielectric constant of hydrogen-bonded liquid is expressed by the Kirkwood relation⁷⁾

$$\epsilon_0 = \epsilon_\infty + \frac{3\epsilon_0}{2\epsilon_0 + \epsilon_\infty} \left(\frac{\epsilon_\infty + 2}{3} \right)^2 \frac{4\pi N \rho \mu_0^2}{3MkT} g$$

where ϵ_0 is the equilibrium dielectric constant, ϵ_∞ the limiting dielectric constant at high frequency characteristic of induced polarization which is taken as $1.1n_D^2$, μ_0 the dipole moment of the molecule in vacuum, M the molecular weight, N Avogadro number, ρ the density, and kT means the thermal energy. The correlation factor g is a measure of the short-range intermolecular forces that lead to

Table 4. Kirkwood's correlation factor g of ethanolamines.

Temp., °C	MEA	DEA	AEAA
50	...	1.52	1.46
40	...	1.53	1.45
30	...	1.52	1.47
20	1.70	1.53	1.47
10	1.72	1.52	1.47
0	1.74	1.52	1.48
-10	1.75	...	1.48
-20	1.77	...	1.48
-30	...	...	1.49
-40	...	...	1.49
-50	...	...	1.49

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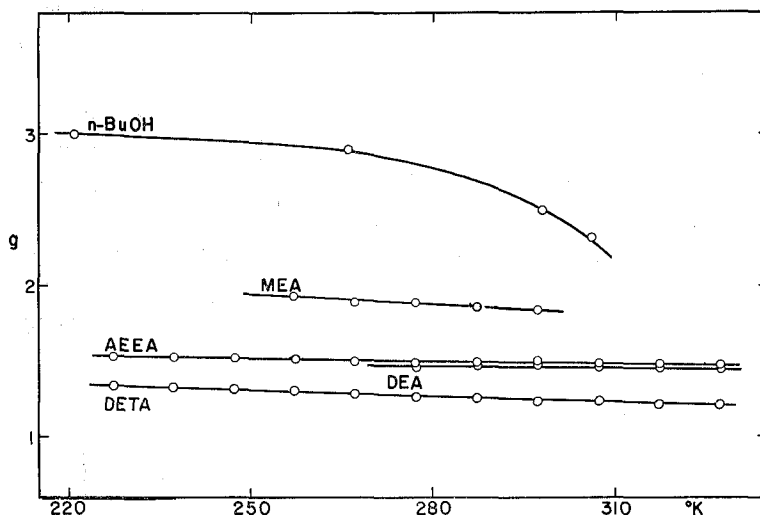


Fig. 2. Plots of Kirkwood's correlation factor g versus temperature for three ethanolamines, n -butanol, and diethylenetriamine.

specific dipole-dipole orientations. In the absence of such forces, g is equal to unity. According to the Kirkwood theory, the g values greater than unity are interpreted as being due to a predominantly parallel alignment of neighboring dipoles; those less than unity to an antiparallel alignment. Kirkwood's g factors for ethanolamine calculated by using the above equation, were tabulated in Table 4 and also compared with those of n -butanol⁸⁾ and diethylenetriamine⁴⁾ in Fig. 2. In ethanolamines the g values are ranging from 1.5 to 2 and approximately independent of temperature. It was considered that the short range interaction force of these compounds are relatively weak although the molecules have more than two functional groups for hydrogen bonding in themselves, or that hydrogen bonded clusters move like one molecule as a whole and cannot be broken by thermal energy in the temperature range studied. Monohydroxyl compounds such as n -alcohols which build up a chain-like structure by $\text{OH}\cdots\text{O}$ hydrogen bonding and are bound each other strongly give larger g values⁹⁾ than those in this case (Fig. 2). Comparatively small Kirkwood's factors in ethanolamines may refer to the following conclusion: first, hydrogen bonding force may be weaker than that of normal alcohols; second, there may be steric hindrance which may interfere with formation of a chain-like structure of alcohols. On the other hand, the g factors are slightly larger than those of ethylenediamine oligomers. This difference may be due to stronger hydrogen bonding of OH group than NH_2 or NH groups.

Dielectric relaxation

The dielectric dispersions of monohydroxyl compounds have been extensively investigated by many workers¹⁰⁾. They concluded that the dispersions were consisted of the principal dispersion characterized by Debye's semi-circle at low frequency and more than two dispersions at higher frequencies. It has been

generally accepted concerning the mechanism of dielectric relaxation that the principal Debye type dispersion takes place by reforming and breaking of hydrogen bonding and that the higher frequency dispersion caused by somewhat like resonance absorption. As to monoethanolamine, on freezing the molecule lost its rotational freedom and the dielectric constant fell abruptly to a much smaller value. Diethanolamine supercooled for a short time, but the whole dielectric dispersion could not be observed because of freezing. In both compounds the wedge type dispersion¹¹⁾ was observed in solid state which was often seen in organic solids. The dielectric properties of aminoethylethanolamine was of much interest, because the dielectric relaxation was observed in a wide range of tem-

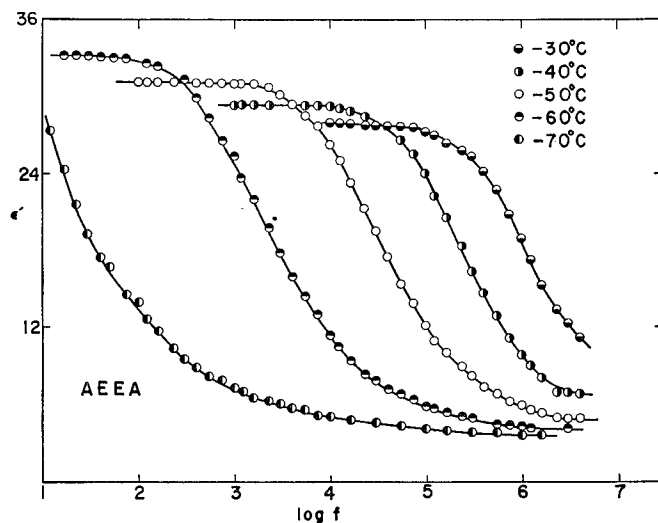


Fig. 3. Frequency dependence of dielectric constants ϵ' for aminoethylethanolamine at various temperatures.

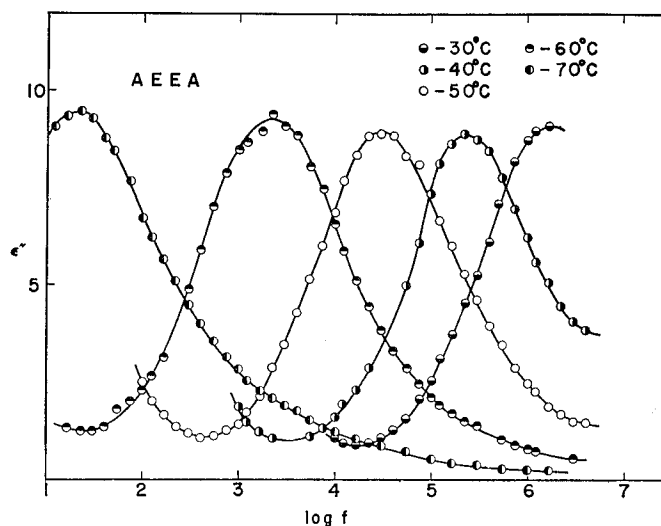


Fig. 4. Frequency dependence of dielectric losses ϵ'' at various temperatures for aminoethylethanolamine.

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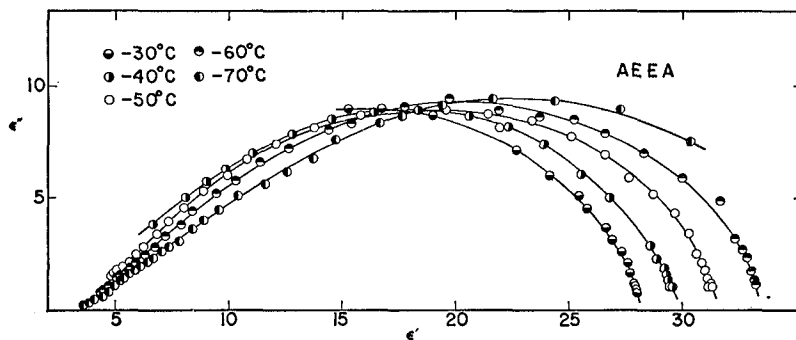


Fig. 5. Complex plane loci of complex dielectric constant ϵ^* for aminoethylethanolamine at various temperatures.

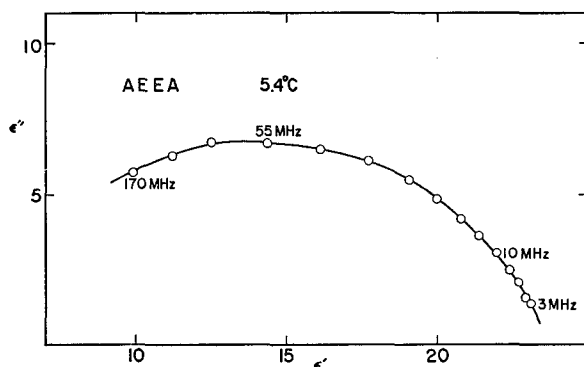


Fig. 6. Complex plane plots of ϵ^* for aminoethylethanolamine at 5.4°C.

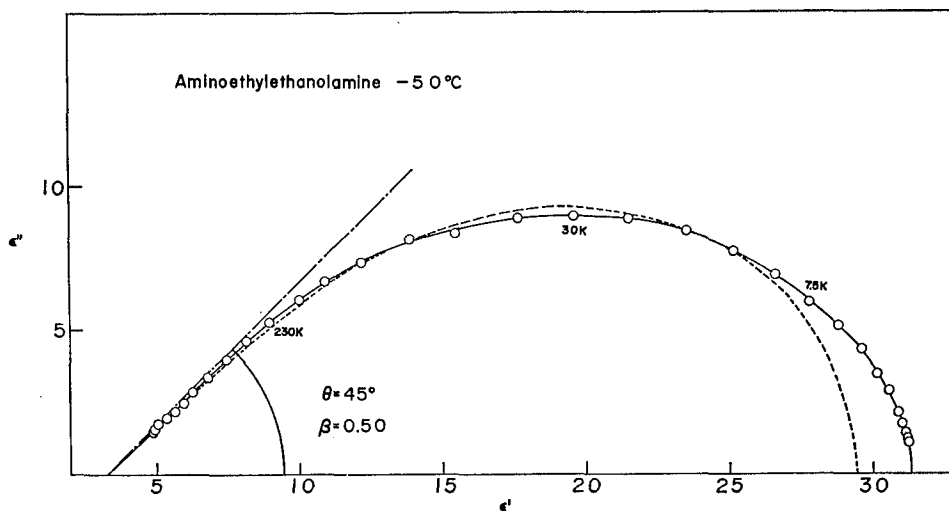


Fig. 7. Comparison between experimental and theoretical loci of complex dielectric constant. The broken line shows the theoretical curve in which β was chosen as 0.5 in the Davidson-Cole equation.

perature with the compound that had hydroxyl, amino, and imino groups. Dielectric dispersion and absorption in AEEA are shown in Figs. 3 and 4, respectively. Fig. 5 illustrates Cole-Cole's plots of complex dielectric constants at different temperatures. The shape of the relaxation was almost the same at a higher temperature, as seen from Fig. 6. The dielectric dispersion spectrum of this compound could not be described simply by any one of the Debye¹²⁾, Cole-Cole¹³⁾, or Davidson-Cole equations¹⁴⁾.

$$\epsilon^* - \epsilon_\infty = \frac{\epsilon_0 - \epsilon_\infty}{1 + j\omega\tau_0} \quad \text{Debye or semi circular equation}$$

$$\epsilon^* - \epsilon_\infty = \frac{\epsilon_0 - \epsilon_\infty}{1 + (j\omega\tau_0)^\beta} \quad \text{Cole-Cole or circular arc equation}$$

$$\epsilon^* - \epsilon_\infty = \frac{\epsilon_0 - \epsilon_\infty}{(1 + j\omega\tau_0)^\beta} \quad \text{Davidson-Cole or skewed arc equation}$$

where ϵ^* is the complex dielectric constant, ϵ_∞ the limiting dielectric constant at high frequency, ω the angular frequency, and τ_0 the mean relaxation time, β the parameter for the distribution of relaxation times. The Cole-Cole plot in Fig. 7 is

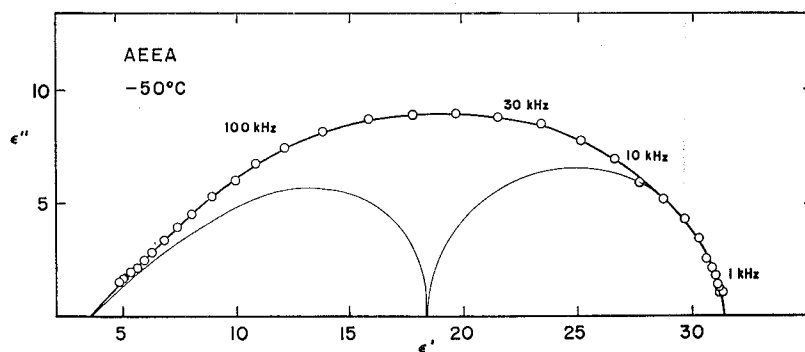


Fig. 8. Complex plane loci of ϵ^* for aminoethylethanolamine. The observed curve is separated into a semi circle and a skewed arc.

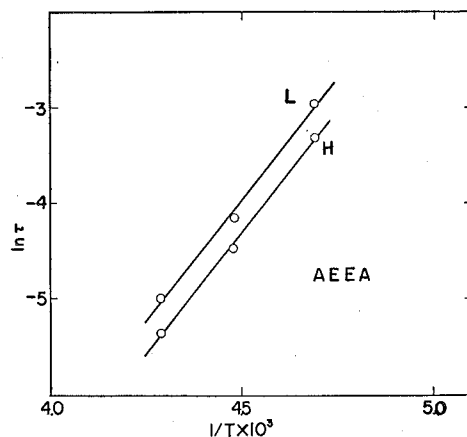


Fig. 9. Arrhenius plots of relaxation times of separated relaxation regions for aminoethylethanolamine. L and H denote relaxation times in low and high frequency relaxations.

very likely to the Davidson-Cole skewed arc, but does not fit this type of dispersion exactly. Particularly at lower frequencies, the observed values of ϵ^* deviated from the theoretical curve. Consequently the relaxation was regarded as the superposition of two dipolar relaxations. The procedure of analysis was as follows: by assuming the Debye equation on the low frequency side, the Debye type relaxation was subtracted from the total dispersion and then the residual was fitted by a dispersion of the Davidson-Cole type. Strictly speaking, the residual dispersion on the high-frequency side showed a slight departure from the theoretical curve. Relaxation times for two dispersions are plotted against reciprocal temperature in Fig. 9. The activation enthalpy and entropy¹⁵⁾ were about 23 kcal/mole and 120 eu, respectively in the low-frequency relaxation process. There was not much difference in these activation parameters between low- and high-frequency relaxation regions. Although the relaxation times of ethanolamines were much greater than those of ethylenediamine oligomers owing to the stronger hydrogen bonding of OH groups, these two different compounds showed the same order of magnitude of the activation parameters.

It was concluded that the Davidson-Cole type dispersion at higher frequencies might be due to the local orientation of polar groups in the molecules and the Debye type dispersion at lower frequencies would be due to the relaxation of molecular reorientation which accompanied the breaking and reforming of the hydrogen bonds.

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