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SOME PHYSICAL PROPERTIES ASSOCIATED WITH THE URETHANE GROUP—I.

N-ETHYL URETHANE

A. T. BULLOCK,* A. M. NORTH† and J. B. SHORTALL
Donnan Laboratories, University of Liverpool, Liverpool

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Abstract—The enthalpy of hydrogen bond formation in N-ethyl urethane is estimated from i.r. and NMR data as about -2kcal.mole^{-1}. From a comparison of the dielectric relaxation properties in the ultra high frequency region with the viscous flow and spectral properties of the N-ethyl urethane, it is concluded that in non-polar solvents dielectric orientation polarization involves the fracture and reformation of long hydrogen-bonded chains of N-ethyl urethane molecules. The activation energies for dielectric relaxation and for viscous flow in undiluted N-ethyl urethane are both 6·5 kcal.mole^{-1}. In ethereal or ester solvents N-ethyl urethane hydrogen-bonds to the solvent and the activation energies for flow and dielectric reorientation processes are reduced; it is suggested that urethane solvent interactions are most important in determining flow or dielectric orientation processes. Dipole moments and NMR chemical shifts for N-ethyl urethanes are also reported.

INTRODUCTION

AN IMPORTANT class of synthetic elastomers exists in which long chain molecules are cross-linked by thermally labile bonds or short chains. These materials are thermoplastic, although they exhibit many of the properties of permanently cross-linked or vulcanized elastomers in the cold. The polyurethane elastomers form one group of such compounds, and in this case the interchain cross-links are thought to be a direct result of NH to O = C hydrogen bonding between urethane chain segments.

In polyurethanes prepared from polyether or polyester diols, the urethane segments may be surrounded by polyether or polyester segments, depending on the other constituents of the polymer chain, or may be in a urethane-rich region if there is any tendancy for phase separation on a submicroscopic scale. Consequently before meaningful observations can be made on polymers of complex composition, it is desirable to study the hydrogen bonding properties of the urethane group in a well-controlled environment. We are not aware of any such studies reported in the literature.

In order to measure some basic properties of the urethane group, we have chosen N-ethyl urethane (ethyl N-ethyl carbamate, $C_2H_5NHCOOC_2H_5$), and carried out an examination of concentrated solutions of N-ethyl urethane in a non-polar solvent (carbon tetrachloride), in ethyl propionate and in 1,2, dimethoxy ethane.

In this work considerable emphasis is on the dielectric properties of the N-ethyl urethane, and these are discussed with reference to certain i.r., NMR, and viscosity observations.

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* Present address: Department of Chemistry, University of Aberdeen, Aberdeen.

† Present address: Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow, C.1.

Hydrogen bonded systems such as urethanes or N-substituted amides(1–3) can exhibit a variety of polarization phenomena,(4–8) any of which could give rise to dielectric relaxation phenomena in the ultra high frequency or microwave region of the electromagnetic spectrum. Dielectric measurements are readily made at these frequencies using a transmission method with the sample contained in the dielectric space of a coaxial or rectangular wave-guide.

EXPERIMENTAL

Materials

Carbon tetrachloride, ethyl propionate and 1,2, dimethoxy ethane were dried and fractionally distilled through a 3 in. column immediately before use. (b.p. 77°, 99°, 85° respectively at 760 Torr). N-Ethyl urethane (Eastman Organic Chemicals) was fractionally distilled under reduced pressure immediately before use (b.p. 80° at 18 Torr). No impurities could be detected by gas liquid chromatography.

Dielectric measurements at 1592 Hz. These were carried out using a Wayne–Kerr B221 transformer ratio arm bridge. The sample was contained in a concentric cylinder rhodium-surfaced cell (Tinsley 4536-A) fitted with a guard ring. *Dielectric measurements between* 10^8 and 3×10^9 *Hz.* These were made using a General Radio type 900-LB precision slotted line. This device[9] can measure voltage standing wave ratios (VSWR) as low as $1\cdot00+0\cdot001\,f_{\mathrm{GHz}}$ at frequencies up to 9 GHz.

Plots of standing wave ratio against liquid depth were constructed. The real and imaginary parts of the complex dielectric constant were then evaluated from the value of the VSWR at the first minimum and maximum as described by Rao.(10) When sufficient maxima and minima were available the calculation was carried out using the values at successive maxima and minima as detailed by Poley.(11)

At the lowest frequencies studied, the slotted line was replaced by an admittance meter (General Radio 1602-B) and the standing wave ratio was obtained from measurements of the reflectance coefficient. In general, standing wave ratios could be measured with an accuracy of better than 1 per cent using the slotted line and of 5 per cent using the admittance meter. The uncertainties in the derived values of ϵ', ϵ'' depend on the values of the loss tangent as well as on frequency. Indeed at high loss values the ambiguity predicted by Rao(10) at sample depths corresponding to quarter wavelengths was observed. The considerable uncertainties caused by this are covered in the discussion section of the paper.

The experimental method used to determine ϵ' and ϵ'' at 9·5 GHz was basically that described by Poley.(11) The principal, and considerable, advantage of this technique lies in the fact that it is unnecessary to determine the phase of the standing-wave pattern. This measurement is a common feature in most other microwave techniques involving reflection methods and is perhaps the greatest single factor contributing to inaccuracies.

The microwave sample cell was designed so that the depth of liquid above a fixed short-circuit could be altered rapidly and continuously by displacement from a storage cylinder. This displacement was effected by inserting a cylindrical plunger into the liquid in the reservoir. The diameters of the plunger and storage cylinder were such that a given linear displacement of the plunger gave rise to a calculable change in liquid depth. The plunger displacement was measured by a dial gauge which could be read to within 0·001 cm.

Refractive indices were measured at room temperature using an Abbé refractometer.

Infra-red spectra were obtained using a Perkin–Elmer 125 Spectrophotometer.

Proton magnetic resonance spectra were kindly measured by Dr. J. Feeney of Varian Associates Ltd. on A60 and H.R.100 spectrometers.

Liquid viscosities were measured using Ubbelohde suspended level viscometers, and the densities in a calibrated dilatometer.

Low temperature experiments were carried out in a Townson & Mercer −70° bath.

RESULTS

Infra-red data

The i.r. spectrum of undiluted N-ethyl urethane at 20° in the N—H stretching region exhibits absorptions due to both free N—H (3428 cm^{-1}) and bonded N—H (3345 cm^{-1}). The relative importance of the bonded species decreases with dilution in carbon tetrachloride as would be expected. The N—H stretching frequencies of a 50 volume per cent mixture of ethyl urethane and carbon tetrachloride have been examined at temperatures between 17° and 74°. The relative importance of the free N—H absorption increases with increasing temperature, and the changes in concentration of each species (assuming temperature independent extinction coefficients) correspond to $\triangle$H of hydrogen bond formation of $-2\cdot2 \pm 0\cdot4$ kcal.mole^{-1}.

The i.r. spectra of mixtures in dimethoxy ethane and ethyl propionate show only a single N—H stretching absorption at 3338 cm^{-1}. The inference is that in these systems the N—H protons are almost completely hydrogen bonded.

Proton magnetic resonance data

The NMR spectrum of N-ethyl urethane, has been measured at 60 MHz at 37°. The chemical shifts are measured in Hz relative to hexamethyl disilane. The spectrum consists of two superimposed methyl triplets centred about 60 Hz, a doublet of quartets at 187 Hz due to the methylene neighbouring the N—H group, a single quartet at 240 Hz due to the methylene neighbouring the oxygen atom and a broad absorption due to the N—H proton which in this spectrum occurs at 373 Hz.

The position of the N—H resonance was dependent on both dilution and temperature. A series of spectra were recorded in which the temperature was varied and the N-ethyl urethane was progressively diluted with carbon tetrachloride. The chemical shifts of the N—H resonance are recorded in Table 1.

TABLE 1. CHEMICAL SHIFTS OF N—H PROTON MAGNETIC RESONANCE

Temperature (°C)	Vol. per cent Urethane in CCl_4	Chemical shift (Hz)
37	100	376
37	100	373
150	100	316
37	50	357
37	50	358
70	50	339
37	2	274

The chemical shift of 274 Hz obtained in the dilute solution must correspond to free N—H. However, it is not possible to obtain the frequency shift for bonded N—H since its concentration in 100 per cent N-ethyl urethane is unknown. On the other hand, if we make the assumption that the observed chemical shift in a rapidly interchanging system varies in a linear fashion with the composition, we can obtain the enthalpy difference between free and bonded protons. This is $-2\cdot0 \pm 0\cdot2$ kcal. mole^{-1} in N-ethyl urethane itself, and $-1\cdot7 \pm 0\cdot2$ kcal.mole^{-1} in 50 per cent carbon tetrachloride solution.

Irradiation of a sample (in a 100 MHz instrument fitted with spin decoupling facilities) at the N—H resonance frequency caused the doublet of quartets due to the α methylene to collapse to a single quartet. This confirmed that the original splitting was due to coupling to the N—H proton, and sets on upper limit of $\sqrt{2}\,\pi J$ (where J is the spin–spin coupling constant) to the rate of any N—H proton intermolecular exchange process.

The 60 MHz NMR spectrum of the mixture (50% v/v in ethyl propionate) shows all the features of the individual components with the N—H proton resonance centred at 358 Hz with respect to hexamethyldisilane. Comparison of this frequency with those reported in Table 1 shows that although the N—H protons are more extensively hydrogen bonded than in pure N-ethyl urethane, the chemical shift is smaller. Consequently, again it seems likely that the hydrogen bonding is predominantly to the ester molecules.

Activation energies for viscous flow

When the viscosities of liquid N-ethyl urethane between −60° and +60° are expressed in the Arrhenius form, the activation energy for viscous flow is 6·5 ± 0·2 kcal.mole^{-1}. For pure carbon tetrachloride the Arrhenius activation energy is 2·5 kcal.mole^{-1} whereas for mixtures containing 60% and 40% v/v N-ethyl urethane the values are 5·1 kcal.mole^{-1} and 4·0 kcal.mole^{-1} respectively. The viscosities of the N-ethyl urethane–ester mixture (50% v/v) are less than those of the carbon tetrachloride mixture, and correspond to an activation energy for viscous flow of 3·1 kcal. mole^{-1}. The corresponding figure for a 50% v/v mixture in dimethoxy ethane is 2·5 kcal.mole^{-1}. These compare with values of 1·7 kcal.mole^{-1} and 2·0 kcal.mole^{-1} respectively for the pure solvents.

Dielectric relaxation

(a) *The solvents.* The three solvents, carbon tetrachloride, ethyl propionate and 1,2-dimethoxy ethane were examined first at temperatures between +60° and their melting points. No dielectric relaxation could be detected in carbon tetrachloride at any frequency up to 9·5 GHz at any temperature.

Pure 1,2-dimethoxy ethane exhibited no dielectric relaxation up to 9·5 GHz at 60° (the real part of the dielectric constant ϵ' was 6·5) or up to 3·0 GHz at 30° (ϵ' was 7·2). However, appreciable relaxation occurs at the higher frequencies at −35°, and this is illustrated as a plot of the imaginary part of the dielectric constant ϵ'', against frequency in Fig. 1.

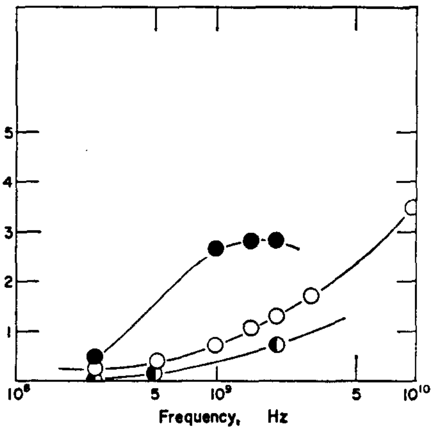

FIG. 1. ϵ'' for ethyl propionate and 1, 2, dimethoxy ethane. ○1,2, dimethoxy ethane at −35°; ◐ ethyl propionate −20°; ● ethyl propionate at −70°.

Pure ethyl propionate exhibited no relaxation up to 9·5 GHz at +60° (ϵ' was 4·8) or at +30° (ϵ' was 5·25). However at −20° the value of ϵ' (6·3 at low frequencies) starts to decrease above 2·0 GHz. Appreciable relaxation over the complete range of frequencies studied was observed at −70°. At this temperature the very low frequency value of ϵ' is 8·0, and the higher frequency values decrease from 8·0 at 250 MHz to 6·7 at 2·0 GHz. The values of ϵ'' at −20° and 70° are illustrated in Fig. 1.

(b) *Undiluted N-ethyl urethane.* Values of ϵ' and ϵ'' for undiluted N-ethyl urethane are illustrated in Figs. 2 and 3. Data are presented as a function of frequency for four temperatures between −20° and 60°. The low frequency dielectric constants (called ϵ_0 and measured at 1592 Hz) and the optical frequency dielectric constant at room temperature (ϵ_{opt}), are also presented in Fig. 2. It can be seen that the dielectric constant is very temperature dependent, and that almost the whole contribution to the polarization relaxes out in this frequency region.

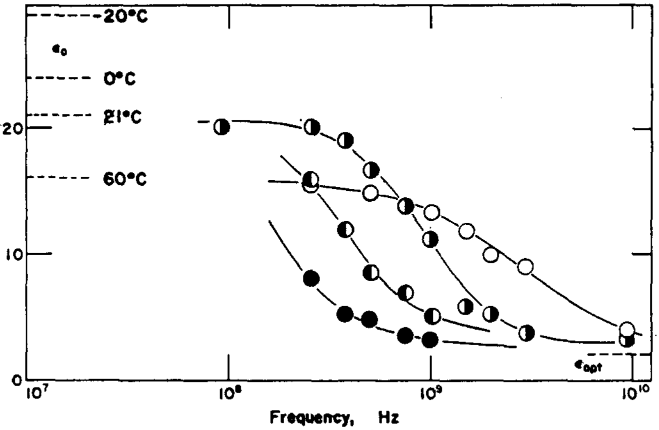

FIG. 2. ϵ' against frequency. ○ 60°; ◑ 21°; ◐ 0°; ● −20°.

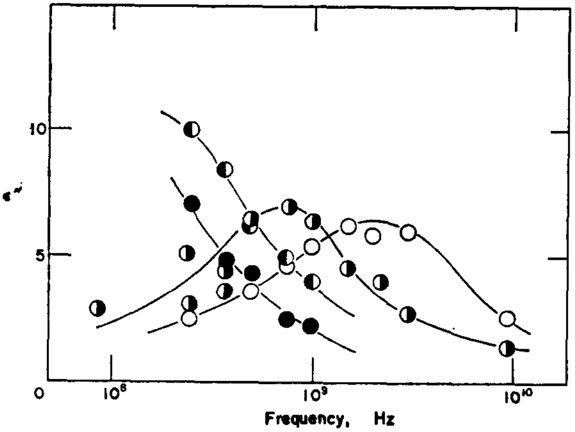

FIG. 3. ϵ'' against frequency. ○ 60°; ◑ 21°; ◐ 0°; ● −20°.

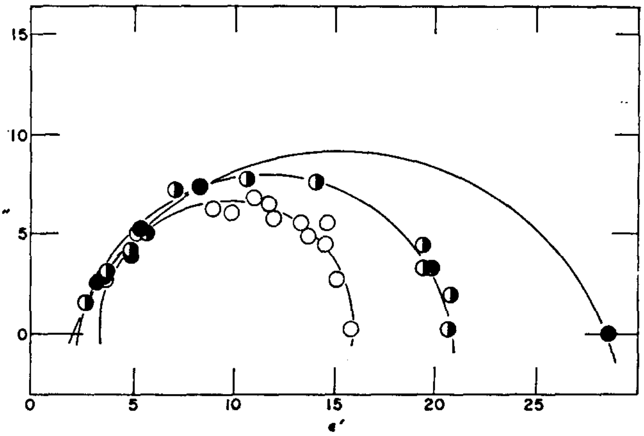

FIG. 4. ϵ'' against ϵ' (Cole–Cole plot). ○60°; ◑ 21°; ● −20°.

Cole–Cole plots(12) in which ϵ'' is plotted against ϵ' are illustrated in Fig. 4. The The Cole–Cole distribution parameter, β, is 1·0, 0·86 and 0·76 at 60°, 21° and −20° respectively.

An Arrhenius plot of the relaxation times ($7{\cdot}5\times10^{-11}$, $2{\cdot}2\times10^{-10}$, $4{\cdot}1\times10^{-10}$ and $1{\cdot}74\times10^{-9}$ sec at 60°, 21°, 0° and −20° respectively) gives an activation energy for the loss process of 6·5 ± 1·0 kcal.mole^{-1}. The estimated uncertainty in the values is 15 per cent.

The calculated effective dipole moments for N-ethyl urethane observed in the pure liquid and also in solution in carbon tetrachloride are listed in Table 2. The calculations were made using the Onsager equation, and show an apparent variation with temperature and dilution.

TABLE 2. EFFECTIVE DIPOLE MOMENTS

Solution	Temperature (°C)	μ_{eff}.
N-ethyl urethane	60	2·95 D
	21	3·03 D
	0	3·01 D
	—20	3·80 D
50/50 v/v N-ethyl urethane in carbon tetrachloride	60	3·88 D
	30	3·99 D
	−35	6·27 D
15/85 v/v N-ethyl urethane in carbon tetrachloride	60	4·12 D
	30	4·41 D
	−20	4·64 D

(c) *N-Ethyl urethane–carbon tetrachloride mixtures.* The dielectric parameters, ϵ' and ϵ'', for two solutions of N-ethyl urethane in carbon tetrachloride (50% v/v and 15% v/v) are illustrated in Figs. 5 and 6. It can be seen that relaxation regions occur at frequencies similar to those observed for pure N-ethyl urethane. However the relaxation times at any temperature decrease with dilution. The relaxation times (τ_1) at the different temperatures are summarized in Table 3, and yield an Arrhenius activation energy of $6 \cdot 0 \pm 1 \cdot 0$ kcal.mole^{-1}.

TABLE 3. DIELECTRIC RELAXATION TIMES OF MIXTURES

Solvent	Volume per cent N-ethyl urethane	Temp. (°C)	$\tau_1 \times 10^{10}$ (sec)
Carbon tetrachloride	50	60	1·1
		30	2·7
		−35	93
	15	60	0·34
		30	1·60
		−20	3·5
Ethyl propionate*	50	60	(0·4)†
		30	2·6
		−20	10
		−70	27
	15	60	0·1
		30	0·4
		−35	15
		−70	10
1,2- Dimethoxy ethane*	50	60	(0·5)†
		30	1·0
		−35	(5·0)†
		−70	100
	15	60	0·20
		30	0·60
		−35	2·0

* For an idealized Debye relaxation. In these cases the τ_1 values have only limited significance.
† Resolution not precise in these cases.

(d) *N-Ethyl urethane–ethyl propionate mixtures.* Values of ϵ' and ϵ'' for mixtures of N-ethyl urethane and ethyl propionate (50% v/v and 15% v/v) are illustrated in Figs. 7 and 8. At 60° the Cole–Cole plots of these results are semi-circular, indicating that the relaxation is predominantly due to a single process. However, at low temperatures the relaxation becomes spread over a relatively wide frequency range.

(e) *N-Ethyl urethane*—1,2-*dimethoxy ethane mixtures.* Values of ϵ' and ϵ'' for mixtures of N-ethyl urethane of ϵ' and ϵ'' for mixtures of N-ethyl urethane and 1,2-dimethoxy ethane (50% v/v and 15% v/v) are illustrated in Figs. 9 and 10. Again the relaxation seems to involve more than one process.

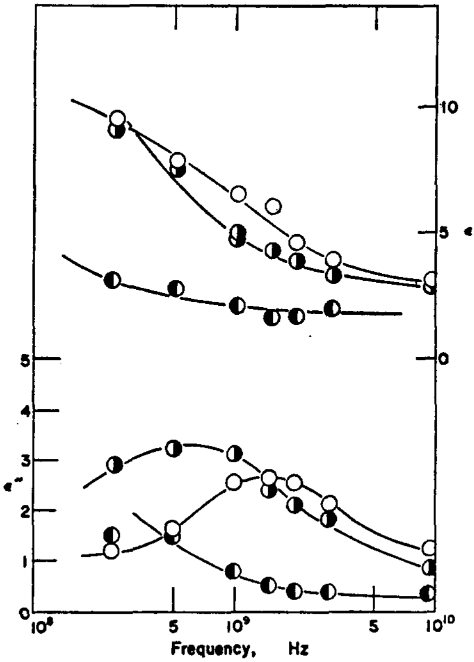

FIG. 5. ϵ' and ϵ'', N-ethyl urethane: carbon tetrachloride 50/50 v/v. ○60°; ◑ 30°; ◐ −35°.

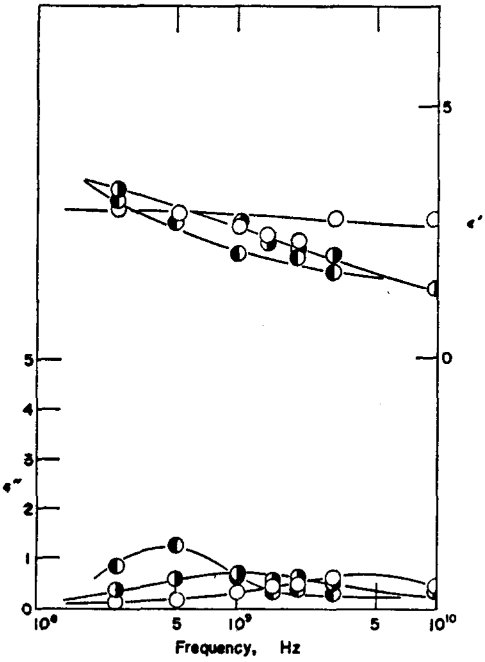

FIG. 6. ϵ' and ϵ'', N-ethyl urethane: carbon tetrachloride 15/85 v/v. ○ 60°; ◑ 30°; ◐ −20°.

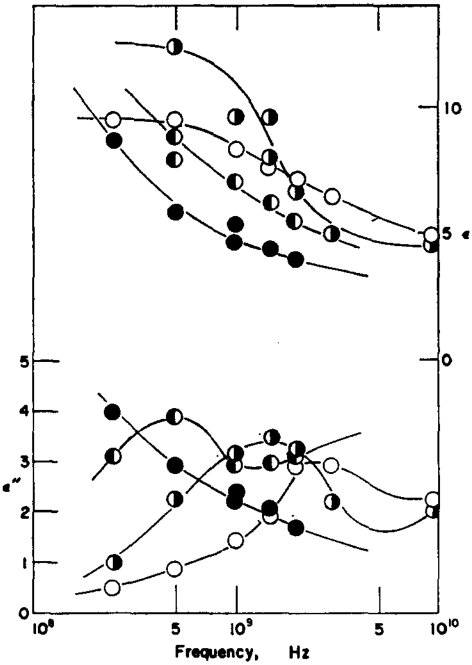

FIG. 7. ϵ' and ϵ'', N-ethyl urethane: ethyl propionate 50/50 v/v. ○ 60°; ◑ 30°; ◐ −20°; ● −70°.

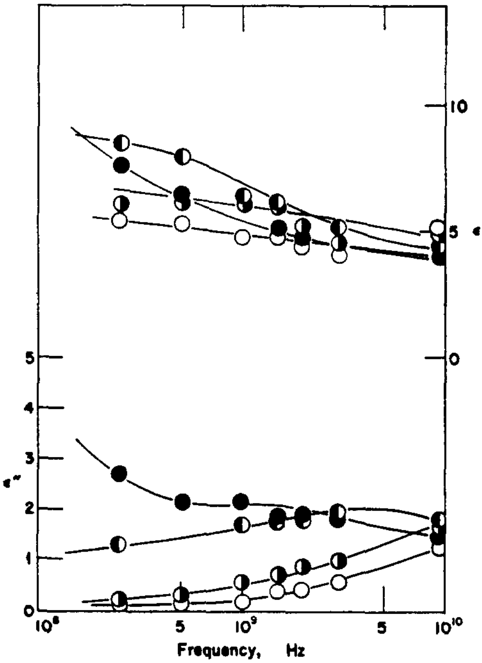

FIG. 8. ϵ' and ϵ'', N-ethyl urethane; ethyl propionate 15/85 v/v. ○ 60°; ◑ 30°; ◐ −35°; ● −70°.

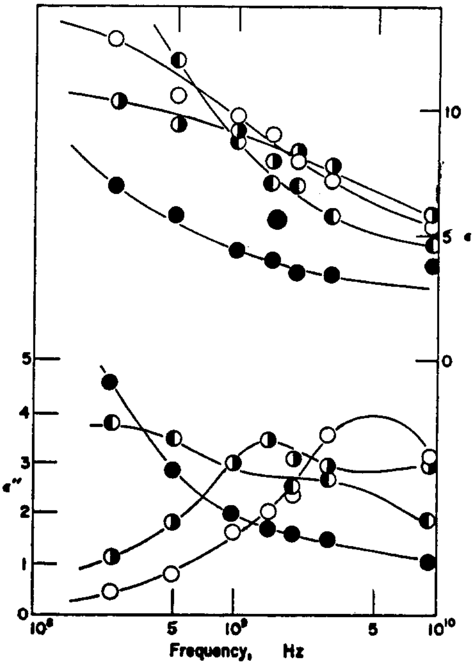

FIG. 9. ε′ and ε″, N-ethyl urethane: dimethoxy ethane 50/50 v/v. ○ 60°; ◑ 30°; ◐ −35°; ● −70°.

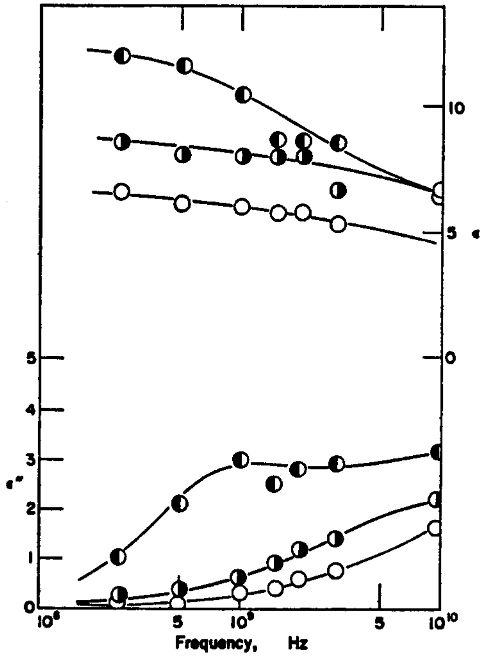

FIG. 10. ε′ and ε″, N-ethyl urethane: dimethoxy ethane 50/50 v/v. ○60°; ◑ 30°; ◐ −35°.

DISCUSSION

The i.r. and NMR observations are consistent with a system in which NH to O=C hydrogen bonding occurs with a hydrogen bond ethalpy of about -2 kcal.mole^{-1}. There is nothing unusual in the spectra, and the details are reported solely because these are the first published measurements of the hydrogen bond strengths in such systems. It is worthy of note that such bond strengths are just over half the magnitude in N-mono-substituted amides.

In discussing the dielectric results, it is necessary first to comment on the significance of the measurements. N-ethyl urethane exhibits a large dielectric loss in the relaxation region. This causes the appearance of an ambiguity in the determination of ϵ'' for medium and high loss liquids first mentioned by Rao,(6) and leads to a large uncertainty in certain values of ϵ''. The tabulated functions or factors listed by Rao become an appreciable fraction of the observed values at tan δ (loss tangent) values greater than 0·5. Furthermore there is an ambiguity in the values of ϵ'' calculated from observations made on sample depths corresponding to a quarter wavelength. When the dielectric constant and frequency were sufficiently high and the loss sufficiently low that measurements could be taken over a large number of quarter wavelengths, this ambiguity could be resolved with certainty. However at the lowest frequencies, measurements could be made only up to one quarter of a wavelength sample length by reason of sample geometry. Under these circumstances, at the highest and lowest losses, the ambiguity was resolved since one possibility was patently absurd. However at medium losses the ambiguity could not be resolved, and occasionally neither alternative agreed well with a smooth curve through the experimental points. This is typically exemplified by the ϵ'' values in Fig. 2 at 21° at 90, 250 and 375 GHz to which we would apply only 25 per cent confidence limits. Consequently, although the apparatus is the most precise currently available or in use, the ϵ'' values are considerably less certain than in the case of other hydrogen-bonded systems studied in solution.(13) We are not aware of any other comparable work where the appearance of this ambiguity, or the use of correction functions at the extreme limit of those tabulated by Rao, have been emphasised. In our view, interest in the system as it stands warrants the presentation of the ϵ'' values despite these uncertainties.

(a) *Undiluted N-ethyl urethane*

There are at least seven dielectric polarization processes which can be postulated in N-ethyl urethane. The elimination of most of these involves lengthy arguments, but the processes which best fit all known observations involve rotational rearrangement of hydrogen-bonded aggregates or chains of molecules, either in their entirety, or with concomitant fracture and reformation.

The presence of hydrogen bonded chains of urethane molecules seems almost unquestionable. The low frequency dielectric constant is high, and decreases markedly with increasing temperature or with dilution by a non hydrogen bonding solvent. Indeed the concentration-dependent changes in dielectric constant or dipole moment of dilute solutions in carbon tetrachloride cannot be fitted to Debye or Looyenga(14) equations for two-component systems. These dielectric features, and observed moments of 3–4 D are also encountered in N-substituted amides,(1,2) in which such chains are believed to exist. The very high viscosity and activation energy for viscous flow are further evidence for the presence of such chains.

If it is accepted that the high dielectric constant of the liquid ethyl urethane is a direct consequence of the existence of these hydrogen-bonded chains, and since almost the whole contribution to the dielectric constant relaxes out in the frequency region of interest, the relaxation must be related to a polarization process of the chains. The chains consist of a large number of N—H - - - O—C units joined head to tail, and so must have a large dipole moment. Polarization can occur either by rotating the whole chain, or by a process in which the chain fractures into smaller units, these are oriented by the electric field, and join other fragments to reform larger units in the aligned position.

It is not easy to decide which of these two processes is more likely to be taking place, and in this context it is relevant to discuss the mechanism for viscous flow. In dilute solutions of stable long chain molecules, the activation energy for viscous flow is usually very close to that of the solvent. In these cases the long chain molecules are rotated and deformed in the shear gradient. On the other hand, in concentrated solutions or in polymer melts where extensive chain entanglement occurs, the activation energy for viscous flow can be very large indeed and may be measured in tens of kilocalories. If we assume that energies of similar magnitude would be required to "untangle" chains in the urethane system, it becomes apparent that the simplest process in tangled chains of very low bond strengths is simply chain fracture. The very close similarities which exist between the temperature dependence of viscous flow and of dielectric relaxation in all the systems studied suggest that this indeed is the mechanism of dielectric orientation polarization.

(b) *Solutions of N-ethyl urethane in ethyl propionate and* 1,2 *dimethoxy ethane*

The existence of at least two major relaxation regions is obvious from Figs. 7–10.

The measurements on the pure solvents show that—at all except the lowest temperatures—the dielectric relaxation associated with orientation polarization occurs at frequencies greater than 10^{10} Hz. Consequently, there can be little doubt that of the major processes observed in the liquid mixtures, the high frequency relaxation is characteristic of the solvent, while the low frequency relaxation is related to the presence of N-ethyl urethane. Because only the low frequency side of the solvent relaxation falls within the scope of these measurements, it is the low frequency process (associated only with the presence of N-ethyl urethane) which is of prime interest.

In order to resolve the observed relaxation in terms of two (solvent-dependent and N-ethyl urethane-dependent) processes, it is necessary to know the mathematical relationship descriptive of each process. In systems of this complexity such relationships are unknown.

As a preliminary semi-quantitative examination of the system we have analysed the data in terms of two independent Debye processes when, for the imaginary component

$$\frac{\epsilon''}{\epsilon_0+\epsilon_\infty} = \frac{C_1\omega\tau_1}{1+\omega^2\tau_1^2} + \frac{C_2\omega\tau_2}{1+\omega^2\tau^2} \tag{1}$$

where ϵ_0, ϵ_∞ represent the values of the dielectric constant at very low, and very high frequencies respectively, τ_1 and τ_2 are the relaxation times of each process and

C_1 and C_2 are the corresponding weight factors. Final values of τ_1, τ_2, C_1, C_2 were obtained by an iterative procedure in which the sum of the squared differences on ϵ'' were minimized.

In terms of this analysis the hypothetical relaxation times, τ_1, for the idealized urethane-dependent process were obtained and are also listed in Table 3.

These idealized values correspond to Arrhenius activation energies of $4 \cdot 0 \pm 0 \cdot 4$ kcal.mole^{-1} in ethyl propionate and $3 \cdot 3 \pm 0 \cdot 3$ kcal.mole^{-1} in 1,2 dimethoxy ethane.

Obviously an analysis in terms of two Debye processes is a gross oversimplification. We present it here only because it does give the suggestion that the activation energy for the N-ethyl urethane polarization process is lessened by the presence of an ethereal or ester solvent. The same suggestion is obtained from other analyses in terms of any two empirical relaxation functions. Since this suggestion is in line with the effect of these solvents on viscous flow, it seems that we can give it qualitative (though not quantitative) significance.

The conclusion can then be drawn that in the ester or ether environment the urethane exists predominantly H-bonded to solvent, and the orientation or polarization of a urethane-solvent "dimer" is only slightly less facile than that of a solvent molecule. On the other hand, in carbon tetrachloride solution the urethane groups exist as long hydrogen-bonded chains, orientation polarization of which is not easy.

This conclusion is of considerable relevance to the behaviour of polyurethanes, since it suggests that in chains containing a high proportion of ether or ester groups, the properties which depend on segmental orientation processes are more likely to be governed by urethane–ether or urethane–ester interactions than by urethane–urethane interactions.

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Résumé—D'après les données de l'i.r. et de la RMN, on estime l'enthalpie de formation d'une liaison hydrogène dans les N-éthyluréthans à environ—2 kcal/mole. Une comparaison entre les propriétées de relaxation diélectrique dans le domaine des hyperfréquences et l'écoulement visqueux et les propriétés spectrales du N-éthyluréthane permettent de conclure que dans les solvants non polaires, la polarisation par oreintation diélectrique met en jeu la rupture et la restauration de longues chaines de molécules de N-éthyluréthane liées par liaisons hydrogènes. Les énergies d'activation de la relaxation diélectrique et de l'écoulement visqueux sont toutes deux de 6,5 kcal/mole pour le N-éthyluréthane non dilué. Dans les solvants à fonction éther out ester le N-éthyluréthane se lie par liaison hydrogène au solvant et les énergies d'activation de l'écoulement et de la réorientation diéelectrique se trouvent réduits. Il est suggéré que les interactions uréthane-solvant sont d'importance primordiale pour déterminer les processus d'écoulement et d'orientation diélectriques.

On présente également des données sur les moments dipolaires et des déplacements de bandes de RMN dans les N-éthyluréthanes.

Sommario—L'entalpia della formazione del legame idrogeno del N-etil-uretano risulta in base ai dati ottenuti col metodo dello infrarosso e della risonanza magnetica nucleare di circa -2 kcal.mole^{-1}. Da un confronto delle proprietà di attenuazione della constante dielettrica nello spettro delle ultrafrequenze con la viscosità e le proprietà spettrali del N-etil-uretano, si è concluso che nei solventi apolari la polarizzazzione dell'orientamento dielettrico comporta la rottura e la ricostituzione di lunghe catene con legame idrogeno di molecole di N-etil-uretano. L'energia di attivazione della attenuazione dielettrica e della viscosità relative al N-etil-uretano non diluito è per entrambe di 6·5 kcal.mole^{-1}. Nei solventi a base di eteri o esteri i legami idrogeno del N-etil-uretano con il solvente e l'energia di attivazione della viscosità e della riorientazione dielettrica sono ridotte; si suppone che l'interazione dell'uretano con il solvente sia quanto mai importante nel determinare la viscosità o l'orientazione dielettrica. Inoltre sono state riscontrate variazioni chimiche dei momenti dipolari e della risonanza magnetica nucleare nei N-etil-uretani.

Zusammenfassung—Aus- i.r. und NMR-Messungen wird die Bildungs-Enthalpie der Wasserstoffbrückenbindungen von N-Äthylurethan auf etwa—2kcal/mol abgeschätzt. Ein Vergleich der dielektrischen Relaxationseigenschaften im Ultra-Hochfrequenzbereich mit den Viskositäts- und spektralen Eigenschaften von N-Äthylurethan läßt darauf schließen, daß die dielektrische Orientierungspolarisation in nicht-polaren Lösungsmitteln mit einer Spaltung und Rückbildung von lagen, durch Wasserstoffbrücken verbundenen Ketten der N-Äthylurethanmole-küle einhergeht. In verdünntem N-Äthylurethan beträgy die Aktivierungsenergie sowohl für die dielektrische Relaxation als auch für das Fließverhalten 6·5 kcal/mol. In Äthern und Estern als Lösungsmittel bestehen Wasserstoffbrückenbindungen des N-Äthylurethans zum Lösungsmittel und die Aktivierungsenergie für Fließ- und dielektrische Reorientierungsprozesse ist verringert. Es wird vorgeschlagen, daß die Wechselwirkungen Urethan-Lösungsmittel eine wesentliche Rolle für das Fließverhalten und die dielektrischen Orientierungs-Prozesse spielen. Es werden ferner für N-Äthylurethan Dipolmomente unde die chemischen Verschiebungen für NMR angegeben.