acid strength of ROH and the ratio [ROH]/[H_2O] in the solvent mixture. The extent to which the carbanion is formed in the equilibrium step of the process (Step 1) undoubtedly depends upon the base level of the system, and a decrease in basicity would, therefore, cause a decrease in rate. It is tentatively suggested that in methanol–water mixtures, the influence of methanol in decreasing the basicity over the entire range of composition is sufficient to more than compensate for the expected increase in rate due to decreasing dielectric constant. It seems logical to assume that ethanol is a weaker acid than methanol and hence has less influence on the basicity. We may assume, at low ethanol concentrations, that the dielectric constant effect is predominant, but that at the higher concentrations the decreased basicity brings about a decrease in rate, thereby accounting for the observed maximum in the rate constants as a function of ethanol composition. The fact that rate constants in the alcohol–water mixtures extrapolate smoothly to the rate constants for reaction with alkoxyl ion in the anhydrous alcohols supports this explanation. Accurate information on acid-base levels in ethanol–water and methanol–water mixtures is sorely needed and is being sought in this laboratory.

Summary

1. The rate of reaction of ethylene chlorohydrin with hydroxyl ion (or with alkoxyl ion) has been measured in 1,4-dioxane–water, methanol–water, ethanol–water, isopropanol–water and *t*-butanol–water mixtures at 30° up to high concentrations of the non-aqueous solvent. Measurements in anhydrous ethanol and methanol are included. For the first three solvent mixtures, rate measurements were also made at 0 and 15°.

2. In methanol–water mixtures, the reaction rate decreased continuously with increase in methanol concentration. With the addition of ethanol to water, the rate at first increased, reached a maximum value at about 38% ethanol (30°), and then decreased at higher ethanol concentrations. In the other solvent mixtures, the rate increased with a decrease in dielectric constant over the entire range of solvent composition.

3. It has been established that ethylene oxide is the principal reaction product in all of the solvents used, including anhydrous ethanol and anhydrous methanol.

4. The Winstein–Lucas mechanism which postulates an initial equilibrium step in which a proton is removed from the chlorohydrin to form an anion, followed by an intramolecular displacement of chloride by the negatively charged oxygen, is consistent with (a) the bimolecular character of the reaction, (b) the absence of an appreciable kinetic salt effect, (c) the formation of ethylene oxide as the principal product, and (d) the increase in rate with decrease in dielectric constant is the principal factor influencing the rate. This mechanism is also capable of giving a qualitative explanation of the unusual results obtained in methanol–water and ethanol–water mixtures by taking into account the possible influence of the acid–base level in these solvents upon the initial equilibrium step.

PITTSBURGH 13, PENNSYLVANIA

RECEIVED FEBRUARY 5, 1948

[CONTRIBUTION FROM BELL TELEPHONE LABORATORIES, INC.]

Measurements on the Absorption of Microwaves. III. Losses of Camphor Dissolved in Cyclohexane

BY D. H. WHIFFEN[1]

The general outline of the type of absorption of electromagnetic radiation of about a centimeter wave length by mobile liquids and solutions has already been established.[2,3] Before investigating some of the details or exceptional systems, it was thought profitable to measure one system carefully; such a system may also be useful for comparing various methods of measurement.

Solutions of camphor in cyclohexane seem to have several advantages for this purpose. Firstly, the use of solutions makes a large range of loss tangents available according to the concentration employed. Secondly, cyclohexane is easily purified so as to give an almost negligible loss; this is in contrast to benzene which is difficult to keep dry. Thirdly, camphor was chosen because of its large dipole moment, its rigidity, its high solubility, the ease of purification by sublimation, and because preliminary experiments had indicated that its solutions in cyclohexane obeyed the Debye loss curve[4] with a relaxation time of 7×10^{-12} sec., which corresponds to a maximum loss at 1.3 cm. wave length.

Experimental

Cavities.—The loss tangents were obtained from the Q of a cavity resonator completely filled with the test liquid. The details of the resonator used at 3.3 cm. are shown in Fig. 1. This is a cylindrical cavity which can be resonant in the $H_{1,1,2}$ mode[5] when filled with a liquid

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(1) Present address: St. John's College, Oxford, England.

(2) Whiffen and Thompson, *Trans. Faraday Soc.*, **42A**, 114 and 122 (1946).

(3) Jackson and Powles, *ibid.*, **42A**, 101 (1946).

(4) Debye, "Polar Molecules," Chemical Catalog Co., Reinhold Publ. Corp., New York, N. Y., Chap. V.

(5) Lamont, "Waveguides," Methuen, New York, N. Y.

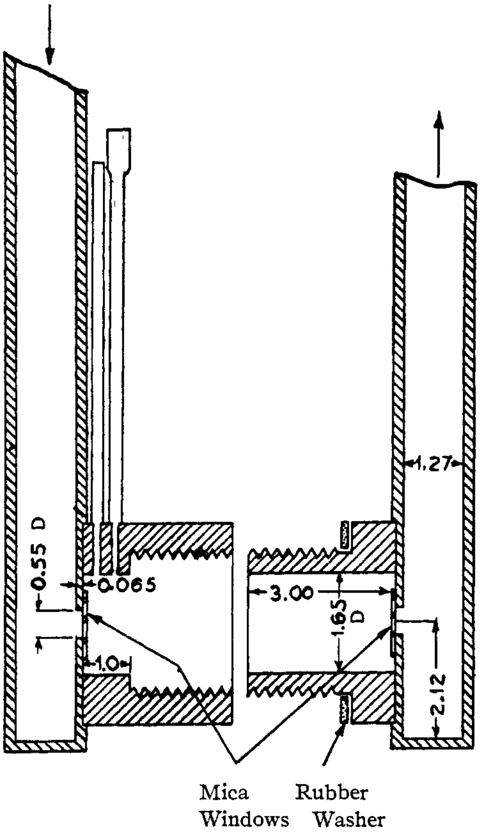

Fig. 1.—3.3-Cm. wave length resonant cavity; dimensions in cm.

of dielectric constant about 2.0 at a frequency near 9,500 Mc./sec. The liquid is contained by two very thin mica windows which are stuck with seccotine over the coupling holes, which are located centrally in each end-plate. The central barrel is in two parts so that the windows could be fixed in position and the cavity can be thoroughly cleaned. When assembled the two parts meet in a butt-joint and this is located one quarter of the way along the barrel, where there is a node in the longitudinal wall currents. The whole is silver-plated and when screwed up the end guides are kept parallel thus ensuring coupling into and out of the same member of the degenerate $H_{1,1,2}$ modes. Since the cavity is not resonant at a convenient wave length when filled with air, the Q due to the wall resistance and the coupling losses must be found with the help of a lossless liquid or by calculation. In this instance the observed Q when filled with the best sample of cyclohexane was 4,050 and the theoretical Q is 7,100, whence the maximum loss tangent of the cyclohexane is 0.00011, which is the difference in the reciprocal Q's; this figure is only a maximum since it has usually been observed[6,7] that the Q's of air filled cavities are lower than the theoretical values calculated from the direct current resistivities of the walls. For work with solutions it is the reciprocal Q of the cavity filled with solvent which must be subtracted from that of the cavity filled with solution to obtain the loss due to the solute molecules, and so the solvent and the resistance losses need not be separated.

The cavity used at 1.3 cm. is essentially a scale model of that already described and has a barrel length of 2.29 cm. and diameter of 0.63 cm. The $H_{1,1,3}$ mode is used and when filled with cyclohexane it has a Q of 2,500; the theoretical Q is 3,800 so that the loss tangent of the cyclohexane is less than 0.00014 at room temperature and 1.3 cm. wave length.

The cavities are immersed in a thermostat whose temperature is held constant to better than 0.1° and the rubber washer indicated in the diagram serves to keep the thermostat liquid from the inside of the cavity.

Q Measurements.—The wave guide bench arrangement is shown in Fig. 2. The signal oscillator is stabilized in frequency by comparison of its output with a cavity resonator, any difference in frequency causing an error voltage to be fed back to the reflector of the oscillator (723A at 3.3 cm.) and also to the thermal tuning grid in the case of the oscillator used at 1.3 cm. (2K50). The error voltage is obtained by a modification of the first Pound[8] circuit or else by a rather different arrangement due to Dr. Townes[9] which involves a very small frequency modulation of the oscillator. The output powers of both the signal and the beat oscillators are monitored with a crystal detector and a microammeter. Superheterodyne detection is employed, the beat oscillator being swept through a small frequency range. The detecting crystal is connected through a calibrated carbon attenuator to a 60 Mc./sec. amplifier and thence to a detecting system whose output meter shows a signal dependent on the peak input during the sweep. The meter is used as a null instrument and the power calibration rests in the attenuator for the 60 Mc./sec. signal.

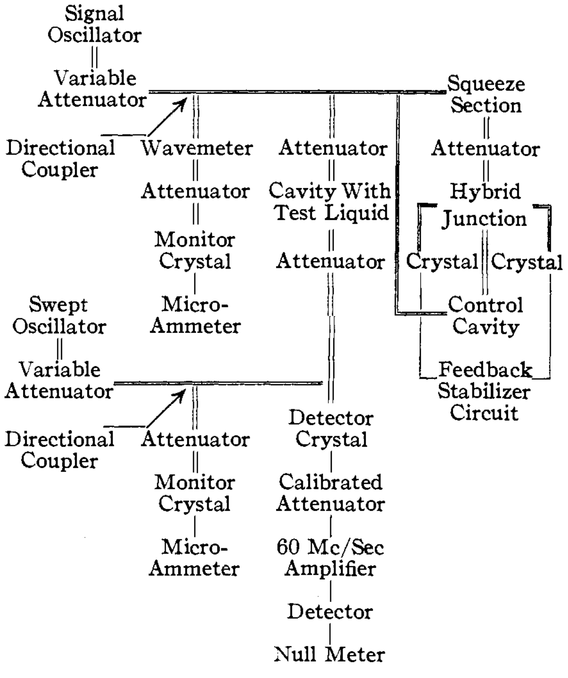

Fig. 2.—Arrangement of the wave-guide bench.

Measurements of the Q are made by observing first the maximum transmission of the cavity and the frequency at which this occurs; then 3 db., or other convenient amount, of attenuation are removed and the frequency of the signal oscillator readjusted so that the output from the cavity is reduced to its former value. From the difference between this frequency and that at the corresponding point on the other side of the maximum the Q can be calculated from the usual formula for a resonance curve

$$Q = f/\delta f(P_{\max.}/P - 1)^{1/2}$$

where f is the frequency, δf the total frequency difference

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(6) Horner, Taylor, Dunsmuir, Lamb and Jackson, *J. Inst. Elect. Engrs.*, **93**, 53 (Part III 1946).

(7) Bleaney, Loubser and Penrose, *Proc. Phys. Soc.*, **59**, 185 (1947).

(8) Pound, *Rev. Sci. Instruments*, **17**, 490 (1946).

(9) To be published.

and $P_{\max.}$ and P are the power transmissions at the peak and at the points of observation of δf. The frequency meter at 1.3 cm. is an $H_{0,1,n}$ cylindrical resonator which has been calibrated against the ammonia spectrum[10,11] while that used at 3.3 cm. is a coaxial line meter checked against a substandard which derives its calibration from quartz crystals. In the measurement of the Q there is a scatter of experimental values corresponding to a probable error of 3% in each reading; several determinations are made on each Q which reduces this error, but there may also be systematic errors due to the small frequency sensitivity of the directional couplers and the monitor crystals so that the results can only be trusted to 5%.

Measurements at 10 cm.—Measurements at 10 cm. wave length are made using a coaxial line after the method of von Hippel and his co-workers.[12] The test liquid at the end of a short-circuited coaxial line has its surface in contact with a quarter wave length plug of Teflon (polyfluorethylene) of negligible loss; the liquid is introduced from a pipe through the reflecting end of the line. The plug is located so as to leave one quarter wave length of liquid at room temperature. However uncertainty in its expansion leads to some uncertainty in the length of the liquid filling at other temperatures, and the observed losses at the higher temperatures may be too low on this account.

Materials.—The cyclohexane was a commercial product dried and purified by shaking with active silica gel. The *dl*-camphor was a commercial resublimed product.

The solutions for the measurements at 3.3 and 1.3 cm. ranged in concentration up to 2.5 g./liter, whereas the smaller loss and the less sensitive technique at 10 cm. wave length necessitated solutions up to 25 g./liter. The density[13] of pure cyclohexane was used to correct for the change of volume concentration with temperature.

Results and Discussion

The losses due to a solute are best expressed as the molecular loss tangent, that is Loss tangent/C where C is the concentration in g. moles/liter; this name and concentration unit have been chosen to be in keeping with general usage in other fields of chemistry. In no case was there any indication of a departure from a linear dependence of loss with concentration. This is shown for the losses at 3.3 cm. in Fig. 3.

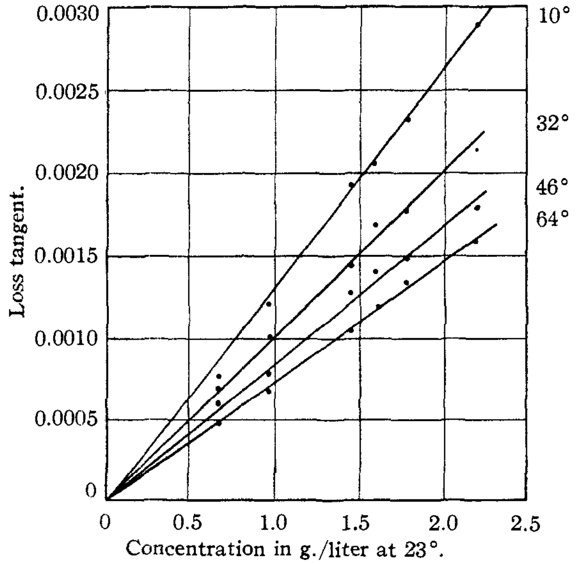

Fig. 3.—Loss of camphor in cyclohexane at 3.3 cm.

The experimental results are summarized in Table I which gives the observed molecular loss tangents; in each case the value is taken from the slope of a graph covering the concentration range. No explanation is offered for the smaller loss at 29° compared to the neighboring temperatures at 1.3 cm. wave length; the reduction is scarcely more than the estimated experimental errors.

Table I

1.3 cm. 24,000–23,500 Mc./sec. T, °C.	 Loss	3.3 cm. 9500–9250 Mc./sec. T, °C.	 Loss	10.0 cm. 3000 Mc./sec. T, °C.	 Loss
10	0.246	10	0.194	12	0.064
29	.226	32	.156	25	.056
46	.235	46	.135	37	.047
62	.202	64	.118	51	.037
				66	.030

For comparison at a common temperature the losses at 10, 30, 50 and 70° were obtained by interpolation and slight extrapolation. These were compared with the Debye loss expression used in the form[2]

$$\text{Loss} = \frac{(\epsilon + 2)^2}{\epsilon} \frac{4\pi N \mu^2}{27kT} \frac{\omega\tau}{1 + \omega^2\tau^2}$$

ϵ, the dielectric constant of the solvent is 2.0 and μ, the dipole moment of camphor, was taken as 3.00 D; Sidgwick's table[14] gives range from 2.94–3.05 D. ω is the angular frequency and τ, the time of relaxation, is the only unknown quantity. The values of this parameter which best fit the results, together with the experimental losses and the calculated losses using these times, are given in Table II. This table shows agreement between the experimental and calculated losses within 5% except for the higher temperature results at 10 cm. wave length and a special experimental error, which would lead to low experimental values here, has been mentioned above.

Table II

Temp., °C.	Time of relaxation, sec.	Losses at 1.3 cm. exp.	1.3 cm. calcd.	3.3 cm. exp.	3.3 cm. calcd.	10 cm. exp.	10 cm. calcd.
10	7.4×10^{-12}	0.246	0.255	0.194	0.190	0.066	0.067
30	6.2×10^{-12}	.228	.235	.159	.155	.052	.053
50	5.3×10^{-12}	.230	.220	.131	.129	.039	.045
70	4.5×10^{-12}	.193	.200	.111	.105	.029	.036

Measurements are at too few frequencies for a claim to be made that the Debye expression with one relaxation time is undoubtedly the proper form for describing the loss, but the agreement is such that it can be said that single relaxation times, one for each temperature, do give a reasonable description of the system. In particular the recipro-

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(10) Strandberg, Kyhl, Wentink and Hillger, *Phys. Rev.*, **71**, 326 (1947).

(11) Coles and Good, *ibid.*, **71**, 383 (1947).

(12) Hippel, Jelatis and Westphal, "Measurements of Dielectric Constant and Loss in Coaxial Waveguides," report from Massachusetts Institute of Technology, 1943.

(13) "International Critical Tables."

(14) *Trans. Faraday Soc.*, **30**, 1934.

cals of these times describe the rate of rotation and the temperature dependance of this rate may be expressed as an activation energy. Figure 4 shows a graph of logτ against $1/T$ and the slope of this line is equivalent to an activation energy, E_τ, of 1.7 kcal. if the time of relaxation is expressed by

$$\tau = Ae^{-E_\tau/RT}$$

This value may be compared with that of 1.7 kcal. for the similar activation energy for the rotation of camphor in n-heptane,[2] and also with the value of 2.3 kcal. for the corresponding activation energy for the viscosity of cyclohexane[13] over the range 15–30°. Further the interpolated value for the relaxation time at 20° which is 6.8×10^{-12} sec. in cyclohexane is very close to the value 6.5×10^{-12} sec. for camphor in n-heptane[2] but these values are by no means proportional to the macroscopic viscosity coefficients which are 0.96 and 0.41 cpoise, respectively.[13]

Acknowledgments.—The author wishes to thank Prof. P. Debye for his interest in the work and Dr. C. H. Townes for many invaluable discussions and suggestions. He also wishes to thank the Commonwealth Fund for the award of a Fellowship and the Bell Telephone Laboratories for granting the use of their facilities so freely during its tenure.

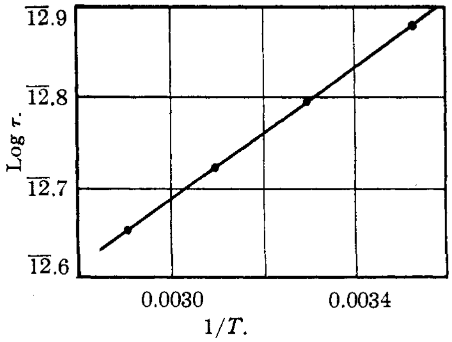

Fig. 4.—Graph of $\log_{10} \tau$ against $1/T$; slope equivalent to 1.7 kcal. energy of activation.

Summary

A description of the measurement of the dielectric loss of liquids at microwave frequencies using a completely filled cavity resonator is given. Solutions of camphor in cyclohexane have been measured over the range 10–70° at three wave lengths, 1.3, 3.3 and 10 cm. The observed losses can be well explained by a single Debye loss curve; the relaxation time is 6.8×10^{-12} sec. at 20° and the temperature coefficient corresponds to an activation energy of 1.7 kcal.

MURRAY HILL, NEW JERSEY

RECEIVED FEBRUARY 20, 1948

[CONTRIBUTION FROM THE UNIVERSITY OF MINNESOTA AND CORNELL UNIVERSITY]

Potentiometric Investigation of Tripyrophosphatomanganic(III) Acid

BY JAMES I. WATTERS AND I. M. KOLTHOFF

Evidence presented in a previous paper[1] indicated that the violet complex ion of manganese (III) and pyrophosphoric acid is a chelate ring complex anion having essentially the formula $Mn(H_2P_2O_7)_3^{-3}$. The ionic weight was estimated by application of Jander's expression[2] to the polarographically determined diffusion coefficients, and the hydrogen content of the complex was deduced from pH, ionic charge, and theoretical considerations. An investigation of the oxidation potential of the manganese(II)–manganese(III) couple in acidic pyrophosphate solutions along with the various factors influencing it is described in the present paper.

A new potentiometric procedure for determining manganese by titrating the trivalent complex with standard iron(II) sulfate solution is also described. Volumetric procedures in which the trivalent complex is titrated with iron(II) sulfate and the end-point detected with diphenylamine sulfonate as indicator, as well as amperometrically, will be described in subsequent papers. On the basis of the present studies,[3] Lingane and Karplus[4] have developed a potentiometric method for determining manganese in which manganese(II) is titrated to the violet manganese(III) pyrophosphate complex with standard permanganate solution. Their titration curves substantiate the authors' results.

Theoretical

In the experimental part it is shown that the potential at a platinum electrode of the complex manganic(III)–manganous(II) system is reversible, and that both complexes are mononuclear. It has been mentioned that the trivalent manganese complex contains three pyrophosphate radicals.[1] The hydrogen content of the pyrophosphate ions, either in the form of complex ions or simple ions, is a function of the pH of the solution. The number of associated hydrogen ions in the various ions at a particular pH, will be indicated by x, y and z. The number of pyrophosphate radicals in the manganese(II) complex will be indicated by m to illustrate the method of its evalua-

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(1) I. M. Kolthoff and J. I. Watters, *Ind. Eng. Chem., Anal. Ed.*, **15**, 8 (1943).

(2) G. Jander and H. Spandau, *Z. physik. Chem.*, **A185**, 325 (1939).

(3) J. I. Watters, Ph.D. Thesis, University of Minnesota, 1943.

(4) J. J. Lingane and Robert Karplus, *Ind. Eng. Chem., Anal. Ed.*, **18**, 191 (1946).