salts exhibit a minimum in their conductance curves and the conductance increases sharply at higher concentrations. The increase is the more pronounced the lower the conductance at the minimum.

3. For salts with large anions, such as the picrate ion, the conductance curves are comparatively simple. With salts of simple ions, the curves are highly inflected.

4. It is suggested that concentrated salt solutions may be looked upon as solution of solvent in fused salt. The properties of concentrated solutions are discussed from this point of view.

PROVIDENCE, R. I. RECEIVED JULY 9, 1949

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

The Mechanism of Rotation of Long-chain Alkyl Bromides and Other Molecules in the Solid State[1]

BY JOHN D. HOFFMAN[2] AND CHARLES P. SMYTH[*]

It has been found that the normal long-chain alcohols rotate about their long molecular axes in the solid state provided the chain contains fourteen or more carbon atoms.[3] Observation of orientation polarization due to molecular rotation was rendered difficult in the study on alcohols by a direct current conductivity effect which resulted in Maxwell–Wagner polarization at low frequencies. Since it is to be expected that the proton transfer mechanism of conductivity postulated for the alcohols could not occur in the bromides the study of molecular rotation in the latter should not be hampered by conductivity effects.

Müller[4] has shown by X-ray techniques that rotation about the long axis in the solid is not observed in the normal long-chain hydrocarbons on warming until the chain contains twenty-two or more carbon atoms. The explanation tentatively advanced by Müller for the onset of rotation in the paraffins at about twenty-two carbon atoms was that the molecules achieved sufficient chain length to overcome end-group forces. It has seemed desirable to reconsider this hypothesis. Data on transition temperatures have been collected from the literature for alcohols, iodides and paraffins for purposes of comparison.

It was also found by Müller[5] that certain long-chain ketones showed a gradual increase in orientation polarization at 1.5×10^8 cycles/sec. prior to melting. This increase was marked even 30° below the melting point, and considerably exceeded the polarization of the corresponding paraffin, thus indicating molecular freedom in the solid state. The term "prerotation" will be used to describe the gradual onset of molecular rotational freedom below the transition or melting point.[6]

In this work, dielectric evidence of prerotation was sought in *n*-dodecyl, *n*-hexadecyl, *n*-octadecyl and *n*-docosyl bromides down to liquid nitrogen temperatures. *n*-Hexadecane was measured for purposes of comparison. The wide temperature range over which prerotation phenomena were observed suggested that Fowler's treatment of rotating diatomic molecules,[7] with extensive modifications, might predict the dielectric constants and rotational specific heats in the solid state at and below the transition point. Formation of liquid due to impurities and premelting[8] does not constitute a true prerotation effect, as has been discussed in a previous paper on molecular freedom in amines,[9] and care has been taken to minimize these effects by using pure materials.

Purification of Materials

We are indebted to Dr. E. Emmet Reid for the samples of pure *n*-dodecyl, *n*-hexadecyl and *n*-octadecyl bromides,[10] and to Dr. Nathan L. Drake of the University of Maryland for the sample of *n*-docosyl bromide. In addition, *n*-octadecyl bromide from the Matheson Co. (Paragon Div.) was purified by twice crystallizing from the melt, and then distilling under vacuum three times, each distillate being cut into five fractions and the product designated as II in Table I. This product is compared with that supplied by Dr. Reid which is designated as I. The sample of *n*-docosyl bromide supplied by Dr. Drake was further purified by high vacuum distillation. *n*-Hexadecane obtained from Paragon

TABLE I

PHYSICAL PROPERTIES OF THE ALKYL BROMIDE SAMPLES

Bromide	Densities 30°	60°	n_D		M. p.
n-Dodecyl	1.029	1.005	1.45747	(25°)	−9.70°
n-Hexadecyl	0.986	0.962	1.46075	(25°)	17.33°
n-Octadecyl(I)	.9760	.952	1.46145	(30°)	27.35°
n-Octadecyl(II)	.9754	.952	1.46105	(30°)	27 15°
n-Docosyl	....	...	1.46 (est.)	(40°)	42.7°

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[*] Harvard University Ph.D., 1921.

(1) This investigation was carried out with the aid of the Office of Naval Research.

(2) Present address: Research Laboratory, General Electric Co., Schenectady, N. Y.

(3)(a) Hoffman and Smyth, THIS JOURNAL, **71**, 431 (1949); (b) Baker and Smyth, *ibid.*, **60**, 122 (1938); (c) Ott, *Z. physik. Chem.*, **193**, 218 (1944).

(4) Müller, *Proc. Roy. Soc. (London)*, **A138**, 514 (1932).

(5) Müller, *ibid.*, **A158**, 403 (1937).

(6) Smyth, *Trans. Faraday Soc.*, **42A**, 175 (1946).

(7) Fowler, *Proc. Roy. Soc. (London)*, **A1419**, 1 (1935).

(8) Oldham and Ubbelohde, *ibid.*, **A176**, 50 (1940).

(9) Hoffman and Smyth, THIS JOURNAL, **71**, 3591 (1949).

(10) Meyer and Reid, *ibid.*, **55**, 1574 (1933).

was also purified by vacuum distillation. The liquid densities, the refractive indices for the D sodium line, and the melting points of these compounds are given in Table I.

An estimated density of *n*-docosyl bromide (0.948 at 40°) was obtained by extrapolation of molar volume data calculated from Table I. The good agreement of the physical constants with the available literature values and the sharpness of the cooling curves indicate an adequate degree of purity for these compounds.

Experimental Results

The details of the method for obtaining dielectric constant–temperature data on an impedance bridge have been described elsewhere.[3a] Each compound was run at least three times, and the data presented here represent the most reproducible run on the purest sample. The dielectric measurements were first made at 0.5, 5.0 and 50 kc., but since no dispersion was ever found, only the 5.0 kc. results are recorded in Table II and plotted in Fig. 1. The precision was better than 0.2% but the accuracy was less due to voids. The quantity of *n*-docosyl bromide available was so small that glass beads had to be used to raise the liquid level in the cell so that the three concentric gold cylinders were filled with dielectric. No beads were between the condenser plates. The material froze just flush with the top of the cylinders so that the dielectric constant values may have been slightly low due to difference in edge effect. It was, therefore, considered inadvisable to measure prerotation effects much below 0°.

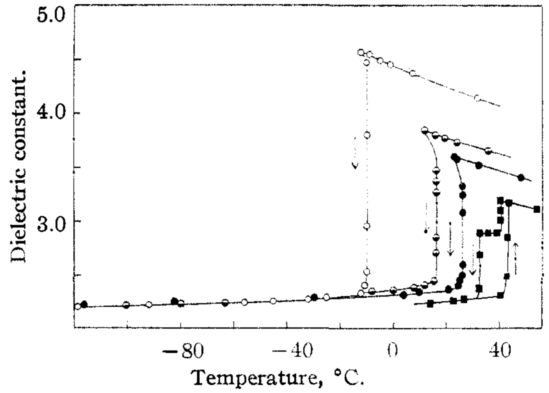

Fig. 1.—Temperature dependence of dielectric constants of long-chain bromides at 5.0 kc.: hollow circles, *n*-dodecyl bromide; half-filled circles, *n*-hexadecyl bromide; filled circles, *n*-octadecyl bromide; and squares, *n*-docosyl bromide. Arrows indicate direction of temperature change.

The increase of density in the cell due to freezing calculated from the dielectric change in *n*-hexadecane is 5%. The presence of some voids causes a smaller density change in the cell than would be obtained under ideal conditions. The average increase in density observed for *n*-octadecyl bromide on freezing in a pycnometer was 4%. The maximum value found was 7%. Approximate values for the other solids were estimated by increasing the liquid densities at the freezing points by 4%.

Table II

Dielectric Constants at 5.0 Kc.

t, °C.	ε′	*t*, °C.	ε′	*t*, °C.	ε′	*t*, °C.	ε′
n-Dodecyl bromide		*n*-Hexadecyl bromide		*n*-Octadecyl bromide		*n*-Docosyl bromide	
Cooling		Cooling		Cooling		Cooling	
31.5	4.15	37.4	3.66	58.4	3.40	55.2	3.12
6.6	4.38	23.5	3.74	32.4	3.52	39.8	3.20
−1.0	4.46	18.7	3.78	24.0	3.59	39.5	3.10
−4.9	4.50	15.7	3.80	22.5	3.60	39.3	3.02
−9.9	4.55	12.0	3.85	25.9	3.32	38.5	2.92
−11.9	4.57	16.0	3.47	26.1	3.24	36.5	2.91
−10.0	4.48	16.2	3.38	26.0	3.08	34.4	2.90
−10.6	3.80	16.2	3.25	25.8	2.60	32.9	2.90
−10.7	2.95	16.1	2.85	25.7	2.50	30.9	2.88
−10.8	2.53	16.0	2.71	25.4	2.45	30.3	2.85
−11.0	2.40	14.9	2.45	24.8	2.40	30.3	2.70
−11.2	2.35	13.9	2.43	21.5	2.35	30.0	2.40
−12.3	2.33	12.2	2.40	9.4	2.34	29.9	2.38
−25.0	2.28	8.6	2.38	−16.0	2.31	27.4	2.27
−32.0	2.27	0.0	2.36	−28.0	2.29	23.0	2.26
−45	2.25	−8.0	2.35	−79.0	2.24	20.7	2.26
−56	2.24	−63	2.24	−120	2.21	14.0	2.25
−92	2.22	−80	2.22	−160	2.20	Warming	
−134	2.20	−102	2.21	−178	2.20	14.0	2.25
Remelted at		−140	2.20	Warming		25.3	2.27
−9.70°		Warming		−53	2.25	29.1	2.30
		−160	2.20	−39	2.30	40.6	2.30
		−60	2.24	−18.0	2.34	41.4	2.35
		9.9	2.39	3.0	2.37	42.1	2.50
		12.0	2.41	25.0	2.42	42.7	2.85
		13.0	2.43	25.5	2.53	42.7	3.20
		14.5	2.48	26.6	2.90	60.2	3.10
		15.0	2.50	27.3	3.54		
		15.4	2.53	30.2	3.53		
		16.3	2.71				
		16.5	2.90				
		16.9	3.48				
		17.0	3.73				
		17.2	3.78				
		17.3	3.83				
		19.9	3.80				

As was to be expected from the absence of the possibility of proton transfer, no high specific conductivities or Maxwell–Wagner effects were encountered, and the dielectric loss factor, ε″, may be taken as < 0.03 throughout.

Discussion of Results

The dielectric behavior of the three shorter bromides is very similar (Fig. 1). All supercool slightly before freezing, and then show a sharp drop in dielectric constant coincident with freezing. There is a slight hysteresis between freezing and melting points as may be seen in Fig. 3, where the dielectric constant–temperature curve of *n*-hexadecyl bromide is depicted on a large scale. In contrast to the behavior of the three shorter compounds, *n*-docosyl bromide shows a relatively high dielectric constant below the freezing point (40°), which remains nearly constant at 2.90 until the substance is cooled to 30.3°, where the dielectric constant drops sharply. This indicates qualitatively that the molecules of *n*-

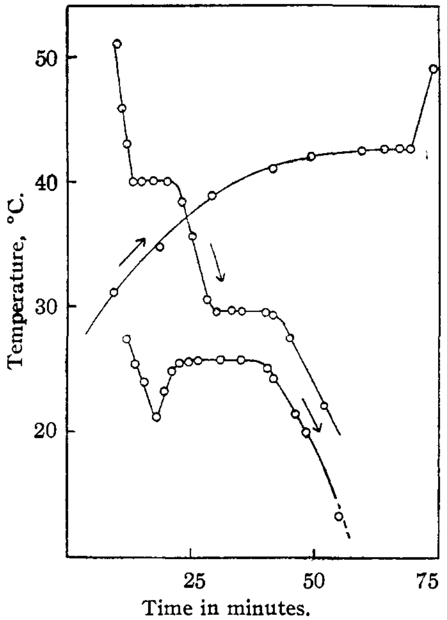

Fig. 2.—Temperature–time curves for *n*-docosyl bromide (upper curves) and *n*-octadecyl bromide (lower curve). Arrows indicate direction of temperature change.

docosyl bromide rotate about their long molecular axes between the freezing and transition points. The transition in the solid state is characterized by rotational freezing of the dipoles and by a sharp heat of transition (Fig. 2). The transition is monotropic, and does not reappear on warming.

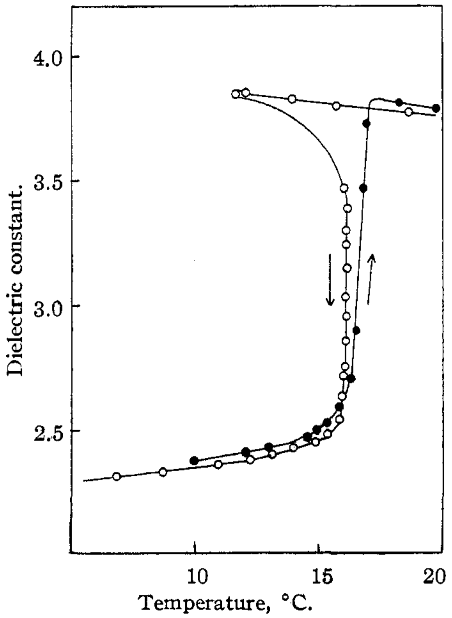

Fig. 3.—Temperature dependence of dielectric constant of *n*-hexadecyl bromide at 5.0 kc. near melting point. Arrows indicate direction of temperature change.

The dielectric constants of the bromides exceed the squares of the refractive indices as corrected for density change even at −100°, and show a continuous rise with rising temperature. This has been shown in detail in Figs. 6, 7 and 8. The comparison with *n*-hexadecane is particularly striking. The fact that the dielectric constant of *n*-hexadecane varies only 0.02 between 18 and −160° indicates that the number of molecules between the plates does not change after the material has solidified. Müller[5] found a similar situation in his study of *n*-docosane and long-chain ketones. It is apparent that the gradual rise in dielectric constant observed in solid bromides may be regarded as an orientation polarization effect.

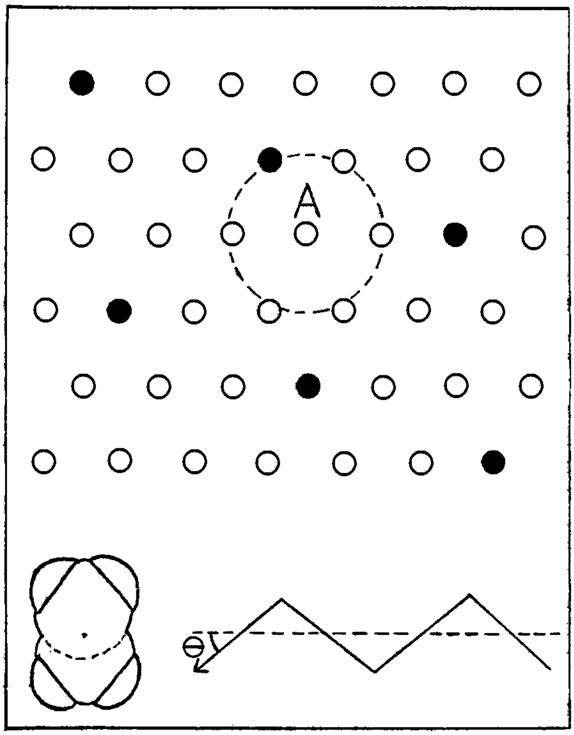

Fig. 4.—Molecular structure of long-chain compounds. Upper part represents end view of long-chain molecules in lattice. Black circles represent rotator molecules. End view of single molecule showing bar shape is depicted on lower left, and a diagrammatic side view of long-chain molecule showing axis of rotation and dipole (arrow) is shown on lower right.

The dipole moment vector, μ_0, in the bromides is inclined at an angle, θ, to the axis of rotation (Fig. 4) so that the effective dipole moment, μ_1, of a molecule rotating about the long axis for a polycrystalline material is given by[5]

$$\mu_1 = \mu_0 \sin \theta$$

where μ_0 is 2.15 D, the gas moment.[11] Since $P_0 = 4\pi N\mu_1^2/9kT$, it is seen that the net result of the dipole vector being inclined at an angle to the axis of rotation would be a reduction in orientation polarization and dielectric constant.

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[11] Smyth and McAlpine, *J. Chem. Phys.*, **3**, 347 (1935).

If one accepts the simple planar model of a long chain bromide, $\theta = 35°$. Dipole induction tends to make θ somewhat smaller, but a slight twisting of the dipole on the chain due to thermal agitation tends to increase θ, so $\theta = 35°$ should be a good approximation. The dielectric constant of the rotator phase in *n*-docosyl bromide can be calculated at 30° using $\mu_0 = 2.15$ D, $M = 389$, d. = 1.00 (extrapolated from Table I with density correction for solidification), $\theta = 35°$, n^2_{D} 2.21 (also corrected for density), $T = 303°$ K., k = Boltzmann's constant and N = Avogadro's number in the Onsager[12] equation, in which the moment, μ_0, is replaced by $\mu_0 \sin\theta$

$$P_0 = \frac{4\pi N(\mu_0 \sin\theta)^2}{9kT} = \frac{M}{d}\frac{(\epsilon' - n^2)(2\epsilon' + n^2)}{\epsilon'(n^2 + 2)^2} \quad (1)$$

The calculated dielectric constant is 2.70 which is 6% lower than the observed value of 2.88. Kirkwood[13] has modified the Onsager equation by multiplying μ_0^2 by $[1 + z\overline{\cos\gamma}]$ which accounts approximately for the dielectric constant of the medium surrounding the dipole. z is the number of dipoles in the first coördination sphere. γ is the angle between dipole moments of a pair of neighboring molecules, and $\overline{\cos\gamma}$ is defined as $\int\int \cos\gamma\, e^{-W_0/kT} d\omega_1 d\omega_2$, where W_0 is the potential of average torque acting on a pair of neighboring molecules. In the present case, following Kirkwood, we assume $W_0 = 0$ (free rotation) so that $\overline{\cos\gamma} = \cos^2\theta$ for the six dipoles which are on molecules alongside the one under consideration. For the six dipoles lying in the head-to-head position $\overline{\cos\gamma} = -\cos^2\theta$, so that the calculated value of $[1 + z\,\overline{\cos\gamma}]$ is unity. The experimental value is 1.2 which indicates Onsager's equation is a fair approximation. The assumption $W_0 = 0$ is not exact, and the small increase in $[1 + z\,\overline{\cos\gamma}]$ emphasizes the fact that the rotation is slightly hindered. In either case the dielectric data quantitatively support the picture of molecular rotation about the long axis. The fact that the dielectric constants of the alcohols[3a,b] showed no drop on solidification to the rotator state may be attributed to the fact that θ for the resultant moment lies close to 90°, at which value $\mu_1 = \mu_0$.

Qualitatively, it may be seen that the pre-rotation effect is due to the gradual lowering of the potential barrier opposing rotation as a solid is warmed. At any given temperature, thermal fluctuations permit a number of molecules to surmount their barriers and rotate or reorient frequently. A rotating molecule, however, should exert much less orienting influence on its neighbors, thus giving rise to a coöperative effect which increases the fraction of molecules rotating. At some temperature, the coöperative effect may cause all of the molecules to attain rotational freedom. If the lattice must expand to permit the molecules to rotate, the tendency to rotate is reduced. The ideas set forth above may be developed to calculate the fraction of molecules rotating, r, as a function of temperature. This relation between r and T is used to calculate the dielectric constant by replacing N by Nr in equation (1). The molecular model is essentially that given by Müller,[4,5] who regarded the long rods as bar shaped, much rounded at the corners. The roughly rectangular cross-section is a result of the fact that carbon atoms in a paraffin chain are arranged in a regular saw-tooth pattern. The essential elements of the model are shown in Fig. 4. The bar shape of the molecule will tend to cause the potential energy to have two minima as one rotates the molecule from $\phi = 0$ to 2π, but the presence of both end-groups on the same side of the axis of rotation for the even bromides and the bromine atom at one end of the chain will greatly deepen one of the minima. The analytic form of the angular dependence of the potential energy may be taken as of the form $^1/_2 V \cos\phi/2$ abbreviated $V(\phi)$, or as a step function with one deep minimum of depth V. The barrier against rotation about the long axis for these rods may be treated as composed of two parts[4]: the first, V_e, is the barrier due to both end groups, and the second, $(n - 2)\ V_{\mathrm{CH_2}}$, is due to the bar shape of the molecules. $V_{\mathrm{CH_2}}$ will be constant for any -CH$_2$- group in the even series. The barrier resisting rotation, V_n (exclusive of lattice expansion energy) will be given by

$$V_n = V_e + (n - 2)V_{\mathrm{CH_2}}$$

where n is the number of atoms in the chain. The barrier is seen to increase linearly with increasing chain length.

Using the Hamiltonian H for a classical rigid rotator with one degree of freedom and denoting the rotation about the long axis in terms of an angle ϕ, we may write

$$H = P_\phi^2/2I - V(\phi) \quad (2)$$

where P_ϕ is the conjugate momentum and I is the moment of inertia. The degree of non-rotation, s, may be defined as

$$s = 1 - r = Q_0/Q_{\mathrm{T}} \quad (3)$$

where Q_{T} is the partition function for all states of a molecule and Q_0 is the partition function which satisfies the condition of non-rotation. The condition of non-rotation is given by

$$P_\phi^2/2I \leqq V \quad (4)$$

which states that a molecule cannot rotate if the kinetic energy available is equal to or less than the prevailing barrier, V. Fowler inserted a factor, β, in the above expression to represent the fraction of the barrier which the molecule had to overcome in order to rotate, and achieved different kinds of behavior by varying β arbitrarily. It is difficult to see how β could be other than 1 unless

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(12) Onsager, This Journal, 58, 1486 (1936).

(13) Kirkwood, *J. Chem. Phys.*, 7, 911 (1939).

tunnelling were important. The partition function which satisfies (4) is given by

$$Q_0 = \frac{1}{h}\int_{-(2IV)^{1/2}}^{(2IV)^{1/2}}\int_0^{2\pi} e^{-H/kT}\mathrm{d}P_\phi \mathrm{d}\phi \qquad (5)$$

After making the substitutions $x^2 = P_\phi{}^2/(2IkT)$ and $B = (V/kT)^{1/2}$ this becomes

$$Q_0 = \frac{(2IkT)^{1/2}}{h}\int_{-B}^{B} e^{-x^2}\mathrm{d}x\int_0^{2\pi} e^{-V(\phi)/kT}\mathrm{d}\phi \qquad (6)$$

The lattice may have to expand to permit rotation of the molecules. There is ample indication from X-ray[4] data that the paraffinic lattice expands rather rapidly below the transition point. If we let ΔE equal the difference per molecule in the lattice energy of the rotator and non-rotator states, the Hamiltonian for the rotator becomes

$$H' = (P_\phi^2/2I) - V(\phi) + \Delta E \qquad (7)$$

ΔE_n is taken as the difference in lattice energy of the rotator and non-rotator molecules before any cooperative loosening has set in. Since

$$Q_T = Q_0 + 2e^{-\Delta E/kT}\frac{(2IkT)^{1/2}}{h}\int_B^\infty e^{-x^2}\mathrm{d}x\int_0^{2\pi} e^{V(\phi)/kT}\mathrm{d}\phi \qquad (8)$$

we see from equation (3) that

$$s = Q_0/Q_T = \psi_B/[\psi_B + e^{-\Delta E/kT}(\pi^{1/2} - \psi_B)] \qquad (9)$$

$$\text{where } \psi_B = \int_{-B}^{B} e^{-x^2}\mathrm{d}x$$

The potential energy, V, is a variable which is dependent on the prevailing degree of rotation. Fowler assumed a coöperative law in the form $V = V_n s$. For a rotator in one degree of freedom we shall adopt a law in the form $V = V_n s^2$, where V is the effective potential barrier resisting rotation for a given degree of rotation, and V_n is the barrier prior to the operation of the coöperative effect. This coöperative law should probably be regarded as an assumption, although the following considerations based on the nature of the paraffinic lattice make it appear reasonable. If we consider an hexagonal lattice of long-chain molecules (viewed end-wise as depicted in Fig. 4) and let 1/6 of the molecules rotate as indicated by black circles so that $s \equiv 5/6$, it is seen that five of the nearest neighbors of a non-rotator, A, possess barriers of 5/6 of the full value on an average since each has one rotating neighbor where the barrier is assumed to be zero. Thus the average barrier for $s \equiv 5/6$ is $V = [(0 + 5(5/6))/6]V_n = (25/36)V_n$ about A. Hence $V = V_n s^2$ is reasonable insofar as this model represents the facts. It is clear that the law $V = V_n s$ is an oversimplification in the present case, since it takes account of the nearest neighbors only, the loosening of the nearest neighbors of A by their neighbors being neglected. ΔE is also a variable depending on the degree of rotation, and will also be assumed to vary with s^2, *i. e.*, $\Delta E = \Delta E_n s^2$. This may be seen to be reasonable in a manner similar to that given to indicate $V = V_n s^2$.

V_n/k is a constant in the dimensions of temperature which we denote as T_c so that the limit B becomes $s(T_c/T)^{1/2}$ when we substitute $V_n s^2$ for V in $(V/kT)^{1/2}$. If we set $\Delta E_n/V_n = \alpha$, equation (8) becomes

$$s = 1 - r = \psi_B/[\psi_B + e^{-\alpha B^2}(\pi^{1/2} - \psi_B)] \qquad (10)$$

where

$$\psi_B = \int_{-s(T_c/T)^{1/2}}^{s(T_c/T)^{1/2}} e^{-x^2}\mathrm{d}x$$

Equation (10) is an implicit equation which describes the variation of r for different values of T/T_c. This relation is found numerically by choosing a value of B, evaluating ψ_B and finding s from equation (10). The corresponding value of T/T_c is found by putting this value of s in $B = s(T_c/T)^{1/2}$. For a given value of α, r snaps up toward 1 at a temperature of $1.275T_c$, which we call T_r. This is shown in Fig. 5.

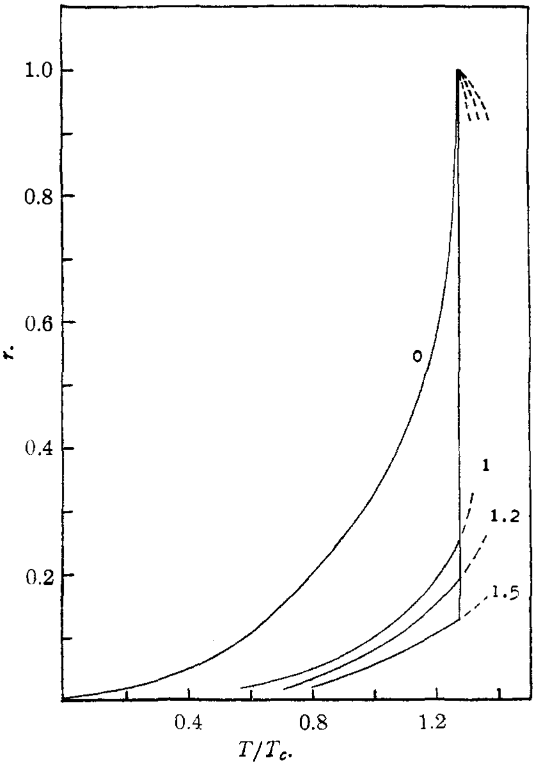

Fig. 5.—Calculated temperature dependence of degree of rotation. Numerals represent values of α.

If $V = V_n s$ had been used as the coöperative law, no snap-up would have developed and r would have risen monotonically to a value near 1 at T_r, then leveled off and become 1 only when T approached infinity. This means the molecule will rotate in a very shallow potential well due to nearest neighbors above T_r.

V_n is obtained from the relation $1.275\ V_n/k = T_r$, where T_r is the observed transition temperature. ΔE_n may be estimated from the relation $\Delta E_n \approx \Delta H_t - V_n$, where ΔH_t is the observed

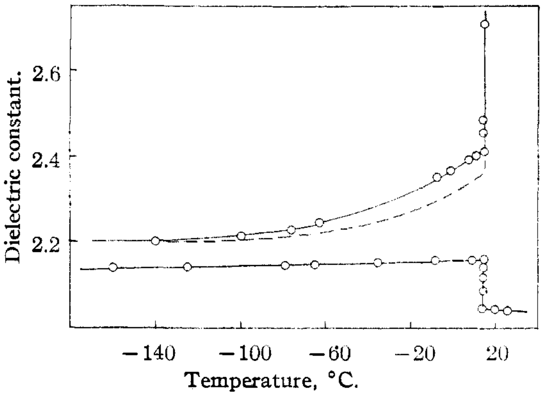

Fig. 6.—Temperature dependence of dielectric constant of *n*-hexadecyl bromide (upper curve) and *n*-hexadecane (lower curve) at 5.0 kc. Dotted line represents calculated prerotation effect using equation (1).

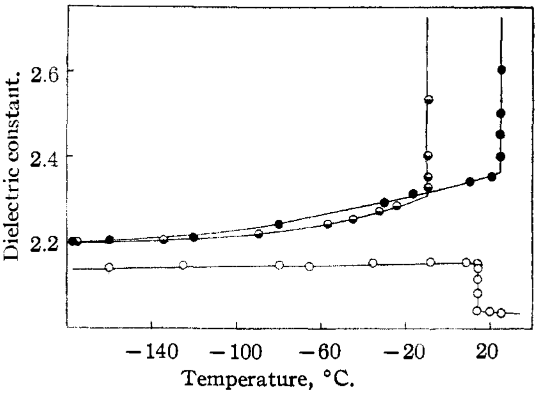

Fig. 7.—Temperature dependence of dielectric constants of *n*-dodecyl bromide (half-filled circles), *n*-octadecyl bromide (filled circles) and *n*-hexadecane (hollow circles) at 5.0 kc.

heat of transition. Ubbelohde[14] has found that hexadecene-1 and *n*-pentadecane show heats of transition of about 1 kcal./mole. In the absence of other data we shall use this figure to obtain an approximate α. Thus, for *n*-docosyl bromide, $T_r = 303°$ K., so $V_n = 0.47$ kcal. and $\alpha = \Delta E_n/V_n = (1.0 - 0.47)/0.47 = 1.2$. Equation (10) has been used to calculate r *vs.* T/T_c using $\alpha = 0$, 1, 1.2 and 1.5, corresponding to an increase in lattice expansion energy. The results (Fig. 5) show that the inclusion of the lattice energy suppresses the degree of rotation. At T_r the solution is double-valued for $\Delta E_n \neq 0$. The solution above T_r may be regarded as an "unstable" solution as in order–disorder theory. The vertical jump of r at T_r obtained when the lattice energy is considered is a first order transition, and the gradual rise in degree of rotation below T_r may be identified with prerotation.

If the treatment presented here is essentially correct, the dielectric constants of the long-chain bromides should be calculable in the region of prerotation for an r *vs.* T/T_c curve based on $\alpha = 1.2$. Further, since $V_n = V_e + (n-2)V_{\mathrm{CH_2}}$ and $T_r = 1.275\ V_n/k$ it is obvious that the transition temperatures in the unassociated compounds should increase nearly linearly with increasing chain length.

The calculation of the dielectric constants will be attempted first, replacing N in equation (1) by Nr, the effective number of orienting molecules, where the values of r are taken from the curve in Fig. 5 for $\alpha = 1.2$, and where the previously used values for density, μ_0 and θ are employed. The calculated dielectric constant of the prerotator state is in good agreement with the observed value as may be seen in Fig. 8. The gradual change in dielectric properties of the prerotator phase and the sharp nature of the transition seem correctly predicted.

A similar calculation has been made for *n*-hexadecyl bromide assuming $T_r = 290°$ K., the freezing point. The agreement (Fig. 6) is seen to be good. It is necessary to estimate T_r for this compound since the transition point is not observable. In the alcohols[3a] the appearance of a transition point on cooling was attributed to an equilibrium between two metastable phases α(rotator) and β_1(non-rotator). The β_1 phase was supposed to transform to β_2, a more stable (tilted) form on standing. Dielectric[3a,b] and X-ray[3c] evidence was cited which strongly supported the existence of these phases. The α phase was somewhat unstable, and transformed to β_2. The failure of a transition to appear in full on rewarming was ascribed to the fact that the more stable β_2 form melted before its transition appeared (*i. e.*, V_n was higher for β_2 so that $T_r > T_{\mathrm{fusion}}$). In the very long hydrocarbons the rotational transitions are enantiotropic[4] and in the shorter ones, monotropic, indicating that the β_1–β_2 transformation is extremely slow for the very long molecules. The activation energy for the β_1–β_2 transformation is probably very high, and nucleation difficult. Thus, *n*-docosyl bromide is comparable to compounds like *n*-octadecane and *n*-octadecyl alcohol, which show monotropic transitions. The shorter bromides, like the alcohols, when cooled slowly probably crystallize directly into the stable β_2 form. It may be expected that with proper experimental methods (probably a quick-freeze technique) the more transient rotator modifications may be found below the chain length normally given as the inception point of rotation. Ideally, prerotation effects should be calculated for substances where the transition is enantiotropic and the ΔH_t known. The application of this statistical mechanical theory to these phase transitions in the present case is legitimate inasmuch as two phases (α and β_1) are in equilibrium at the transition point.

In Fig. 10 it is seen, for iodides and paraffins,[15] that the transition points of the paraffins in-

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[14] Ubbelohde, *Trans. Faraday Soc.*, **34**, 289 (1938).

[15] Deffet, "Composés Organique Polymorphes," Desoer, Liége, 1942.

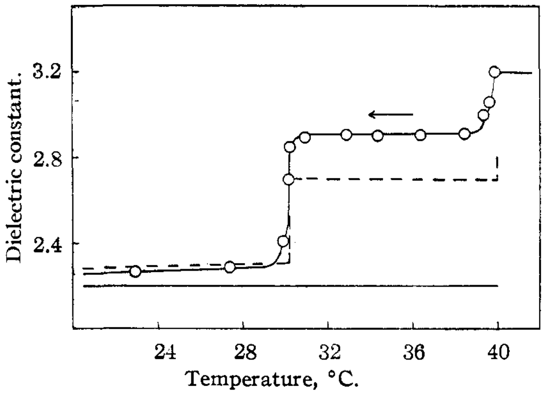

Fig. 8.—Temperature dependence of the dielectric constant of *n*-docosyl bromide near the freezing and transition point at 5.0 kc. The dotted lines represent the dielectric constants calculated by equations (1) and (10). The horizontal line at $\epsilon' = 2.21$ is the value of the index of refraction squared for the liquid corrected for density change.

crease nearly linearly with increasing chain length in accord with prediction. The transition temperatures of the iodides do not vary quite linearly with chain length, probably because V_e cannot be regarded as strictly constant with temperature since molecular dipole interactions vary as $1/T$. The slopes and intercepts of the lines indicate that $V_e \cong 500$ cal./mole and $V_{CH_2} \cong 5$ cal. The total barrier against rotation ranges around 1.0 kcal., before any coöperative lowering of the barrier occurs. This is considerably smaller than the potential barrier for internal rotation about the carbon–carbon bond, so it is easier for a molecule to rotate as a whole than to permit the dipole to turn independently of the remainder of the molecule. This is also borne out by the close correspondence of X-ray[3c] and dielectric data[8a] for alcohols, which indicate that rotation of the paraffin chain and dipole orientation effects appear simultaneously. The alcohols show a non-linear variation of T_r with chain length as expected from the temperature sensitive nature of the hydrogen-bond. The unassociated compounds show a convergence of the melting point and transition point curves at high chain lengths owing to the flattening off of the melting point and the approximately linear rise of T_r with increasing chain length.

Fowler's original treatment of rotating polar molecules predicted a dielectric Curie point far below T_r. The absence of such a Curie point in the present treatment is a result of using the Onsager rather than the Debye expression to relate polarization and dielectric constant. Since we find no dielectric Curie point experimentally, a serious objection to Fowler's treatment is eliminated.

Müller's concept[4] that the sudden appearance of a rotator at a given chain length was due to overcoming end-group forces must be modified. In our view the sudden appearance of a rotator state at a given chain length is due to the fact that the β_1–β_2 and α–β_2 transitions are very rapid for the shorter compounds owing to lower activation energies and greater ease of nucleation. At a somewhat greater chain length the α form is stable and a transition appears.

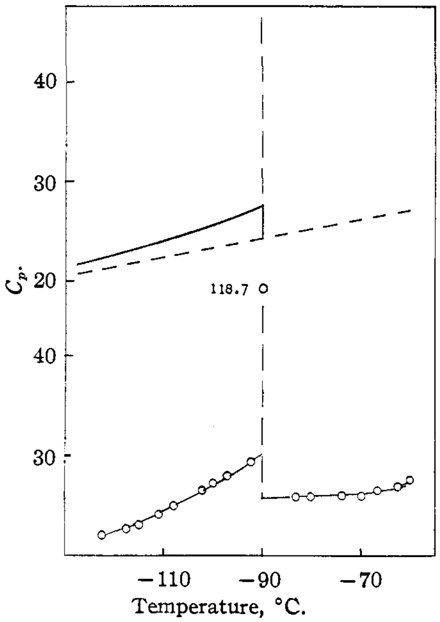

Fig. 9.—Variation of specific heat of *t*-butyl chloride with temperature for low temperature solid transition. Lower curve observed, upper curve calculated. The horizontal dashed line represents the assumed vibrational specific heat and the vertical dashed line represents the heat of transition.

Kirkwood[16] has advanced a rigorous treatment of phase transitions in solids due to hindered rotation which is able to predict the dielectric constant near the broad lambda point in hydrobromic acid[17] at 89° K. with fair accuracy. If a two-minima potential between neighboring molecules had been used, first order transitions could have been obtained. Kirkwood also surmises that first order transitions could arise from the sensitivity of barrier height to lattice parameters. Although no explicit case of first order transitions was discussed in detail, it may be profitable to attempt an interpretation of our data with Kirkwood's theory, but this is beyond the scope of the present paper.

Frank[18] has developed a theory for a rotator with one frozen position. Then, employing an expression of the form $n_{\text{rot.}}/n_{\text{frozen}} = ge^{-E/kt}$ and applying the Bragg–Williams[19] coöperative approximation to the energy, E, Frank obtains *r vs. T* curves for different values of *g* indicating first order transitions similar to ours. When

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(16) Kirkwood, *J. Chem. Phys.*, **8**, 205 (1940).

(17) Smyth and Hitchcock, THIS JOURNAL, **55**, 1830 (1933).

(18) Frank, *Trans. Faraday Soc.*, **A42**, 32 (1946).

(19) Bragg and Williams, *Proc. Roy. Soc.* (*London*), **A145**, 699 (1934).

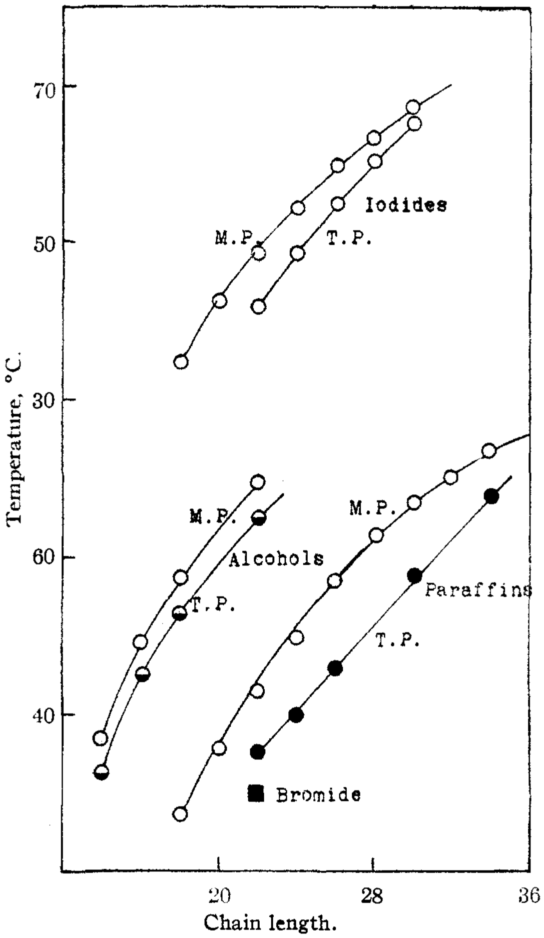

Fig. 10.—Melting points and transition points in long-chain compounds.

the statistical weight of the rotators, g, is set equal to 13, the results are nearly identical. The assignment of g seems rather arbitrary.

Fröhlich[20] has developed a theory of the dielectric properties of long-chain compounds based on order–disorder in the dipole array, in which it is assumed that the interaction energy is due solely to dipolar forces. As was pointed out in the addendum to his paper, the calculations suggest a transition of the second order, and do not agree with experiment. Another objection to Fröhlich's theory, as he apparently realized, is that the transitions in the paraffins must remain unexplained since they possess no dipole array and could therefore have no solid transition. Actually, the close parallelism between the transitions in paraffins, bromides, alcohols and iodides (Fig. 10) with such varying polar nature strongly suggests that the dipole interactions are quite weak in comparison to the London forces at the end-group and along the chain.

The energy required to cause a molecule to rotate at a given temperature is given by $\Delta H_T s^2/N$, where N is the Avogadro number and $\Delta H_T = V_n + \Delta E_n$. The heat capacity due to molecules overcoming the barriers may be obtained by multiplying the energy required for rotation per mole, $\Delta H_T s^2$, by the rate at which the molecules are assuming the rotational state, dr/dT. Thus

$$C_r \cong (\Delta E + V_n)s^2 \frac{dr}{dT}$$

dr/dT may be read from Fig. 5 for the appropriate α. If one plots C_r against T for $\alpha = 0$ the specific heat passes through a distinct maximum below T_r. If α is about 1/2 or greater, the specific heat rises slowly up to T_r, and then the latent heat of transition appears (Fig. 9). No specific heat data of high precision are available for long-chain compounds. Certain solid transitions involving only one degree of freedom of rotation have been studied, however, and the treatment given here should be applicable. The heat capacity has been calculated for *t*-butyl chloride which shows a transition,[21,22] probably involving one degree of freedom at $-90°$. The motion is presumably around the dipole axis ($\theta = 0$), since only a slight change in dielectric constant is observed. $\Delta H_T = 0.41$ kcal., $T_r = 183°$ K., so $V_n = 0.28$ kcal., and, therefore, $\Delta E_n = 0.41 - 0.28$, or 0.13 kcal. and $\alpha = 0.13/0.28$ or about 1/2. Using a plot of r *vs.* T/T_c calculated for $\alpha = 1/2$ in conjunction with the expression for C_r, the specific heat has been calculated at various temperatures by adding C_r to a roughly estimated curve (dashed line, Fig. 9) for the vibrational heat capacity and compared with experiment in Fig. 9. We are indebted to Mr. R. W. Crowe[22] for the use of these data. The vibrational contribution to the heat capacity was assumed continuous as the transition took place. Heat capacity data on such compounds are customarily obtained with rather rapid warming. This tends to smear out transitions and give them the appearance of lambda points, *e. g.*, a calorimeter warmed at 1°/min. caused carbon tetrachloride to "melt" over a range of 9°, while warming at half this rate narrowed the melting range to 5°.[22] This may be the cause of the breadth of the transitions observed by Ubbelohde.[14] A small amount of true broadening of transition and melting points in long-chain compounds may be due to premelting[8] or chain twisting as treated by Fröhlich,[23] but the transition points and melting points observed in alcohols,[3a,b] bromides, and paraffins[24] seem sharp within the limits of purity, so premelting phenomena are little in evidence. It should be recognized that α–β_2 and β_1–β_2 transitions may slowly take place during dielectric and calorimetric measurements thus obscuring the true nature of other phase changes. Heat capacity should be measured with lowering temperature to avoid this difficulty.

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(20) Fröhlich, *Proc. Roy. Soc.* (*London*), **A185**, 399 (1946).

(21) Kushner, Thesis, Princeton University, 1948.

(22) Crowe, unpublished measurements in this Laboratory.

(23) Fröhlich, *Trans. Faraday Soc.*, **41**, 90 (1945).

(24) Seyer, Patterson and Keyes, THIS JOURNAL, **66**, 179 (1944).

In any event, the treatment which has been developed gives the correct shape and magnitude for the specific heat curve in Fig. 9.

The absence of dielectric dispersion in the prerotator state of long-chain ketones[5] even at frequencies up to 1.5×10^8 cycles/sec. (2 meters) has already been mentioned. Daniels[25] has found that mixtures of long-chain ketones and paraffins show dielectric transitions similar to that described in this paper for *n*-docosyl bromide. No dispersion was found in the rotator or prerotator state between 10^3 and 3×10^6 cycles/sec. It may be inferred that the dispersion region in certain solid rotator states may occur at a wave length corresponding to about 1.5×10^9 cycles/sec. (20 cm.) or less. Heston, Hennelly, Laquer and Smyth[26,27,28] have investigated the wave length, λ_m, where maximum dielectric loss occurs for many liquid long-chain bromides. It is interesting to note that λ_m for liquid *n*-hexadecyl bromide at 25° is about 10 cm., which corresponds to a free energy barrier of $\Delta F^{\ddagger} =$ 3.5 kcal./mole as calculated from the Eyring rate theory[27,29] using the formula $\lambda_m = (h/kt)\ (2\pi c)\cdot e^{\Delta F^{\ddagger}/RT}$, where h = Planck's constant and c = velocity of light. The orientation process in the solid is evidently very rapid, so it is reasonable to treat the transitions as involving momenta rather than configurational degrees of freedom such as are concerned in the glass transformation defined by Kauzmann[30] where relaxation times of several hours or more are often encountered. The theory presented in this paper should be used only where there is evidence of rapid orientation.

Fowler's original theory implicitly involves the notion of free molecular rotation above T_r as oirginally suggested by Pauling.[31] Actually, of course, the nature of rotation is not determined only by the moment of inertia, but also by potential barriers which may be present. The treatment of rotation here developed clearly refers to the breakdown of long-range order, as may be seen in the derivation of $V = V_n s^2$. The short-range order corresponding to the law $V = V_{n_1} s$, which considers nearest neighbors only, persists in the rotator state above T_r so that free rotation is approached only at very high temperatures. V_{n_1}, the barrier associated with short-range order, may be expected to be small so that ϵ' will be reduced by only a small amount above T_r. For example, if V_{n_1} were 300 cal./mole, r would be 0.95 at the transition point and rise gradually to unity as T approached infinity. The gradual loss of short-range order with increasing temperature in the rotator state is emphasized by the slight rise in ϵ' in *n*-docosyl bromide between the transition and melting point, and the flat portion of the C_p curve of *t*-butyl chloride above T_r. Frenkel[32], concludes that the thermal motions of molecules above T_r are of the same character as below T_r, partly from the consideration that the additional drop in specific heat expected for a hindered rotator transforming to a free rotator (one-half R cal./mole/degree of freedom) is not found experimentally, but is in fact replaced by an increase in specific heat. The latter statement is not correct in the cases of methane,[33] *t*-butyl chloride, and other compounds where drops in specific heat are found, but this does not revive the concept of free rotation. Long-range rotational order is destroyed at T_r, but local order remains and maintains a relatively small hindrance to rotation which prevents the molecules from performing free rotation, although this condition may be approached[32] at high temperatures in certain symmetrical compounds. Insight into the nature of the change in molecular rotation at T_r may be gained by measuring λ_m in the rotator and prerotator states of polar long-chain molecules.

The general picture of the rotational transitions in the bromides is as follows: *n*-dodecyl, *n*-hexadecyl and *n*-octadecyl bromides show a marked but gradual increase in dielectric constant due to prerotation. This is due to coöperative loosening of the bar-shaped molecules in the lattice, which permits some of the molecules to rotate. *n*-Docosyl bromide shows a similar effect as well as an observable rotator phase. The dielectric properties of the rotator phase were shown to be consistent with the picture of the molecules rotating about their long axes, as in the alcohols and paraffins. It was indicated that the three shorter bromides did not show transitions because they crystallized directly into stable modifications. The failure of the transition to reappear on warming was ascribed to a β_1–β_2 transformation in the solid, as was shown for alcohols. Fowler's theory of rotating molecules has been modified by (1) solving for molecules with one degree of rotational freedom, (2) removing the parameter β, (3) changing the assumed coöperative law from $V = V_n s$ to $V = V_n s^2$, (4) taking into account the lattice expansion energy and its coöperative nature and (5) using Onsager's and Kirkwood's relations to calculate dielectric constant from polarization. The results of the calculations indicate that the dielectric constant and specific heat should show prerotation and then snap up sharply at a transition point. Such behavior was shown by *n*-docosyl bromide on cooling, and by certain very long hydrocarbons and alcohols on warming and cool-

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[25] Daniels, *Nature*, **163**, 725 (1949).

[26] Heston, Hennelly and Smyth, THIS JOURNAL, **70**, 4093 (1948).

[27] Hennelly, Heston and Smyth, *ibid.*, **70**, 4102 (1948).

[28] Laquer and Smyth, *ibid.*, **70**, 4097 (1948).

[29] Glasstone, Laidler and Eyring "Theory of Rate Processes," McGraw-Hill Book Co., New York, N. Y., 1941, Chap. IX.

[30] Kauzmann, *Chem. Rev.*, **43**, 219 (1948).

[31] Pauling, *Phys. Rev.*, **36**, 430 (1930).

[32] Frenkel, "Kinetic Theory of Liquids," Oxford University Press, 1946, Chap. II.

[33] Clusius and Perlick, *Z. physik. Chem.*, **24**, 313 (1924).

ing. The theory also is useful in calculating the dielectric constant due to prerotation in the three shorter bromides. The model required that the transition temperatures should rise nearly linearly with increasing chain length in agreement with experiment. Polarity seems to affect the transition points only slightly. In certain cases it is possible to estimate the additional heat capacity and the dielectric constant due to prerotation given ΔH_T and T_r. The theory does not imply free rotation above the transition point. The theory of rotating molecules presented in this paper, in conjunction with the concept of an equilibrium between metastable phases, seems able to give an account of the gross features of the rotational behavior in long chain molecules.

Acknowledgments.—The authors wish to express their indebtedness to Professor W. J. Kauzmann, Dr. A. D. Franklin and Dr. R. A. Oriani for many helpful conversations.

Summary

The dielectric constants and cooling curves of *n*-hexadecane, *n*-dodecyl, *n*-hexadecyl, *n*-octadecyl and *n*-docosyl bromide have been measured over a large temperature range. Prerotation was found in the bromides even at very low temperatures. On cooling, *n*-docosyl bromide froze at 40° and showed a sharp transition at 30°, and a suitable analysis showed that the molecules rotated about the long molecular axis between the freezing and transition point. No unsharp transitions were found. A theory of molecular rotation has been developed and the dielectric properties of long-chain bromides have been discussed in terms of the results. Heat capacity also has been discussed. Comparisons have been made between the properties of long-chain bromides, alcohols, iodides and paraffins.

PRINCETON, NEW JERSEY RECEIVED JUNE 7, 1949

[CONTRIBUTION FROM THE STERLING CHEMISTRY LABORATORY OF YALE UNIVERSITY]

Polarographic Studies of Metal Complexes. II. The Copper(II) Citrates[1]

BY LOUIS MEITES*

Other papers in this series have dealt with the polarographic characteristics of copper(II) in oxalate[1] and tartrate[2] media. The present paper includes the results of a similar study of the various citrate complexes.

Experimental

The apparatus used will be described elsewhere.[3]

Data and Discussion

Figure 1 shows the variation in the half-wave potential of copper(II) in 0.5 *F* potassium citrate as a function of *p*H. There are four major sections of interest, bounded, at this citrate concentration, by the *p*H limits 2.5–5.5, 5.5–7.4, 7.4–11.8, and 11.8–14.

In the most acid range, as a first approximation, the half-wave potential is related to the *p*H by the equations

$$E_{1/2} = 0.112 - 0.0523\,p\mathrm{H}\ (0.5\ F\ \text{citrate}) \quad (1)$$

and

$$E_{1/2} = 0.142 - 0.050\,p\mathrm{H}\ (0.05\ F\ \text{citrate}) \quad (2)$$

The working formula for the half-wave potential of a metal complex, neglecting activities, is

$$\Delta E_{1/2} = \frac{0.0591}{n}\log K_\mathrm{d} - \frac{0.0591}{n}\,p\log\,[\mathrm{X}] \quad (3)$$

where $\Delta E_{1/2}$ is the algebraic difference between the half-wave potentials of, here, the citrato- and aquo-copper ions, K_d is the dissociation constant of the complex, p is the number of complexing groups attached to one copper atom, n is 2 for reduction to the metallic state, and [X] is the concentration of the citrate species involved in the complex. Laitinen, Onstott, Bailar and Swann[4] have recently rewritten equation (3) in the related form

$$\Delta E_{1/2} = \frac{0.0591}{n}\log K_\mathrm{d} - \frac{0.0591}{n}p(p\mathrm{H} - pK + \log\,[\mathrm{HX}]) \quad (4)$$

where [HX] and K_a are the concentration and dissociation constant, respectively, of the acid corresponding to the complexing anion. They state that "from this equation it is apparent that the half-wave potential will be a linear function of *p*H if the dissociation of the acid is small...." This is only true within the accuracy of the measurements when $p\mathrm{H} \leqslant pK_\mathrm{a} - 1$, and, as this is not the case here, equations (1) and (2) would not be expected to be as accurate as the data themselves.

The four regions of the graph can hardly indicate anything but the formation of complexes with, successively, the dihydrogen and monohydrogen citrate ions, the citrate ion itself, and, at high *p*H values, with both hydroxyl ion and citrate. In solutions more acid than *p*H about 5, the dihydrogen citrate ion predominates. Its

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* Harvard University Ph.D., 1947.

[1] L. Meites, THIS JOURNAL, **71**, 184 (1949).

[2] L. Meites, *ibid.*, **71**, 13269 (1949).

[3] L. Meites and T. Meites, to be submitted.

[4] H. A. Laitinen, E. I. Onstott, J. C. Bailar, Jr., and S. Swann, Jr., THIS JOURNAL, **71**, 1550 (1949).