cant change in dielectric constant once solidification has taken place. The increase in density accompanying solidification of this compound has been found by direct means[31] to be 5.2%, while that calculated here from the change in dielectric constant at the freezing point is 4.2%. Considering the fact that complete filling of the cell with solid is difficult, this agreement may be considered satisfactory. It is impossible, however, to account for the gradual decrease in dielectric constant with decrease in temperature, as well as the sharp decrease below the transition point, unless it is assumed that a decrease in polarization is involved. It may be that the force fields in the crystals increase the binding forces on the electrons so as to decrease the molecular polarizabilities, the effect becoming more pronounced as the distance between neighboring molecules decreases (increase in density). This could account for the gradual decrease in dielectric constant with decrease in temperature down to the transition point. Since the number of molecules between the condenser plates remains approximately constant, the increase in density which, presumably, accompanies the transition to the low temperature form can, by the same argument, cause the observed drop in dielectric constant at this point. Measurements upon solid carbon tetrachloride, carried out recently in this Laboratory,[32] have indicated similar behavior for the substance.

[31] L. Rotinjanz and N. Nagornow, *Z. physik. Chem.*, **A169**, 20 (1934).

[32] A. DiGiacomo, unpublished measurements.

PRINCETON, NEW JERSEY RECEIVED MAY 16, 1951

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF WASHINGTON]

Studies on Sulfonates. XI. Electrical Conductances of Aqueous Solutions of Some Magnesium *n*-Alkane Sulfonates[1]

BY A. L. M. LELONG, H. V. TARTAR, E. C. LINGAFELTER, J. K. O'LOANE AND R. D. CADLE

Magnesium hexane, octane, decane and dodecane sulfonates have been prepared, and the conductances of their aqueous solutions measured at 25 and 40° for the C_6 salt; at 25 and 60° for C_8; and at 60 and 80° for the C_{10} and C_{12} salts. The critical concentrations for micelle formation are given, for the C_{12}, C_{10} and C_8 magnesium salts, as shown by conductance data; for the C_6 magnesium salt and C_6 and C_8 sodium salts, as determined by the pinacyanol dye method. The values of the heat of micelle formation over the range 60–80° have been calculated for the C_{10} and C_{12} magnesium salts. The variation of the critical concentrations for micelle formation (cmc) with carbon chain length has been discussed. The change with carbon chain length of the slope of the Λ *vs.* $\sqrt{Nv}$ curves immediately above the critical concentrations has been shown to be a function of $\sqrt{\text{cmc}}$. The Krafft points of magnesium octane, decane and dodecane sulfonates have been determined.

The results herein reported are a continuation of earlier work in this Laboratory, on the properties of paraffin chain salts. The previous investigations have dealt with aqueous solutions of uni-univalent electrolytes. This report is concerned with some properties of magnesium alkane sulfonates (salts of the 2–1 type), with particular reference to their conductance and behavior toward micelle formation. The hydrocarbon chains are unbranched in all cases. For simplicity the prefix *n*-(normal) will be omitted from the names of the alcohols, bromides and salts.

Experimental

Preparation of Salts.—Octyl and decyl bromides were prepared from the corresponding alcohols by the method of Kamm and Marvel.[2] The octyl alcohol was purchased from the Eastman Kodak Company. Decyl alcohol was obtained from repeated fractionation of lorol. Hexyl and dodecyl bromide were from the Eastman Kodak Company and Halogen Chemicals Inc., respectively. The bromides were further purified by fractionation under reduced pressure: the hexyl and decyl bromides in an efficient Widmer column 61 cm. long; the octyl and dodecyl bromides in a column 1.2 meters in length and filled with small glass helices, which gave a performance equivalent to 19 theoretical plates. The bromides prepared during the latter part of the work (hexyl, octyl and dodecyl) were more carefully checked for boiling point and refractive index.

The uncorrected boiling points and corresponding pressures were: decyl alcohol, 119° (10 mm.); the bromides: hexyl, 87.8–88.8° (90 mm.); octyl, 97.0° (20 mm.); dodecyl, 160–161° (25 mm.). The refractive indices of three of the bromides were determined at 25°; the data (including those of other investigators) were as follows: hexyl, 1.4451, 1.4452[3]; octyl, 1.4504, 1.4503[3]; dodecyl, 1.4562, 1.4563.[4]

Sodium alkane sulfonates were prepared by the Strecker reaction: the hexane, octane and dodecane salts by the method of Houlton and Tartar,[5] the decane salt by treating the bromide with sodium sulfite in an autoclave at 150–200°, and recrystallizing several times from alcohol.

Magnesium hexane, octane and dodecane sulfonates were prepared by obtaining the sulfonic acids from the sodium salts: hexane and octane by the method of Zuffanti[6]; dodecane by the method of Reychler,[7] and neutralizing the acid with magnesium oxide or hydroxide, the excess of which was separated by centrifugation. Magnesium decane sulfonate was prepared from the sodium salt by double decomposition with magnesium chloride. The salts were all recrystallized from water, except the hexane sulfonate, which was recrystallized from alcohol.

The criterion for purity used in the recrystallizations was the absence of chloride ion, and negligible amount of sodium, as evidenced by the flame test. This degree of purity was generally reached after five recrystallizations. It was found that filtrations through a büchner funnel are greatly improved by the use of a covering of rubber dam, which reduces the formation of foams occurring when air is sucked through the wet precipitate.

The magnesium salts were dried in a vacuum oven at 130° and analyzed for magnesium; the hexane sulfonate, by the method of Fleck and Ward,[8] the octane and dodecane sul-

---

[1] For detailed tables of data order Document 3302 from American Documentation Institute, 1719 N Street, N. W., Washington 6, D. C., remitting $1.00 for microfilm (images 1 inch high on standard 35 mm. motion picture film) or $1.00 for photocopies (6 × 8 inches) readable without optical aid.

[2] Kamm and Marvel, "Organic Syntheses," Coll. Vol. I, 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1941, p. 25.

[3] Ellis and Reid, THIS JOURNAL, **54**, 1674 (1932).

[4] Heston, Hennelly and Smyth, *ibid.*, **72**, 2071 (1950).

[5] Houlton and Tartar, *ibid.*, **60**, 544 (1938).

[6] Zuffanti, *ibid.*, **62**, 1044 (1940).

[7] Reychler, *Kolloid-Z.*, **13**, 277 (1913).

[8] Fleck and Ward, *Analyst*, **58**, 388 (1933).

fonates, by the pyrophosphate method after igniting in a porcelain dish; and the dodecane sulfonate by careful ignition in a platinum dish, and conversion to magnesium sulfate.

The results of the analyses, expressed in per cent. of magnesium, were as follows: magnesium hexane sulfonate: calcd. 6.92, found 6.89; octane sulfonate: calcd. 5.92, found 5.93; decane sulfonate: calcd. 5.20, found 5.12; dodecane sulfonate: calcd. 4.65, found 4.63.

Preparation of Solutions.—Most of the solutions were prepared individually by weight, so that, in general, each point on the conductance plots corresponds to a separately prepared solution. A few, however, were prepared by dilution. In the case of the decane and dodecane sulfonates, with Krafft points of 41 and 54°, respectively, the solutions required the use of an air-bath provided with glass windows, and held above 60°, to avoid precipitation of the salt during the filling of the conductivity cells and pycnometers. Magnesium octane and hexane sulfonate solutions, the former with a Krafft point of 15°, the latter with no Krafft point, were handled at room temperature.

Conductance Measurements.—The conductance measurements were performed with the equipment described in previous papers,[9] the only modification being the use of a cathode ray oscilloscope as balance point detector. The temperature was kept constant to ±0.001°, and measured frequently with a 4-lead platinum resistance thermometer and a Mueller bridge. The thermometer was calibrated using three thermometric points: ice point,[10] sodium sulfate decahydrate,[11] and sodium bromide dihydrate.[12,13] The conductivity cells were calibrated with 0.1 demal potassium chloride solutions (7.41913 g. of KCl in 1000 g. of solution, calculated to weight *in vacuo*) κ_{25} = 0.0128560 mho cm.$^{-1}$.[14] The cell constants at 40, 60 and 80° were then calculated on the basis of their value at 25°, their geometry, and the coefficients of thermal expansion of Pyrex glass and platinum,[15] and from those values and the measured resistance of the cell with KCl solution, the specific conductance for 0.1 demal potassium chloride at 60° was calculated: κ_{60} = 0.021853 mho cm.$^{-1}$. The solutions were prepared with water obtained by distillation in a tin-lined still, and allowed to come to equilibrium with air. The conductance of the water was measured simultaneously with that of the solutions; it was of the order of 2 × 10^{-6} mho cm.$^{-1}$ at 25° and 4 × 10^{-4} mho cm.$^{-1}$ at 60°.

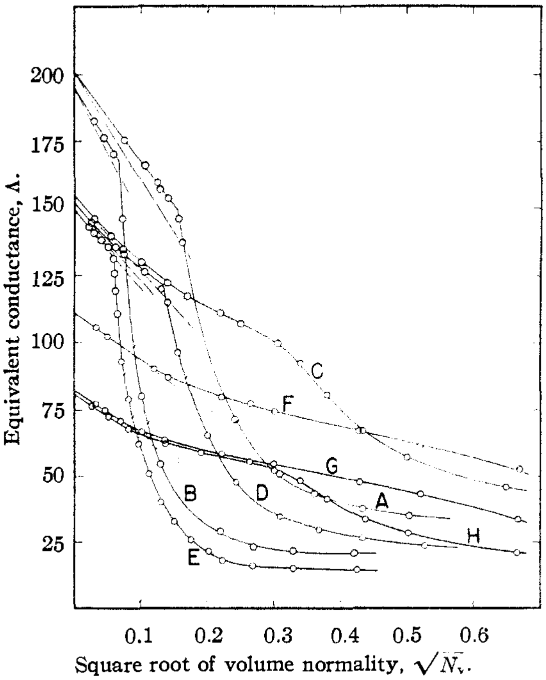

Fig. 1.—The equivalent conductance of magnesium alkane sulfonate solutions. Curves A and B correspond, respectively, to the C_{10} and C_{12} salts at 80°; C, D and E, to C_8, C_{10} and C_{12} at 60°; F to C_6 at 40°; G and H to C_6 and C_8 at 25°.

Density Measurements.—Density measurements were performed with pycnometers of the type described by Scott and Tartar.[16] The purpose of the density measurements was to convert weight normalities (equiv. per 1000 g. solvent) to volume normalities.

Solubility measurements were carried out by the technique described by Tartar and Wright.[17]

The critical concentrations for the formation of micelles (later designated cmc) were determined for some of the salts by the use of pinacyanol chloride dye,[18,19] in concentrations 10^{-5} molar.

Results and Discussion

The results of the conductance measurements are shown graphically in Figs. 1 and 2.[20] Although these plots are closely related, each brings out certain features in a unique way; the former (Fig. 1) describes better the behavior of the salts below the cmc, where they show the behavior of normal electrolytes and the normality is clearly defined; the latter (Fig. 2) is of significance above the cmc, where the plot is remarkably linear.

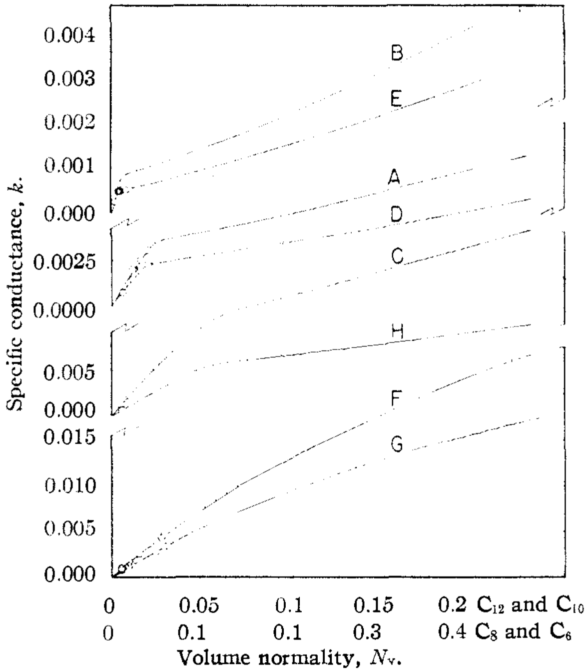

Fig. 2.—The specific conductance of magnesium alkane sulfonate solutions. The lettering of the curves corresponds to that of Fig. 1.

To obtain the limiting equivalent conductances of the sulfonate anions, that of the magnesium ion at different temperatures was taken or estimated

---

(9) Sivertz, Reitmeier and Tartar, This Journal, **62**, 1379 (1940).

(10) White, *ibid.*, **56**, 20 (1934).

(11) Dickinson and Mueller, *Bur. Standards, Bull.*, **3**, No. 1, 641 (1907).

(12) Richards, *Proc. Amer. Acad. Arts Sci.*, **41**, 436 (1905–1906).

(13) Richards and Wells, *Z. physik. Chem.*, **56**, 349 (1906).

(14) Jones and Bradshaw, This Journal, **55**, 1780 (1933).

(15) Washburn, *ibid.*, **38**, 2431 (1916).

(16) Scott and Tartar, *ibid.*, **65**, 692 (1943).

(17) Tartar and Wright, *ibid.*, **61**, 539 (1939).

(18) Sheppard and Geddes, *J. Chem. Phys.*, **13**, 63 (1945).

(19) Corrin, Klevens and Harkins, *ibid.*, **14**, 480 (1946).

(20) The tabulated numerical data for this paper have been filed with the American Documentation Institute, Washington, D. C., and are available for microfilm and photoprint distribution.

by graphical interpolation from the data given by Landolt and Börnstein.[21] The limiting equivalent conductances in mhos cm.$^{-1}$ of the anions of the respective salts at the different temperatures are: (25°), C_6, 29; C_8, 25: (40°), C_6 39.5: (60°), C_8, 55; C_{10}, 53; C_{12}, 51: (80°), C_{10}, 68; C_{12}, 63.

The dotted lines in Fig. 1 at small concentrations represent the conductances calculated in accordance with Onsager's equation. In all cases where the experimental values are at sufficiently low concentrations, the agreements are exceedingly good.

From the break in the conductance curves, the cmc values for the dodecane, decane and octane magnesium salts have been determined. The cmc for the hexane salt was found by using pinacyanol dye, and lies outside the concentration range studied here by conductance measurements. For comparion, the cmc for the corresponding sodium salts are given; the values for the tetradecane, dodecane, decane and pentane salts were taken from the literature[22,23]; those for the octane and hexane salts were determined by the dye method. The logarithm of the cmc is a linear function of the number of carbon atoms in the paraffin chain (see Fig. 3). To permit comparison, the values for the salts with 10 carbon atoms or more have been adjusted to 25° by linear extrapolation from the values at higher temperatures. For the magnesium and sodium salts, the slopes of the plots are somewhat greater and smaller, respectively, than those for the fatty acid soaps studied by Harkins,[24] and used by Debye in his sketch of a theory of the micelle.[25] According to his theory, however, all slopes should be the same.

It is noteworthy that these cmc curves for magnesium and sodium salts intersect; below 7 carbon atoms, the sodium salts form micelles at concentrations lower than the magnesium salts. Hence it does not appear that, in general, the bivalent cations are more effective than univalent in producing micelle formation as stated by Lottermoser and Puschel.[26]

From each pair of cmc values for a given salt it is possible to estimate the heat content change, ΔH, of the formation of micelles from paraffin chain anions and magnesium cations. The calculations were made in accordance with the method and with the assumptions used by Stainsby and Alexander.[27] The values obtained in kilocalories per equivalent weight are −2.6 and −3.6 for the decane and dodecane sulfonates, respectively, and appear to be of reasonable order of magnitude when compared with the values obtained by Alexander and Stainsby for the corresponding sodium salts.

There is an interesting relationship at a given temperature between the slopes for the Λ *vs.* $\sqrt{N_v}$ curves immediately above the cmc, the carbon chain length and the specific conductance. The slopes increase with increasing chain length; this has also been observed by Grieger and Kraus[28,29] for some quaternary ammonium salts, and can be observed in Fig. 1 for the C_8, C_{10} and C_{12} salts at 60°. An expression for this relationship can be obtained in the following manner: let s_1 and s_2, represent the slopes of the specific conductance curves below and above the cmc; represent the specific conductance κ by $\kappa_{cmc} + \kappa'$ (κ_{cmc} = the specific conductance at cmc = const.), and the volume normality N_v by cmc + N_v'.

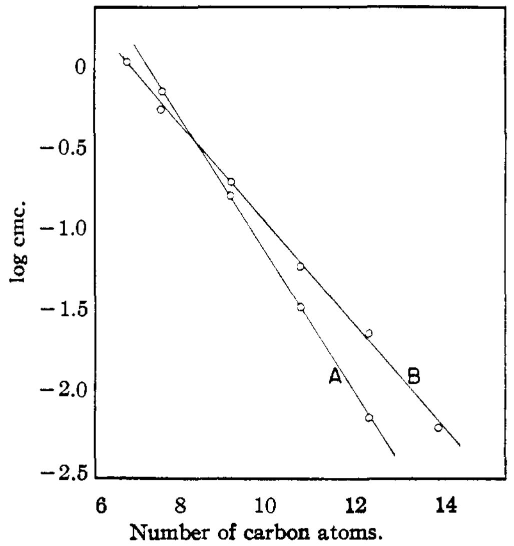

Fig. 3.—Critical concentrations for the formation of micelles, extrapolated to 25°. Curves A and B represent the magnesium and sodium salts, respectively.

Substituting in the usual formula $\Lambda = \frac{1000\ \kappa}{N_v}$, we obtain

$$\Lambda = \frac{1000(\kappa_{cmc} + \kappa')}{\text{cmc} + N_v'}$$

Let S represent the slope of the Λ *vs.* $\sqrt{N_v}$ plot immediately above the cmc. Then

$$\frac{d\Lambda}{d\sqrt{N_v}} = \frac{d\Lambda}{dN_v}\cdot\frac{dN_v}{d\sqrt{N_v}} = \frac{d\Lambda}{dN_v}(2\sqrt{N_v})$$

$$\frac{d\Lambda}{dN_v} = \frac{1000\left[\frac{d\kappa'}{dN_v}(\text{cmc} + N_v') - \frac{dN_v'}{dN_v}(\kappa_{cmc} + \kappa')\right]}{(\text{cmc} + N_v')^2}$$

For

$$N_v = \text{cmc},\ N_v' = 0,\ \kappa' = 0,\ \frac{d\kappa}{dN_v} = S_2 \text{ and } \frac{dN_v'}{dN_v} = 1$$

Then

$$S = \frac{1000[s_2\ \text{cmc} - \kappa_{cmc}]\ 2\ \sqrt{\text{cmc}}}{(\text{cmc})^2}$$

$$= 2000\left[\frac{s_2}{\sqrt{\text{cmc}}} - \frac{\kappa_{cmc}}{\text{cmc}}\frac{1}{\sqrt{\text{cmc}}}\right]$$

But

$$\kappa_{cmc}/\text{cmc}$$

is essentially equal to s_1 and therefore

$$S = 2000\left(\frac{s_2 - s_1}{\sqrt{\text{cmc}}}\right)$$

The data indicate that change of S with carbon

---

(21) Landolt and Börnstein, "Physikalisch Chemische Tabellen," 5th Ed. supp. 3, part 3, p. 2059, Springer, Berlin, 1936.

(22) Gordon R. Shuck, University of Washington, Thesis, 1947.

(23) Wright, Abbot, Sivertz and Tartar, THIS JOURNAL, **61**, 549 (1939).

(24) Harkins, Miltelman and Corrin, *J. Phys. Colloid Chem.*, **53**, 1350 (1949).

(25) Debye, *Ann. N. Y. Acad. Sci.*, **51**, 575 (1949).

(26) Lottermoser and Puschel, *Kolloid-Z.*, **63**, 191 (1933).

(27) Stainsby and Alexander, *Trans. Faraday Soc.*, **46**, 587 (1950).

(28) Grieger, *Ann. N. Y. Acad. Sci.*, **51**, 827 (1949).

(29) Grieger and Kraus, THIS JOURNAL, **70**, 3803 (1948).

chain length is chiefly determined by the variation of the value of $\sqrt{\text{cmc}}$.

The densities of the magnesium alkane sulfonate solutions did not show any abrupt deviation of trend within the range of cmc. To the contrary, some of the densities in this region are remarkably linear. The solubilities show the same general behavior as the sodium salts,[17] but the increase in solubility is much more abrupt at the Krafft point.

SEATTLE 5, WASH. RECEIVED APRIL 14, 1951

[CONTRIBUTION FROM THE GULF RESEARCH & DEVELOPMENT COMPANY]

Infrared Absorption Study of Hydrogen Bonding Equilibria

BY NORMAN D. COGGESHALL AND ELEANOR L. SAIER

A study has been made of hydrogen-bonding equilibria using the infrared absorption due to the unassociated hydroxyl group. Sterically unhindered molecules associate in polymeric complexes. Agreement between theory and experiment obtained by the use of two dissociation equilibria constants, one for the dissociation of dimeric complexes and one for the dissociation of higher order complexes is better than that obtained by the single dissociation equilibrium constant scheme of Kempter and Mecke. These constants have been evaluated for a series of simple alcohols and phenols. If a phenol has one ortho position occupied by a large substituent such as a *t*-butyl group it will be sterically hindered and will associate almost entirely in dimeric complexes. The equilibrium constants for several such partially hindered phenols have been evaluated. Hydrogen bonding occurs between hydroxylated materials and proton-acceptor compounds. Equilibrium constants have been evaluated for the systems of benzyl alcohol and methyl ethyl ketone and of benzyl alcohol and 1,4-dioxane.

The present report is of some studies of the equilibrium of hydroxylated materials between the free or unassociated state and the hydrogen-bonded or associated state. The data for this were obtained by infrared absorption measurements wherein the absorption due to the "free" hydroxyl group was correlated with the amount of unassociated material present. Fox and Martin[1] reported in 1937 some studies on phenol from which they concluded that at moderate concentrations an equilibrium is set up between single and double (associated) phenol molecules. More recently Kempter and Mecke[2] examined phenol using the second overtone of the free hydroxyl stretching frequency. They assumed that complexes of all orders were possible and that all the equilibrium coefficients for the dissociation of complexes were the same, and their data appeared to check the theory satisfactorily. In the present work it was found that better agreement between theory and experiment was obtained if two equilibrium coefficients were used: one for the dissociation of the dimer complexes, and one which was applicable to the dissociation of the higher order complexes. It was found that the association of the partially hindered phenols is almost entirely dimer in nature. In addition, the association between benzyl alcohol and methyl ethyl ketone and between benzyl alcohol and dioxane has been studied.

Equilibrium Equations

Case of a Single Equilibrium Constant.—Kempter and Mecke[2] considered equilibria of the type

$$(\mathrm{ROH})_n + \mathrm{ROH} \rightleftarrows (\mathrm{ROH})_{n+1}$$

where the subscripts n and $n + 1$ refer to complexes of the nth and $n + 1$th order. They assumed that the dissociation constants were equal for all orders of complexes and hence derived the equation

$$K_c = \alpha C/(1 - \sqrt{\alpha}) \tag{1}$$

where K_c is the general dissociation constant applicable to each order complex, α is the fraction of hydroxylated molecules which are unassociated, and C is the concentration in moles per liter of hydroxylated material. When they plotted αC *vs.* $\sqrt{\alpha}$ for phenol, Kempter and Mecke obtained a straight line plot from which they concluded that agreement between their theory and experiment was satisfactory. It has not been possible to obtain agreement between our data and this simple theory and this led to a modification of the theory as given in the next section.

Case of Two Equilibrium Constants.—Here the assumption of equality of all dissociation constants is rejected. Instead we use a distinct constant K_1 for the dissociation of dimer complexes and a general constant K_c for all others, *i.e.*, $K_2 = K_3 = K_4 \ldots . = K_c$. This procedure is based on evidence from three different considerations: (a) the shape and wave length maxima of the association bands at low concentration, (b) the disagreement with data encountered using the simpler scheme, and (c) the evidence that the potential energy in the formation of a dimer complex is considerably less than the potential energy change when an n-fold complex adds a member to become an $n + 1$-fold complex. A discussion of these points will be given later.

Utilization of the equilibrium conditions between the various orders of complexes leads to the relation

$$\alpha_n = n\alpha \frac{K_c}{K_1}\left\{\frac{\alpha C}{K_c}\right\}^{n-1} \tag{2}$$

where α_n refers to the fraction of hydroxylated molecules bound in complexes of the $n + 1$th order. With the use of the relation $\Sigma\alpha_n = 1$ one may then derive the expression for K_c, namely

$$K_c = \frac{\alpha C}{2(K_1 - \bar{K}_1)}\left\{2K_1 - \frac{\bar{K}_1}{2} + \sqrt{2K_1\bar{K}_1 + \frac{\bar{K}_1^2}{4}}\right\} \tag{3}$$

where $\bar{K}_1 = 2\alpha^2C/(1 - \alpha)$. To evaluate K_c from Eq. 3 one must first evaluate K_1. It may be shown from operations on Eq. 3 that $\lim \alpha^2C/(1 - \alpha) = K_1/2$ as $C \rightarrow 0$. Therefore, K_1 may be evaluated by plotting $\bar{K}_1 = 2\alpha^2C/(1 - \alpha)$ *versus* C and extrapolating to zero concentration.

Experimental Details

All infrared absorption data were obtained on a Perkin-Elmer Model 12B spectrometer equipped with a LiF prism. The transmission measurements were made manually using a null system previously described.[3] Three different cell thicknesses were used. For the study of association between hydroxylated molecules and other materials such as ketones, etc., a cell of 1.4 cm. thickness was used. For the studies on alcohols a cell of 0.036″ thickness was used. For the phenols a cell of 0.006″ thickness was used. The difference in the latter two cell thicknesses is a result of the wide difference of extinction coefficients for the alcohols as a

---

[1] J. J. Fox and A. E. Martin, *Proc. Roy. Soc. (London)*, **162**, 419 (1937).

[2] H. Kempter and R. Mecke, *Z. physik. Chem.*, **46**, 229 (1941).

[3] N. D. Coggeshall and E. L. Saier, *J. Applied Physics*, **17**, 450 (1946).