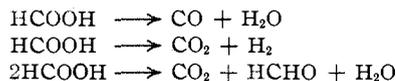


400, and at 425° the reaction rates were determined for the principal primary reaction. Evidence is presented concerning the other reactions involved.

2. The principal primary reaction is shown to be



This is followed by the decomposition of formic acid



3. Evidence is presented that minor primary reactions occur, and the nature of these reactions is suggested.

4. Calculated from the present data, the energy of activation of the reaction producing ethylene is 40,010 cal.

HOUGHTON, MICHIGAN

RECEIVED AUGUST 10, 1939

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY No. 427]

## Vapor-Liquid Equilibrium. IV. Carbon Tetrachloride-Cyclohexane Mixtures<sup>1</sup>

BY GEORGE SCATCHARD, S. E. WOOD AND J. M. MOCHEL

In the third paper of this series,<sup>2</sup> we showed that benzene-cyclohexane mixtures have an entropy increase on mixing which is larger than that of an ideal solution even at constant total volume, and which we attributed tentatively to some lack of randomness in at least one of the pure liquids. Since earlier calculations<sup>3</sup> had given no indication of such an effect for benzene-carbon tetrachloride mixtures, and since cyclohexane has an unusually small entropy of fusion, we have next studied carbon tetrachloride-cyclohexane mixtures. Although there is a slight excess entropy of mixing at constant total volume, it is less than a tenth of that for benzene-cyclohexane mixtures. Mixtures of cyclohexane with carbon tetrachloride agree with simple theory in every respect more closely than do those with benzene.

The cyclohexane was purified as in III. Merck c. p. carbon tetrachloride was refluxed for eleven hours with an aqueous solution 10% in potassium permanganate and 10% in sodium hydroxide. The carbon tetrachloride was distilled off, dried with calcium chloride and rectified in the column described in Paper III. The boiling points of the products and of the rejected portions were measured in a small Cottrell apparatus with a five-junction thermocouple. The normal boiling points, which should be used for relative values only, are:

	CCl <sub>4</sub>	Product	76.69
Tops	75.93	76.54	76.67
Bottoms	76.72	76.69	76.68
	C <sub>6</sub> H <sub>12</sub>	Product	80.73
Tops	79.29	80.41	80.69
Bottoms	82.64	80.99	80.74

(1) Presented before the Division of Physical and Inorganic Chemistry of the American Chemical Society, September 14, 1939.

(2) I and II are published in THIS JOURNAL, **60**, 1275, 1278 (1938), and III in *J. Phys. Chem.*, **43**, 119 (1939).

(3) George Scatchard, *Trans. Faraday Soc.*, **33**, 160 (1937).

The gas heater for the equilibrium still was replaced by an electrical heater with a Variac control which greatly increased the accuracy of the regulation of the boiling. To prevent direct radiation to the thermometer, the bottom of the glass still is painted with black stovepipe enamel which is renewed when necessary. A hood of aluminum foil is placed over the top of the still, and for temperatures of 60° or higher a shield of aluminum foil is placed around the still. This protection prevents the increase of material in the inner boiler during the runs at high temperatures, but does not affect the decrease during the low temperature runs.

The thermocouple was recalibrated from 60 to 100° as before by measuring the vapor pressure of water and determining the temperature from this pressure by the equation of Smith, Keyes and Gerry,<sup>4</sup> and the low temperature calibration was checked by a determination of the transition point of sodium sulfate decahydrate. Measurements of the vapor pressure of cyclohexane agreed with those with the gas heated still except at 30 and 35°. Apparently there had been radiation from the flame to the thermometer which cancelled out at those temperatures at which the calibration had also been carried out in the still. So the measurements for benzene at 30, 35 and 40° were repeated, and new equations were derived for cyclohexane and benzene. The equations are

$$\begin{aligned} \text{CCl}_4: \log p_1 &= 6.68148 - 1045.022/T - 99,577/T^2 \\ \text{C}_6\text{H}_{12}: \log p_2 &= 6.65859 - 1040.641/T - 104,865/T^2 \\ \text{C}_6\text{H}_6: \log p_3 &= 6.66457 - 1007.742/T - 116,197/T^2 \end{aligned}$$

( $T = t + 273.16$ .) The standard (root mean square) deviations are 0.5, 1.3 and  $1.5 \times 10^{-4}$ , respectively. The normal boiling point of carbon tetrachloride is 76.687°. Timmermans and Martin<sup>5</sup> give 76.75. The new boiling points of cyclohexane and benzene are 80.73° and 80.10°, which are 0.004 lower and 0.005° higher than our former values. The values of the vapor pressures of these three substances at rounded temperatures are given in Table II.

(4) L. B. Smith, F. G. Keyes and H. T. Gerry, *Proc. Am. Acad. Arts and Sci.*, **69**, 137 (1934).

(5) J. Timmermans and F. Martin, *J. chim. phys.*, **23**, 747 (1926).

The compositions were determined from the densities at 25°, which are given by the equation

$$d = (0.77383 + 0.81031 z_1)/(1 + z_1 z_2/150) \quad (1)$$

$$z_1 = 1 - z_2 = 1/(1 + w_2 d_1/w_1 d_2) \quad (2)$$

in which  $w_1$  is the weight of carbon tetrachloride,  $d_1$  its density, and  $z_1$  its volume fraction, and  $w_2$ ,  $d_2$  and  $z_2$  are the corresponding quantities for cyclohexane. In Table I are given the weight fractions and mole fractions of carbon tetra-

TABLE I  
DENSITIES OF CYCLOHEXANE-CARBON TETRACHLORIDE MIXTURES AT 25°

Weight fraction CCl <sub>4</sub>	Mole fraction CCl <sub>4</sub>	Density	Deviation from eq. 1	100V <sup>M</sup> /V <sup>0</sup>
0.0000	0.0000	0.77383	.....	...
.2053	.1238	.86401	-0.00003	0.069
.3744	.2466	.95609	+ .00008	.108
.5177	.3699	1.05106	+ .00011	.140
.6369	.4897	1.14605	+ .00016	.151
.6434	.4968	1.15162	+ .00006	.161
.7530	.6251	1.25638	- .00018	.175
.7530	.6251	1.25646	- .00010	.168
.8458	.7500	1.36199	- .00009	.139
.9268	.8738	1.47019	+ .00010	.078
1.0000	1.0000	1.58414	.....	...

chloride, the measured densities, the difference of these densities from those calculated by equation 1, and the measured values of 100V<sup>M</sup>/V<sup>0</sup>.  $V$  is the volume of the mixture,  $V^0$  that of the unmixed components, and  $V^M = V - V^0$ . From equation 1, it follows that

$$V^M/V^0 = z_1 z_2/150 \quad (3)$$

There is a systematic error in these results which corresponds to a loss of 2-4 mg. of the component first weighed out, and which we confirmed later as the approximate loss by evaporation between the two weighings. Since this corresponds to only 0.01-0.02% in the composition, it was not considered worth while to repeat these measurements with a different technique, but we have used equation 1 to determine the equilibrium compositions.

Vapor-liquid equilibrium measurements were made at intervals of approximately one-eighth in the mole fraction at 40 and 70° and for a single mixture, about 50 mole per cent., at 30, 50 and 60°. For mixtures containing more than 40% carbon tetrachloride, nitrogen replaced helium as the confining gas. The measurements at 40° are shown in Fig. 1, in which the curves are determined from equations 6, 7, 14 and 15 and the circles are the individual experimental points. The top curve gives the equilibrium pressure as ordinate

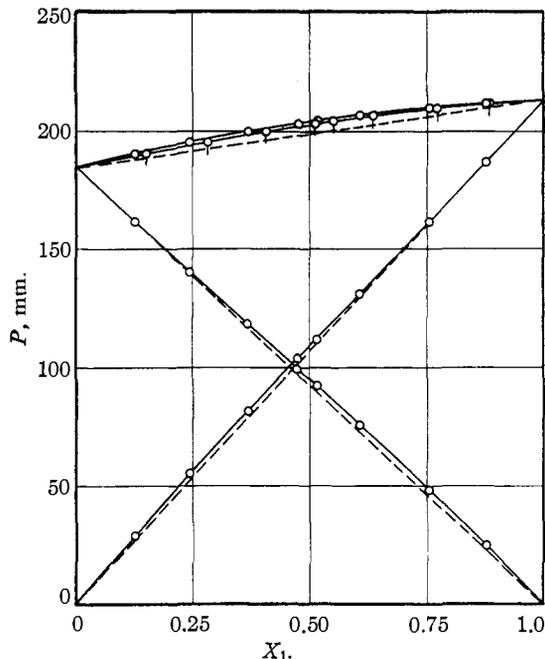


Fig. 1.—Vapor pressure vs. mole fraction for carbon tetrachloride-cyclohexane at 40°.

and the liquid composition as abscissa. The curve just below it and the flagged circles have the vapor composition as abscissa, and the two lower curves are the derived partial pressures with the liquid composition as abscissa. The broken lines are the Raoult's law lines for the total and partial pressures vs. liquid composition.

TABLE II  
VAPOR PRESSURES OF PURE SUBSTANCES

Temp., °C.	Carbon tetrachloride, mm.	Cyclohexane, mm.	Benzene, mm.
30	141.55	121.60	119.16
40	213.34	184.61	182.70
50	312.04	271.80	271.34
60	444.28	389.29	391.66
70	617.43	543.95	551.03
80	....	743.27	757.56

The measurements are reported in detail in Table III as mole fraction of carbon tetrachloride in the liquid and in the vapor, equilibrium pressure, and the derived excess free energy of mixing. After each of the last three is given the deviation of the corresponding quantity from that calculated by equations 6, 7, 14 and 15.

After the measurements with mixtures there was a distinct odor of phosgene which was stronger from the condensate than from the liquid and which increased after each measurement. Therefore three approximately equimolar mixtures

TABLE III  
 VAPOR PRESSURES OF MIXTURES

$t$	Mole fr. of Liquid ( $x_1$ )	of $\text{CCl}_4$ Vapor ( $y_1$ )	Dev. in $y_1$	Pressure $P$	Dev. in $P$	$F_x^E$	Dev. in $F_x^E$
40°	0.1262	0.1515	-0.0008	190.62	=0.00	6.77	+0.05
	.2453	.2822	- .0008	195.62	+ .01	11.50	+ .10
	.3669	.4066	- .0008	200.08	+ .02	14.62	+ .18
	.4739	.5103	- .0010	203.40	- .06	15.61	- .13
	.5151	.5474	- .0029	204.59	- .05	15.90	+ .09
	.4753	.5116	- .0010	203.45	- .05	15.65	- .07
	.6061	.6341	- .0008	206.97	- .06	15.16	- .11
	.7542	.7702	- .0004	210.15	- .03	12.01	- .06
	.8756	.8822	- .0002	212.04	- .03	7.10	- .09
	70°	.1248	.1458	- .0002	558.78	+ .06	5.98
.2468		.2787	+ .0002	571.59	+ .05	10.19	+ .04
.3640		.3981	- .0003	582.59	+ .17	13.03	+ .02
.4836		.5150	- .0003	591.97	- .11	13.89	- .10
.5153		.5473	+ .0017	594.42	= .00	13.90	- .15
.4796		.5113	= .0000	591.73	- .05	13.92	- .06
.6074		.6320	- .0004	600.52	- .09	13.48	- .08
.7535		.7680	- .0001	608.79	+ .05	10.79	+ .06
.8757		.8818	- .0001	613.97	+ .10	6.50	+ .12
30°		.4728	.5114	- .0010	134.73	= .00	16.38
50°	.4829	.5173	- .0006	298.44	+ .01	15.23	+ .07
60°	.4810	.5137	- .0006	425.34	- .04	14.57	= .00

were studied at 40 and at 70°. The first was the last of a series which included all those preceding it, the third was the last of a series which included all those following it run in the order opposite to that of the table, and the second was made up fresh from the components. The first and third check extremely well, and the deviations of the third are in opposite directions at the two temperatures. A test with *p*-dimethylaminobenzaldehyde<sup>6</sup> indicated less than 0.005% phosgene. This confirms the evidence from the equilibrium measurements that the effect of the phosgene is negligible.

In II it was shown<sup>2</sup> that, if the liquid and vapor volumes are given, respectively, by

$$V/(N_1 + N_2) = V_1x_1 + V_2x_2 \quad (4)$$

$$V'/(N_1 + N_2) = RT/P + \beta_1y_1 + \beta_2y_2 \quad (5)$$

the excess chemical potentials and other excess thermodynamic functions are given by

$$\mu_1^E = RT \ln P y_1 / P_1 x_1 + (\beta_1 - V_1)(P - P_1) \quad (6)$$

$$\mu_2^E = RT \ln P y_2 / P_2 x_2 + (\beta_2 - V_2)(P - P_2) \quad (7)$$

$$F_x^E = F^E / (N_1 + N_2) = x_1 \mu_1^E + x_2 \mu_2^E \quad (8)$$

$$S_x^E = -(\partial F_x^E / \partial T)_{P, N} \quad (9)$$

$$H_x^E = H_x^M = F_x^E + T S_x^E \quad (10)$$

in which  $N_1$  and  $N_2$  are the numbers of moles of the two components,  $x_1$  and  $x_2$  are the mole fractions in the liquid,  $y_1$  and  $y_2$  the mole fractions in the vapor,  $P$  is the vapor pressure of the solution,  $P_1$  and  $P_2$  are the vapor pressures of the components,  $V_1$  and  $V_2$  are the molal volumes of the liquid components, and  $\beta_1$  and  $\beta_2$  are functions of the temperature, each characteristic of one of the components. The effect on the subsequent

(6) L. Rosenthaler, *Pharm. Acta. Helv.*, **12**, 6 (1937).

equations of the deviations from equation 4 is entirely negligible, and the effect of deviations from equation 5 may probably be neglected.

For  $\beta_1$  and  $\beta_2$  we have used 0.9 the value calculated by the theory of corresponding states from the equation of Keyes, Smith and Gerry<sup>7</sup> for water vapor. The values for carbon tetrachloride are one-sixth to one-third larger than those measured by Eucken and Mayer,<sup>8</sup> but their measurements with carbon tetrachloride do not seem consistent with those on other gases.

These results may be expressed by the equations

$$F_x^E = (1.3335 - 0.0022916T) V_{x_1 z_2}^0 \quad (11)$$

in which  $V_x^0 = x_1 V_1 + x_2 V_2 = V^0 / (N_1 + N_2)$

$$H_x^M = 1.3335 V_{x_1 z_2}^0 \quad (12)$$

$$S_x^E = 0.0022916 V_{x_1 z_2}^0 \quad (13)$$

$$\mu_1^E = (1.3335 - 0.0022916T) V_{1 z_2}^0 \quad (14)$$

$$\mu_2^E = (1.3335 - 0.0022916T) V_{2 z_1}^0 \quad (15)$$

The calculated results from which the deviations in Table III are calculated are from equation 11 for  $F_x^E$ , and from the combination of equations 6, 7, 14 and 15 for  $P$  and  $y_1$ .

The constants are chosen to give the average of  $F_x^E$  at 40 and 70° and a linear variation of  $F_x^E$  with the temperature. The average deviation is 0.07% in  $y_1$  and about 0.01% in  $P$ . Although the equation is simpler than that of III, the agreement is considerably better than in that paper. There is no indication that a more complicated function of the composition or of the temperature would be preferable. The solutions are far from regular. The ratio of the temperature coefficient of equation 11 to the constant term is 0.0017. The corresponding coefficient for benzene-cyclohexane mixtures is 0.0019.

For theoretical purposes we are interested in the mixing process at constant total volume.<sup>3</sup> We will designate the functions calculated for this process with a subscript  $v$ , and the values measured at constant pressure with a subscript  $p$ . We apply the equations as in III, using for the coefficients of thermal expansion and of compressibility and their ratio at 25°

$$\alpha_0 = 1.228(1 - 0.018z_2) \times 10^{-3}$$

$$\beta_0 = 1.10(1 + 0.009z_2) \times 10^{-4}$$

$$(\alpha_0/\beta_0) = 11.16(1 - 0.027z_2)$$

$(d \ln \beta) / dT = 0.0076$ , which is its value for carbon tetrachloride as well as for benzene.

$$V_x^0 = 97.111 / (1 - 0.10706z_2) \text{ cc./mole}$$

(7) F. G. Keyes, L. B. Smith and H. T. Gerry, *Proc. Am. Acad. Arts and Sci.*, **70**, 319 (1936).

(8) A. Eucken and L. Mayer, *Z. physik. Chem.*, **B5**, 452 (1929).

Then at 25°

$$A_v^E - F_p^E = (V^0/2\beta)(V^M/V^0)^2$$

$$(A_v^E - F_p^E)_x = 0.004891 \times 97.111 z_1^2 z_2^2 / (1 + 0.009z_2) \\ (1 - 0.10706z_2) \text{ cal./mole} \quad (16)$$

$$S_v^E - S_p^E = -V^M \alpha_0 / \beta_0 + (V^0/2\beta)(V^M/V^0)^2 d \ln \beta / dT \\ (S_v^E - S_p^E)_x = -0.001802 \times 97.111 (1 - 0.027z_2) z_1 z_2 / (1 - \\ 0.10706z_2) + 0.0076(A_v^E - F_p^E) \text{ cal./mole } ^\circ\text{C.} \quad (17)$$

$$(E_v^M - H_{px}^M)_x = T(S_v^E - S_p^E)_x + (A_v^E - F_p^E)_x \quad (18)$$

In Fig. 2 are shown  $F_{px}^E$  at 25° and at 70° from equation 11,  $H_{px}^M$  from equation 12, and  $E_{vx}^M$  at 25°, calculated from  $H_{px}^M$  and equation 18. The difference between  $A_{vx}^E$  and  $F_{px}^E$  at 25° is less than half the width of the line, so the same curve may serve for both.  $TS_{px}^E$  is the difference between the top curve and the third, and  $TS_{vx}^E$  is the difference between the second curve and the third. This second difference is less than a quarter of the first, so three-quarters of the deviation from regularity is accounted for by the change in volume on mixing.

These mixtures are so nearly ideal that we should expect the deviations from random distribution to have a very small effect. Using, as in III, Kirkwood's equation<sup>9</sup> for this effect for a mixture of spheres of equal radii, each with eight nearest neighbors, and with the same value of  $E_{vx}^M$  for an equimolal mixture as for carbon tetrachloride-cyclohexane, 20.7 cal./mole, we obtain

$$E_{vx}^M = B_{12}x_1x_2 - (B_{12}^2/4RT)x_1^2x_2^2 \quad (19)$$

$$20.7 = B_{12}/4 - B_{12}^2/64RT$$

$$B_{12} = 84$$

$$E_{vx}^M - A_{vx}^E = (-84^2/8RT)x_1^2x_2^2 \\ = -0.09 \text{ cal./mole, when } x_1 = 0.5 \quad (20)$$

This effect is very small compared to the measured difference of +4.0 cal./mole.

The difference of 4 cal./mole is so small that it is well to consider the corresponding difference in the more familiar quantities which are directly measured. The effect on  $y_1$  is very small and may be neglected. In an equimolal mixture the measured pressure is 2.63% greater than that calculated by Raoult's law at 40°, and 2.17% greater at 70°. This decrease of 0.46% would be only 0.18% if the solutions were regular. Of the remaining 0.28%, 0.22% is accounted for by the volume change on mixing, and there is only 0.06% left unexplained. However, our measurements are so precise that we believe that the uncertainty of this figure is less than 0.02% or less than one-third its value.

(9) J. G. Kirkwood, *J. Phys. Chem.*, **43**, 97 (1939).

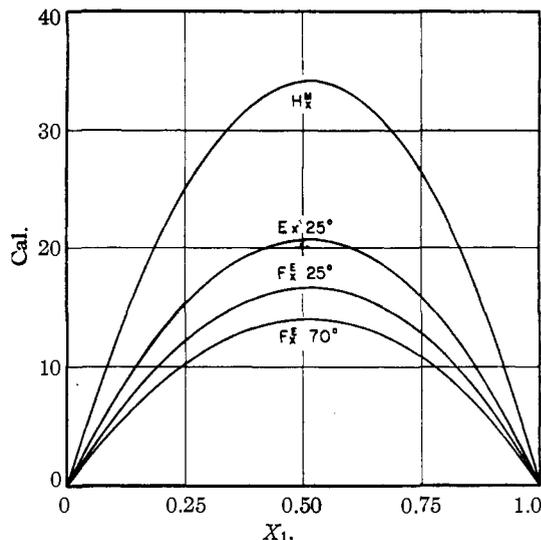


Fig. 2.—Various thermodynamic functions for carbon tetrachloride-cyclohexane.

We are particularly interested in the comparison with benzene-cyclohexane mixtures, for which the unexplained difference is 50 cal. per mole, or thirteen times as great as for carbon tetrachloride-cyclohexane. If the explanation is to be sought in incomplete randomness in one of the component liquids, not more than one-thirteenth is contributed by the cyclohexane unless there are compensating effects in the mixtures of cyclohexane with carbon tetrachloride. However, earlier measurements indicate that benzene-carbon tetrachloride mixtures are almost regular.<sup>3</sup> We are at present making further measurements on this system.

With the assumptions that the cohesive energy density,  $a = (E - E_0)/V$ , is equal to  $-(\partial E/\partial V)_T$  and that  $S_v^E$  is zero,  $E_v^M$  may be computed from  $V^M$  and  $\beta$  by the equation

$$E_v^M = V^M/\beta \quad (21)$$

This leads to a value of 41 cal. per mole for an equimolal mixture, which is approximately twice as great as the directly determined value of 21 cal. per mole and is even larger than the heat of mixing at constant pressure, which is 34 cal. per mole. The absolute difference is not, however, so very great.

From the equations for the vapor pressures of the components, the equations for the deviations from the perfect gas laws, and the densities of the components at 25°, the cohesive energy densities of the components are calculated as  $a_{11} = -72.96$  and  $a_{22} = -66.54$ . The assumption

that the mutual energy per unit volumes,  $a_{12}$ , is equal to  $\sqrt{a_{11}a_{22}}$  leads to the result

$$E_{vz}^M = -(\sqrt{a_{11}} - \sqrt{a_{22}})^2 V_z^0 z_1 z_2 \quad (22)$$

For an equimolal mixture this yields  $E_{vz}^M = 3.8$  cal. per mole instead of the measured 20.7. However, if we calculate  $-a_{12}$  from the relation

$$E_{vz}^M = (2a_{12} - a_{11} - a_{22}) V_z^0 z_1 z_2 \quad (23)$$

and the measured 20.7 for equimolal mixtures, we obtain  $-a_{12} = 69.34$ , which is only 0.5% less than  $\sqrt{72.96 \times 66.54} = 69.67$ . So, quadratic combination gives a very good approximation for  $a_{12}$ , and the small error is in the direction predicted by the quantum theory. The treatment of solutions makes too drastic demands for a simple theory in requiring a small difference between large numbers. On the other hand, measurements on solutions afford a correspondingly accurate measure of one of these quantities if the others are known.

### Summary

The vapor-liquid equilibrium pressure and compositions of carbon tetrachloride-cyclohexane mixtures have been measured at 40 and 70° over the whole composition range, and at 30, 50, and 60° for approximately equimolal mixtures. The densities have been determined at 25°.

These measurements have been expressed analytically, and corresponding equations derived for the thermodynamic functions, including the energy and entropy of mixing at constant total volume.

The dependence upon composition agrees with the predictions of the simple theory. The deviation from regularity is relatively large but most of it is explained by the volume change on mixing.

The unexplained entropy increase on mixing is only one-thirteenth as large as for benzene-cyclohexane mixtures.

CAMBRIDGE, MASSACHUSETTS RECEIVED AUGUST 29, 1939

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STANFORD UNIVERSITY]

## Solutions of the Paraffin-Chain Sulfonic Acids as Colloidal Electrolytes

BY EVELYN LAING MCBAIN, WALTER B. DYE AND STEWART A. JOHNSTON

Colloidal electrolytes since their first recognition by McBain in 1913 have received steadily increasing attention, because of their interesting departures from the behavior of ordinary electrolytes and because they embrace such large groups of substances. The soaps originally studied do not lend themselves to precise examination in very dilute solution on account of the prominent effects of hydrolysis. It remained therefore for Lottermoser and Püschel<sup>1</sup> to show that in great dilution many non-hydrolyzable salts of alkyl sulfuric acids conform to the behavior of the Debye-Hückel theory, rather suddenly departing from it at a very low concentration designated, by Bury and collaborators, the critical concentration for micelles. This has been confirmed by many subsequent investigators, and necessitated a modification of the original formulation to conform more closely to later conceptions of interionic attraction. Different authors, however, differ in their formulations. It is desirable to have exact measurements of many different properties of a non-hydrolyzable pure

material of simple chemical composition sufficiently soluble that it may be studied over a wide range of concentrations.

The present communication comprises measurements of lowering of freezing point, conductivity, viscosity and density of straight chain sulfonic acids with special emphasis upon dodecyl sulfonic acid. The results for diffusion have been published<sup>2</sup> and a provisional discussion is being given elsewhere,<sup>3</sup> although it is not until our measurements of transport number are completed that a sufficient number of equations will be available for a definitive solution of the problem, except in its principal outlines which are already generally known.

### Experimental

An especially pure preparation of laurylsulfonic acid was made by M. E. Synerholm by the method of Noller and Gordon<sup>4</sup>; its equivalent weight by titration was 100.05% of the theoretical, the excess probably being water. The other sulfonic

(2) Evelyn Laing McBain, *Proc. Roy. Soc. (London)*, **A170**, 415 (1939).

(3) Van Rysselberghe, *Colloid Symposium*, 1939.

(4) Noller and Gordon, *This Journal*, **55**, 1090 (1933).

(1) Lottermoser and Püschel, *Kolloid Z.*, **63**, 175 (1933).