does methylene or ethylene dichloride react with amylsodium in the manner expected.

The result of nearness of groups to each other upon the nature of the products is discussed.

High boiling products are formed during reaction of these organosodium compounds with alkyl halides.

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[CONTRIBUTION FROM THE WILLIAM H. CHANDLER CHEMISTRY LABORATORY OF LEHIGH UNIVERSITY]

The Solubility Curves of the Systems Carbon Tetrachloride–*n*-Alkyl Acids–Water at 25°

BY HILTON A. SMITH AND M. BERMAN

In connection with studies of certain ternary alloys, Wright[1] investigated the system chloroform–acetic acid–water, giving his results in weight per cent. on a triangular coördinate system. Subsequently considerable data have been reported giving distribution coefficients of various organic acids between numerous organic solvents and water, but little work has been done in connection with locating the solubility curves of such three phase systems.

The present paper gives the results of investigations into the composition of homogeneous phases having the maximum possible concentration of carbon tetrachloride in water containing varying amounts of straight chain acids. The solubility curves are given in mole per cent. instead of weight per cent. in order to show the effect of the length of the carbon chain of the acids on the size and shape of the areas of mutual solubility.

Experimental

Materials.—Pure formic acid was prepared from the analytical reagent (89%) acid by distillation in a fractionating column, following the method of Ewins.[2] The pure acid froze at 8.3°. C. P. glacial acetic acid and C. P. carbon tetrachloride were used without further purification. The best grades of Eastman chemicals were used in the case of propionic and higher acids.

Methods.—The limits of mutual solubility of the three components were determined by titration of mixtures of two of the components with the third until two phases merged into a single phase or, when the two starting components were miscible, until a second phase separated. Calibrated burets were used, and all experiments were carried out at 25°. In the case of acids which were only partially miscible with one of the other components, the mutual solubility of each in the other was also determined by allowing the two to remain in contact with each other in a 25° thermostat for forty-eight hours after having first been shaken vigorously. Samples of each layer were then withdrawn and analyzed using standard potassium hydroxide solution.

Results and Discussion

The results of the determinations are given in Table I. The figures represent the maximum mole per cent. of carbon tetrachloride which may be dissolved in the indicated mixtures of acid and water. The solubility of water in carbon tetrachloride and that of carbon tetrachloride in water have been determined accurately by Clifford,[3] by Rosenbaum and Walton,[4] and by Gross and Saylor.[5] These values were not redetermined, but the figures given in the table were calculated from those given in the literature.

TABLE I

Mole % CCl_4	Mole % Acid	Mole % H_2O
	Formic Acid	
0.01	0	99.99
.15	40	60
.30	49	51
.40	55	44
.60	63	36
.90	74	24
2.2	94	3.9
2.7	97.3	0
91.2	8.8	0
99.9	0	0.1
	Acetic Acid	
0.01	0	99.99
.3	5.2	94.5
.3	9.5	90
.4	14.4	85
.4	20	79
.5	28	72
2.4	46	52
5.2	54	41
9.2	58	33
11.4	58	31
15	58	27
23	57	20
27	55	18
32	53	15
48	44	8.0
55	39	6.2
61	34	4.4
69	29	1.9
99.9	0	0.1
	Propionic Acid	
0.01	0	99.99
.2	5.7	94
.5	19	80
1.5	26	72
5.0	33	62
13	40	47
17	44	39
31	47	22
42	46	12
49	43	8.3
55	40	5.5
63	35	2.4
75	25	0.1
99.9	0	0.1

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(1) Wright, *Proc. Roy. Soc.* (London), **49**, 174 (1891); **50**, 375 (1892).

(2) Ewins, *J. Chem. Soc.*, **105**, 350 (1914).

(3) Clifford, *Ind. Eng. Chem.*, **13**, 631 (1921).

(4) Rosenbaum and Walton, THIS JOURNAL, **52**, 3568 (1930).

(5) Gross and Saylor, *ibid.*, **53**, 1744 (1931).

TABLE I (*Concluded*)

Mole % CCl_4	Mole % Acid	Mole % H_2O
n-Butyric Acid		
0.01	0	99.99
0.1	4.7	95
1.4	22	76
4.8	35	60
7.7	40	52
15	50	35
28	51	21
45	47	7.7
56	39	5.0
59	37	4.1
64	33	3.0
68	30	2.1
79	21	0.3
99.9	0	0.1
n-Valeric Acid		
0.01	0	99.99
0	0.695	99.3
0	50.5	49.5
7.1	58	35
17	62	21
24	61	15
40	57	3.1
73	26	0.6
99.9	0	0.1
n-Caproic Acid		
0.01	0	99.99
0	0.16	99.84
0	69.5	30.5
5.7	73	21
14	72	14
22	68	9.5
44	53	2.6
72	28	0.4
99.9	0	0.1
n-Heptylic Acid		
0.01	0	99.99
0	0.053	99.95
0	78.3	21.7
5.9	80	14
11	78	11
22	73	5.2
29	67	4.2
38	60	2.1
69	31	0.3
99.9	0	0.1

The relative accuracy of the methods used may be seen from a comparison of the figures in Table II.

TABLE II

	Analysis by titration to appearance or disappearance of two phases	Analysis using standard base
CCl_4	3.0	2.7
HCOOH	97	97.3
H_2O	50	49.5
n-Valeric acid	50	50.5
H_2O	99.3	99.31
n-Valeric acid	0.7	0.695
H_2O	70	69.5
n-Caproic acid	30	30.5

The seven phase diagrams resulting from the values in Table I are shown in Fig. 1. Points in the ranges where the curves merge together have not been indicated for sake of clarity of the figure. These curves show that starting with formic acid an increase in the carbon chain length at first expands the single phase area, apparently due to the increased attraction of the alkyl radical for the carbon tetrachloride. The maximum single phase area is found with propionic acid. With still higher acids, this area decreases, due to the decreased solubility of the alkyl radical in water.

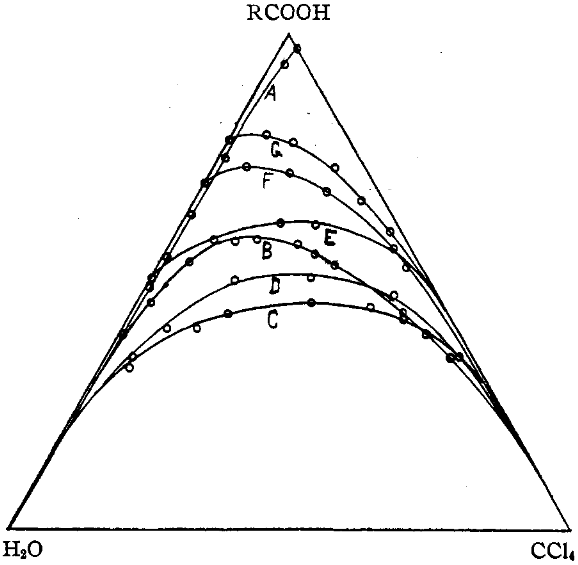

Fig. 1.—Ternary phase diagrams of the systems CCl_4–$RCOOH$–H_2O at 25°: A, formic acid; B, acetic acid; C, propionic acid; D, *n*-butyric acid; E, *n*-valeric acid; F, *n*-caproic acid; G, *n*-heptylic acid.

Summary

The solubility curves of the systems CCl_4–$RCOOH$–H_2O have been studied in the case of straight chain acids having from one to seven carbon atoms. Increasing the length of the carbon chain first causes an increase in the area of mutual solubility, but later causes a decrease. The maximum area occurs when propionic acid is used.

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