

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

The Solubility Curves of the Systems Carbon Tetrachloride–Branched Chain Alkyl Acids–Water at 25°

BY HILTON A. SMITH AND HAROLD TAYLOR

In an earlier paper¹ the effect of the length of the carbon chain of normal organic acids on the solubility curves of the systems carbon tetrachloride–*n*-alkyl acids–water was demonstrated. The present paper gives the results of investigations concerning the effect of branched chain acids on the solubility curves of similar systems.

Experimental

All acids used were the best grade of Eastman chemicals. C. P. carbon tetrachloride was used without further purification since the solubility of water in pure carbon tetrachloride is not great enough to affect the results within the limit of experimental error.

As in the earlier investigation, 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. In the case of acids which were only partially miscible with water, the mutual solubility of each in the other was also determined by titration methods.

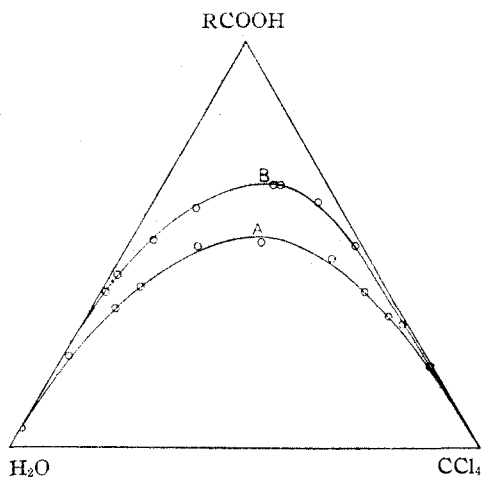


Fig. 1.—Solubility curves of the systems $\text{CCl}_4\text{--C}_3\text{H}_7\text{COOH--H}_2\text{O}$ at 25°: A, *n*-butyric acid; B, isobutyric acid.

Results and Discussion

The results of the determinations are given

(1) Smith and Berman, *THIS JOURNAL*, **59**, 2390 (1937).

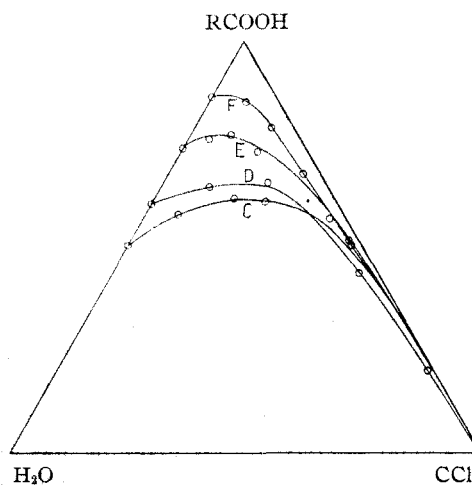


Fig. 2.—Solubility curves of the systems $\text{CCl}_4\text{--C}_4\text{H}_9\text{COOH--H}_2\text{O}$ at 25°: C, *n*-valeric acid; D, isovaleric acid; E, methylethylacetic acid; F, trimethylacetic acid.

in Table I. The values represent the maximum mole per cent. of carbon tetrachloride which may be dissolved in the indicated mixtures of acid and water. As in the earlier paper, the solubility of water in carbon tetrachloride and that of carbon

TABLE I

Mole % CCl_4	Mole % acid	Mole % H_2O	Mole % CCl_4	Mole % acid	Mole % H_2O
Isobutyric Acid			Isovaleric Acid		
0.01	0	99.99	0.01	0	99.99
1.3	39	60	0	0.95	99.05
1.8	43	55	0	60.60	39.40
5.0	51.5	43.5	10	65	25
10	59	31	22	66	12
22	62	16	52	44	4.0
23	65	12	79	20	1.0
25	65	10	99.9	0	0.1
40	59	0.8			
49	51	.5			
99.9	0	.1			
Methylethylacetic Acid			Trimethylacetic Acid		
0.01	0	99.99	0.01	0	99.99
0	0.56	99.44	0	0.55	99.45
0	74.0	26.0	0	86.4	13.6
4.3	76.5	19	7.9	85	7.5
8.7	77	14	17	79	4.4
17	73	10	28	68	3.8
35	62	3.0	48	50	1.7
46	52	1.9	99.9	0	0.1
99.9	0	0.1			

tetrachloride in water were calculated from the data of Clifford,² Rosenbaum and Walton³ and Gross and Saylor.⁴

Figure 1 shows the solubility curves of the systems carbon tetrachloride-acid-water at 25° for butyric and isobutyric acids. The curve for *n*-butyric acid was taken from the data of Smith and Berman.¹ Figure 2 shows the diagrams for similar systems using *n*-valeric acid, isovaleric acid, methylethylacetic acid, and trimethylacetic acid. Again the curve for *n*-valeric acid was taken from the data of Smith and Berman.¹

An examination of these curves shows that in all cases the mutual solubility area is decreased

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

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

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

by substitution of a branched chain acid for a normal acid. The curves for isovaleric acid and methylethylacetic acid indicate that a methyl group substituted in the alpha position is more effective in decreasing the mutual solubility area than a methyl group substituted in the beta position.

Summary

The solubility curves at 25° of the systems CCl₄-RCOOH-H₂O have been studied for the following acids: isobutyric, isovaleric, methylethylacetic, and trimethylacetic. The curves show that the mutual solubility area decreases with increased chain branching.

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The Action of Aluminum Chloride on Fluorinated Compounds

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In an effort to establish the orientation effect of a CF₃ group by the synthesis of CF₃C₆H₄COCH₃, benzotrifluoride was allowed to react with acetyl chloride and aluminum chloride. Instead of the expected products, the reaction gave benzotrichloride and aluminum fluoride in excellent yield and purity. In the absence of acetyl chloride, the reaction was not clean-cut and produced a large amount of tar; only a small quantity of benzotrichloride was isolated. In neither reaction was there a copious evolution of hydrogen halide; in the first case only hydrogen chloride came off, while in the second case a small amount of hydrogen fluoride was present in the hydrogen chloride.

From these results, it is concluded that the principal reaction is an exchange of halogen atoms between the organic fluoride and the inorganic chloride. In the presence of acetyl chloride, a complex presumably is formed between this compound and the aluminum chloride, and the exchange of halogen atoms is smooth because it occurs between the complex and the organic fluoride. In the absence of acetyl chloride, the exchange occurs directly and the benzotrichloride produced is subjected to the action of free aluminum chloride. This is known to cause tar formation.¹

(1) Wohl and Wertyporoch, *Ann.*, **461**, 30 (1930).

The fact that some hydrogen fluoride comes off indicates that either benzotrifluoride or the intermediate benzofluoro-chloride is also involved in the condensation.

The replacement of organically bound fluorine by chlorine in the presence of aluminum chloride suggests a reason for the repeated failures² to effect Friedel-Crafts condensations between organic fluorides and chlorinated ethylenes or benzene.³ The reactions involving only aliphatic compounds always gave tarry materials, which were abandoned. The reactions involving benzene were tried with the following fluorides: CCl₂FCCl₂F, CCl₂FCClF₂, CClF₂CClF₂, CHClF₂ and CCl₂F₂. In the last two cases, the fluorinated compound was passed as a gas through benzene containing aluminum chloride. In the other cases, aluminum chloride was dropped in small portions into a cooled solution of the fluoride in an excess of benzene. In general, a vigorous but controllable reaction started at once but soon stopped; it was started again every time a portion of aluminum chloride was added. The gas evolved was mostly hydrogen chloride which contained only a very small amount of hydrogen fluoride. After completion of the reaction, and decomposition with water in the usual way, the

(2) Henne and Leicester, *THIS JOURNAL*, **60**, 864 (1938).

(3) The use of metalloids fluorides instead of aluminum chloride is now under investigation.