[CONTRIBUTION FROM THE INSTITUTE OF EXPERIMENTAL BIOLOGY OF THE UNIVERSITY OF CALIFORNIA]

Distribution Coefficients of Some Monocarboxylic Acids and Esters between Immiscible Solvents

BY H. J. HENRIQUES

Introduction.—The present paper continues the work of R. C. Archibald[1] and of A. E. Smith and J. W. Norton.[2] The use of distribution coefficients in the separation of vitamins in a pure form is the ultimate aim and, since linoleic acid and linolenic acid have been claimed to be forms of vitamin F,[3] the fatty acid series and some of the esters have been investigated.

Experimental Methods.—Determinations were made at 0 and −19.5°, and, in the case of the acids, at three concentrations. The solvents and acids (or esters) were placed in 250-cc. flasks in an ice-bath and allowed to remain, with frequent shaking until temperature equilibrium had been established, when two 25-cc. portions of each layer were removed for titration with 0.1 *N* sodium hydroxide in 95% ethyl alcohol. The flasks with the remainder of the solutions were then cooled to −19.5°, when the second series of samples was drawn.

In the case of the esters the usual saponification methods gave very erratic results, apparently due to alkali dissolved from the glass and to the low concentrations of esters used. The determination finally employed consisted in saponifying with excess sodium hydroxide in 95% ethyl alcohol, adding water and distilling until the solvent had been entirely driven off, liberating the fatty acid with hydrochloric acid, and extracting the water layer with purified isopropyl ether. The ether layer was washed with water and titrated with 0.1 *N* sodium hydroxide in 95% ethyl alcohol.

The −19.5° bath was essentially that of R. C. Archibald[4] made to accommodate seven samples.

Materials.—The 2,2,4-trimethylpentane was prepared in this Laboratory,[5] and was of very great purity. The β-methoxyethanol (Carbide & Carbon Chemicals Corporation) was rectified in a 6.09 meter Raschig column[6] and boiled within less than 0.1°. The methanol was a commercial product rectified in the same column, after having been made alkaline with sodium hydroxide.

The formic, acetic and butyric acids were commercial C. P. products. The caprylic, lauric, myristic and palmitic acids were very kindly provided by S. Lepkovsky and G. Feskov, of this Laboratory, and were of very high quality. These acids were used in the preparation of the esters.

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[1] R. C. Archibald, THIS JOURNAL, **54**, 3178–3185 (1932).

[2] A. E. Smith and J. W. Norton, *ibid.*, **54**, 3811–3818 (1932).

[3] G. O. Burr and M. M. Burr, *J. Biol. Chem.*, **82**, 345–367 (1929); **86**, 587–621 (1930); G. O. Burr, M. M. Burr and E. S. Miller, *ibid.*, **97**, 1–9 (1932).

[4] R. C. Archibald, THIS JOURNAL, **54**, 3886 (1932).

[5] See H. M. Evans, E. A. Murphy, R. C. Archibald and R. E. Cornish, to be published.

[6] See Evans, Cornish, Lepkovsky, Archibald and Feskov, *Ind. Eng. Chem., Anal. Ed.*, **2**, 339 (1930).

Portions of the solvents in equilibrium with each other at 0° were titrated with 0.1 *N* sodium hydroxide in 95% ethyl alcohol, and the blank titration was subtracted from the experimental concentration of the acid samples. Later work showed that had the β-methoxyethanol been made alkaline before rectification, its acidity would have been negligible. The blank values in millimols per liter were: 0.08 for 2,2,4-trimethylpentane saturated with β-methoxyethanol, 0.3 for β-methoxyethanol saturated with 2,2,4-trimethylpentane, < 0.04 for 2,2,4-trimethylpentane saturated with methanol, < 0.04 for methanol saturated with 2,2,4-trimethylpentane.

Results

TABLE I

DISTRIBUTION RATIOS BETWEEN 2,2,4-TRIMETHYLPENTANE AND β-METHOXYETHANOL AT 0 AND −19.5°, AND CONCENTRATIONS IN MILLIMOLES PER LITER

Hydroc. layer, C_1	Ether layer, C_2	Ratio	Ratio when $C_2 = 0$
Formic acid at 0°			
1.1	248.3	0.0046	
3.4	667.9	.0051	0.0053
4.6	720.7	.0064	
4.9	961.7	.0051	
Acetic acid at 0°			
3.3	156.3	.021	
4.6	161.3	.028	
8.4	361.9	.023	.024
10.5	330.2	.032	
16.9	621.2	.027	
Butyric acid at 0°			
3.4	77.7	.044	
4.0	79.9	.050	
4.9	104.2	.047	
9.9	196.2	.050	.045
12.4	247.0	.050	
16.4	302.2	.054	
21.1	382.7	.055	
Formic acid at −19.5°			
1.3	252.9	.0051	.0048
3.3	703.6	.0046	
Acetic acid at −19.5°			
1.3	170.9	.0078	
2.9	374.3	.0077	.0084
6.4	665.2	.0096	
Butyric acid at −19.5°			
1.9	82.2	.023	
5.8	215.4	.027	.023
10.4	410.3	.025	
Caprylic acid at −19.5°			
3.9	52.2	.075	
12.2	144.7	.084	.074
20.0	234.4	.085	
Caprylic acid at 0°			
5.8	48.2	0.12	
17.7	132.8	.13	0.12
29.1	215.9	.14	
Lauric acid at 0°			
7.3	33.8	.22	
23.5	99.0	.24	.20
42.4	155.0	.27	
Myristic acid at 0°			
8.5	26.9	.32	
24.5	69.0	.36	.30
48.0	122.3	.39	
Palmitic acid at 0°			
5.8	11.8	.49	.47
Oleic acid at 0°			
7.5	18.8	.39	
41.1	87.0	.47	
Lauric acid at −19.5°			
6.4	36.6	.18	
19.6	103.3	.19	.16
35.8	168.9	.21	
Myristic acid at −19.5°			
8.2	26.8	.31	.25
10.2	41.4	.25	
Palmitic acid at −19.5°			
9.5	22.7	.42	.39
Oleic acid at −19.5°			
6.7	20.0	.34	
39.6	92.1	.43	

In Table I the value of the ratio when $C_2 = 0$ was obtained for each acid by plotting C_1/C_2 against C_2 and extrapolating a weighted curve through these points. This method of calculation is based on the assumption that the variation in C_1/C_2 is due to formation of double acid molecules in the hydrocarbon layer. The accuracy of the results is evidently not great,

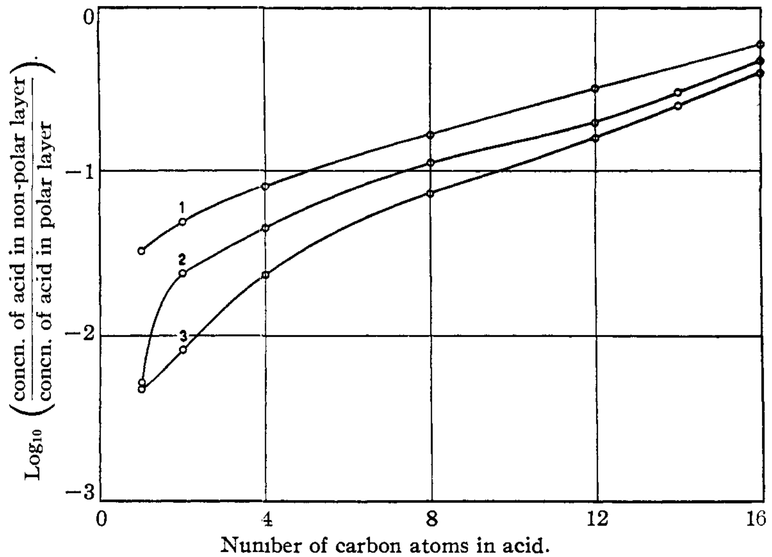

Fig. 1.—Distribution ratios of saturated monocarboxylic acids: 1, from data of A. E. Smith and J. W. Norton, using 2,2,4-trimethylpentane and methanol at 0° [THIS JOURNAL, 54, 3812 (1932)]; 2, 2,2,4-trimethylpentane and β-methoxyethanol at 0°; 3, 2,2,4-trimethylpentane and β-methoxyethanol at −19.5°.

TABLE II

DISTRIBUTION RATIOS OF ESTERS AT 0 AND −19.5°

	At 0°			At −19.5°		
Methyl esters	Hydroc. layer	Alc. layer	Ratio	Hydroc. layer	Alc. layer	Ratio
Caprylate	107.5	109.2	0.98	122.0	109.6	1.1
Laurate	94.8	50.8	1.87	101.5	43.2	2.4
Palmitate	100.7	35.2	2.9	58.8	12.1	4.8
Oleate	83.2	24.9	3.3	143.4	28.2	5.1
Linoleate 66% (found)	99.0	36.2	2.7	106.3	28.5	3.7
Linoleate 100% (calcd.)	53.0	21.4	2.5	67.9	21.0	3.2
β-Methoxy-ethanol esters						
Caprylate	64.5	112.9	0.57	65.0	112.2	0.6
Laurate	80.4	63.4	1.27	80.1	65.2	1.2
Palmitate	44.0	21.0	2.1	41.1	23.5	1.8
Oleate	80.5	38.9	2.1	82.8	38.1	2.2

but was adequate for our purposes.[7] For palmitic acid the association constant was taken as the mean of those for lauric and myristic acids.

Grossfeld and Battay[8] state that petroleum ether is about two and one-half times as effective as ethyl ether for the separation of butyric and caproic acids. If the values of Behrens[7] for the distribution of butyric and caproic acids between ethyl ether and water are compared with those of Grossfeld and Battay for the same acids between petroleum ether and water *at the same concentration in the petroleum ether layer*, it will be found that both solvent pairs are more nearly equally effective for this separation. (It may be noted that the paper by Grossfeld and Battay contains several typographical errors.)

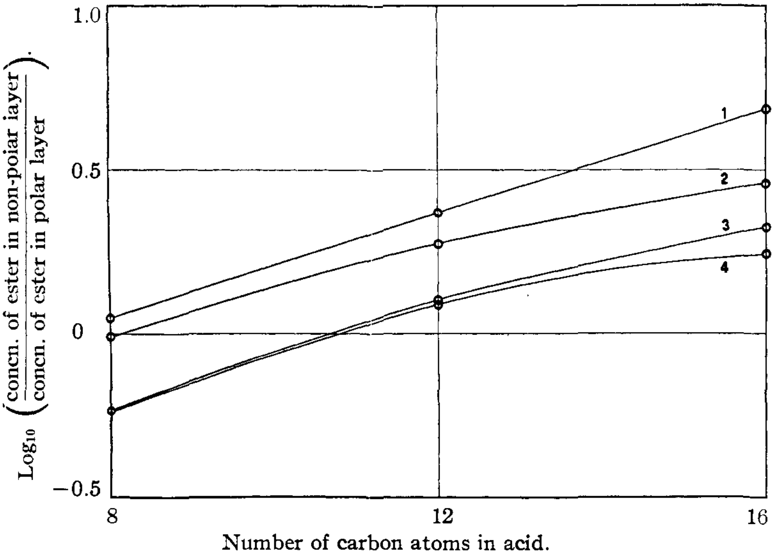

Fig. 2.—Distribution ratios of saturated esters: 1, methyl esters between 2,2,4-trimethylpentane and methanol at −19.5°; 2, methyl esters between 2,2,4-trimethylpentane and methanol at 0°; 3, β-methoxyethanol esters between 2,2,4-trimethylpentane and β-methoxyethanol at 0°; 4, β-methoxyethanol esters between 2,2,4-trimethylpentane and β-methoxyethanol at −19.5°.

It will be noted that there are two values for methyl linoleate in Table II. The material used had an iodine number of 143, equivalent to 34% methyl oleate, the only impurity. In calculating the value for 100% methyl linoleate, the assumption was made that the distribution of the methyl oleate was unaffected by the presence of the linoleate.

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(7) For further discussion of this method see W. U. Behrens, *Z. anal. Chem.*, **69**, 97–107 (1926); H. J. Almquist of this University, yet unpublished.

(8) J. Grossfeld and F. Battay, *Z. Untersuch. Lebensm.* **62**, 99–126 (1931).

Summary

The distribution ratios at 0 and −19.5° of seven fatty acids and five esters of β-methoxyethanol have been determined between 2,2,4-trimethylpentane and β-methoxyethanol. The distribution ratios at 0 and −19.5° of four esters of methanol have been determined between 2,2,4-trimethylpentane and methanol.

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Azulene[1]

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Our knowledge of the chemistry of the blue hydrocarbons known as the azulenes is practically summed up in two papers by Ruzicka and his collaborators,[2] who give a full bibliography of earlier work on the subject.

The azulene used in this investigation was obtained partly by the dehydrogenation of the sesquiterpenes of the essential oil of *Wintera Colorata*[3] and partly by the dehydrogenation *in toto* of guaiacum wood oil. The picrates of the azulene from both sources melted at 121–122°, as did also a mixture of the two, so that the materials are identical. It is probably the sulfur-guaiazulene described by Ruzicka and hereinafter will be called azulene.

The hydrogenation curve of azulene was traced, following the procedure developed by Lebedev and his collaborators.[4] Three hydrogenations were carried out and, although they show slight variations among themselves, the curves have the same general characteristics. A typical example is shown in Fig. 1. There is a short induction period with a slow rate of hydrogenation, rising to give a fairly steady but slowly decreasing rate up to the critical point. The critical point, which can easily be determined as the point at which the blue color disappears, occurs at 55% hydrogenation. A slight but definite increase in the rate was observed immediately after the critical point (*cf.* diisopropenyl and piperylene).

The rate of hydrogenation decreases fairly sharply to a very low value at a point corresponding to 72% saturation, *i. e.*, 3.6 double bonds, and continues to decrease until full saturation is attained. No distinct break occurs at 80% saturation as implied by Sherndal,[5] and the materials described in the literature as octahydroazulene are probably mixtures of this material with hexa- and decahydroazulene.

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(1) This work was carried out while the author was the holder of the John Edmond Fellowship.

(2) Ruzicka and Rudolph, *Helv. Chim. Acta*, **9**, 118 (1926); Ruzicka and Haagen-Smit, *ibid.*, **14**, 1104 (1931).

(3) Melville, THIS JOURNAL, **55**, 2462 (1933).

(4) Lebedev and collaborators, *J. Chem. Soc.*, 823, 2190 (1928).

(5) Sherndal, THIS JOURNAL, **37**, 1537 (1915).