[Contribution from the Research Division of Armour & Company]

SOLUBILITIES OF SATURATED FATTY ACID ESTERS

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The physical properties of the simple alkyl esters (1) of the fatty acids have probably been the subject of more extensive investigation than those of any other class of fatty acid derivatives. These studies have included determination of boiling points, freezing points, melting points, densities, refractive indices, specific heats, heats of crystallization, heats of transition, dielectric constants, and crystal spacings, and investigation of the behavior of binary systems of adjacent homologs. In fact, it would seem that most physical properties with the exception of solubilities have been thoroughly examined. Beyond a recent report (2) of the solubilities of some of the methyl esters in *n*-hexane, no quantitative data have been published.

This paper presents solubility data for the methyl esters of caprylic, lauric, myristic, palmitic, and stearic acids in benzene, cyclohexane, carbon tetrachloride, chloroform, ethyl acetate, butyl acetate, methanol, 95% ethanol, *n*-butanol, acetone, and acetonitrile, with data for methyl tridecanoate, and ethyl, *n*-propyl, and *n*-butyl stearates in several of these solvents for comparison.

The methyl esters were those used in the previous investigation (2). They and the other esters used in this study were prepared by direct esterification of highly purified fatty acids with the appropriate alcohol. The products, after fractionation under a vacuum in a Stedman-packed column, had the following freezing points: methyl caprylate, −33.8°; methyl laurate, 5.08°; methyl tridecanoate, 6.52°; methyl myristate, 18.39°; methyl palmitate, 28.90°; methyl stearate, 37.85°; ethyl stearate, α-form 31.36° (m.p. β-form 33.9°); *n*-propyl stearate, 28.87°; and *n*-butyl stearate, 26.61°.

The solubilities were determined by observing visually the temperature at which crystals appear upon cooling and dissolve upon heating solutions containing known concentrations of solutes. The procedures and equipment used have been described elsewhere (3). The solvents were of the best grade available and were freshly distilled before use.

RESULTS AND DISCUSSION

The solubilities of the alkyl esters are listed in Tables I–XI, inclusive, and some of the representative systems are shown graphically in Figs. 1–5, inclusive.

In a general way, the solubility curves resemble those of the saturated fatty acids (4–6). The esters, having considerably lower freezing points than the acids, are, for the most part, somewhat more soluble on a weight basis than the corresponding fatty acids. The general configuration of the solubility curves of the esters conforms to that of the fatty acids possessing melting points of corresponding magnitude rather than to that of the fatty acids of the same number of carbon atoms. Thus, the solubility of methyl laurate in benzene resembles that

TABLE I

SOLUBILITIES OF ALKYL ESTERS IN ANHYDROUS BENZENE

ESTER	GRAMS OF ESTER PER 100 GRAMS OF BENZENE		
	10.0°	20.0°	30.0°
Me caprylate	∞	∞	∞
Me laurate	∞	∞	∞
Me myristate	355	∞	∞
Me palmitate	107	345	∞
Me stearate	45.5	119	400
Et stearate	66	182	900
n-Pr stearate	102	333	∞
n-Bu stearate	125	455	∞

TABLE II

SOLUBILITIES OF ALKYL ESTERS IN CYCLOHEXANE

ESTER	GRAMS OF ESTER PER 100 GRAMS OF CYCLOHEXANE		
	10.0°	20.0°	30.0°
Me caprylate	∞	∞	∞
Me laurate	∞	∞	∞
Me myristate	275	∞	∞
Me palmitate	67	250	∞
Me stearate	21.2	71	290

TABLE III

SOLUBILITIES OF ALKYL ESTERS IN CARBON TETRACHLORIDE

ESTER	GRAMS OF ESTER PER 100 GRAMS OF CARBON TETRACHLORIDE					
	−20.0°	−10.0°	0.0°	10.0°	20.0°	30.0°
Me caprylate	∞	∞	∞	∞	∞	∞
Me laurate	33.0	78	145	∞	∞	∞
Me myristate	11.1	24.7	62	100	∞	∞
Me palmitate	5.0	10.1	23.8	63	210	∞
Me stearate	0.8	3.3	10.6	26.6	72	25.0

TABLE IV

SOLUBILITIES OF ALKYL ESTERS IN CHLOROFORM

ESTER	GRAMS OF ESTER PER 100 GRAMS OF CHLOROFORM								
	−50.0°	−40.0°	−30.0°	−20.0°	−10.0°	0.0°	10.0°	20.0°	30.0°
Me caprylate	120	375	∞	∞	∞	∞	∞	∞	∞
Me laurate	25.0	33.3	48	77	140	440	∞	∞	∞
Me myristate	10.2	12.8	18.3	29.2	51	103	285	∞	∞
Me palmitate	1.8	3.1	6.4	12.3	24.0	50	106	290	∞
Me stearate	<0.1	0.3	1.9	5.9	13.6	28	54	120	360

TABLE V

SOLUBILITIES OF ALKYL ESTERS IN ETHYL ACETATE

ESTER	GRAMS OF ESTER PER 100 GRAMS OF ETHYL ACETATE								
	−50.0°	−40.0°	−30.0°	−20.0°	−10.0°	0.0°	10.0°	20.0°	30.0°
Me caprylate	76	340	∞	∞	∞	∞	∞	∞	∞
Me laurate	0.4	1.9	5.4	20.0	80	460	∞	∞	∞
Me myristate	—	0.3	1.2	4.1	12.4	40	225	∞	∞
Me palmitate	—	—	0.3	1.0	2.7	8.6	34.8	215	∞
Me stearate	—	—	—	0.1	0.5	2.1	8.6	42	350
Et stearate	—	—	—	.3	1.0	3.1	14.0	87	1050
n-Pr stearate	—	—	—	.6	1.5	3.9	21.9	160	∞
n-Bu stearate	—	—	—	.9	1.8	4.3	27.2	250	∞

TABLE VI

SOLUBILITIES OF ALKYL ESTERS IN BUTYL ACETATE

ESTER	GRAMS OF ESTER PER 100 GRAMS OF BUTYL ACETATE								
	−50.0°	−40.0°	−30.0°	−20.0°	−10.0°	0.0°	10.0°	20.0°	30.0°
Me caprylate	51	164	∞	∞	∞	∞	∞	∞	∞
Me laurate	0.7	1.8	6.9	22.2	62	260	∞	∞	∞
Me myristate	—	<0.1	0.9	3.5	11.9	39.7	172	∞	∞
Me palmitate	—	—	.2	0.8	3.4	10.8	36.0	147	∞
Me stearate	—	—	—	<.1	0.7	3.3	11.1	41.8	233

TABLE VII

SOLUBILITIES OF ALKYL ESTERS IN ACETONE

ESTER	GRAMS OF ESTER PER 100 GRAMS OF ACETONE								
	−50.0°	−40.0°	−30.0°	−20.0°	−10.0°	0.0°	10.0°	20.0°	30.0°
Me caprylate	64	380	∞	∞	∞	∞	∞	∞	∞
Me laurate	0.2	0.9	3.6	12.5	67	645	∞	∞	∞
Me myristate	—	—	0.5	2.1	7.1	28.7	248	∞	∞
Me palmitate	—	—	0.1	0.4	1.3	5.2	21.0	250	∞
Me stearate	—	—	—	—	0.1	0.7	3.6	19.9	450
Et stearate	—	—	—	—	.4	1.5	5.2	40.5	1100
n-Pr stearate	—	—	—	—	.9	2.0	6.0	185	∞
n-Bu stearate	—	—	—	—	1.2	2.4	6.7	345	∞

TABLE VIII

SOLUBILITIES OF ALKYL ESTERS IN METHANOL

ESTER	GRAMS OF ESTER PER 100 GRAMS OF METHANOL								
	−50.0°	−40.0°	−30.0°	−20.0°	−10.0°	0.0°	10.0°	20.0°	30.0°
Me caprylate	4.2	78	∞	∞	∞	∞	∞	∞	∞
Me laurate	—	—	0.1	1.3	5.3	80	∞	∞	∞
Me tridecanoate	—	—	—	0.3	2.9	36.5	∞	∞	∞
Me myristate	—	—	—	—	<0.1	1.9	25.0	∞	∞
Me palmitate	—	—	—	—	—	0.1	1.4	27.0	∞
Me stearate[a]	—	—	—	—	—	—	—	0.6	7.2

[a] Miscible above 40.8°.

TABLE IX

SOLUBILITIES OF ALKYL ESTERS IN 95.0% ETHANOL

ESTER	GRAMS OF ESTER PER 100 GRAMS OF 95.0% ETHANOL								
	−50.0°	−40.0°	−30.0°	−20.0°	−10.0°	0.0°	10.0°	20.0°	30.0°
Me caprylate	7.5	57	∞	∞	∞	∞	∞	∞	∞
Me laurate	<0.1	0.3	1.1	3.8	13.2	120	∞	∞	∞
Me tridecanoate	—	<0.1	0.5	2.7	11.2	70	∞	∞	∞
Me myristate	—	—	—	0.3	2.0	6.7	30.8	∞	∞
Me palmitate	—	—	—	—	0.2	1.1	5.0	30.4	∞
Me stearate	—	—	—	—	—	0.1	1.2	4.4	40
Et stearate	—	—	—	—	.2	0.7	2.1	6.6	180
n-Pr stearate	—	—	—	—	.6	1.5	3.4	11.5	∞
n-Bu stearate	—	—	—	—	1.0	2.1	4.2	18.2	∞

TABLE X

SOLUBILITIES OF ALKYL ESTERS IN *n*-BUTANOL

ESTER	GRAMS OF ESTER PER 100 GRAMS OF *n*-BUTANOL								
	−50.0°	−40.0°	−30.0°	−20.0°	−10.0°	0.0°	10.0°	20.0°	30.0°
Me caprylate	33.3	135	∞	∞	∞	∞	∞	∞	∞
Me laurate	0.3	0.7	2.3	6.3	18.9	165	∞	∞	∞
Me tridecanoate	.1	.4	1.8	5.4	15.9	111	∞	∞	∞
Me myristate	—	—	<0.1	1.0	3.8	10.7	49	∞	∞
Me palmitate	—	—	—	0.1	0.7	2.2	8.3	50	∞
Me stearate	—	—	—	—	<0.1	0.7	2.3	7.4	5.7

TABLE XI

SOLUBILITIES OF ALKYL ESTERS IN ACETONITRILE

ESTER	GRAMS OF ESTER PER 100 GRAMS OF ACETONITRILE								
	−50.0°	−40.0°	−30.0°	−20.0°	−10.0°	0.0°	10.0°	20.0°	30.0°
Me caprylate	12.7	177	∞	∞	∞	∞	∞	∞	∞
Me laurate	—	—	0.4	2.1	6.5	310	∞	∞	∞
Me tridecanoate	—	—	<.1	1.6	5.8	86	∞	∞	∞
Me myristate	—	—	—	—	<0.1	0.9	12.2	∞	∞
Me palmitate[a]	—	—	—	—	—	<.1	0.9	7.1	42.5
Me stearate[b]	—	—	—	—	—	—	<.1	1.1	5.9
Et stearate[c]	—	—	—	—	—	—	.2	1.5	7.2
n-Pr stearate	—	—	—	—	—	.1	.7	23	3.4
n-Bu stearate	—	—	—	—	—	.3	.9	2.6	3.9

[a] Miscible above 31.0°.

[b] Miscible above 53.1°.

[c] Miscible above 65.5°.

of caprylic acid in this solvent, and the solubilities of methyl palmitate and ethyl and *n*-propyl stearates are similar to that of capric acid in benzene. Likewise, in

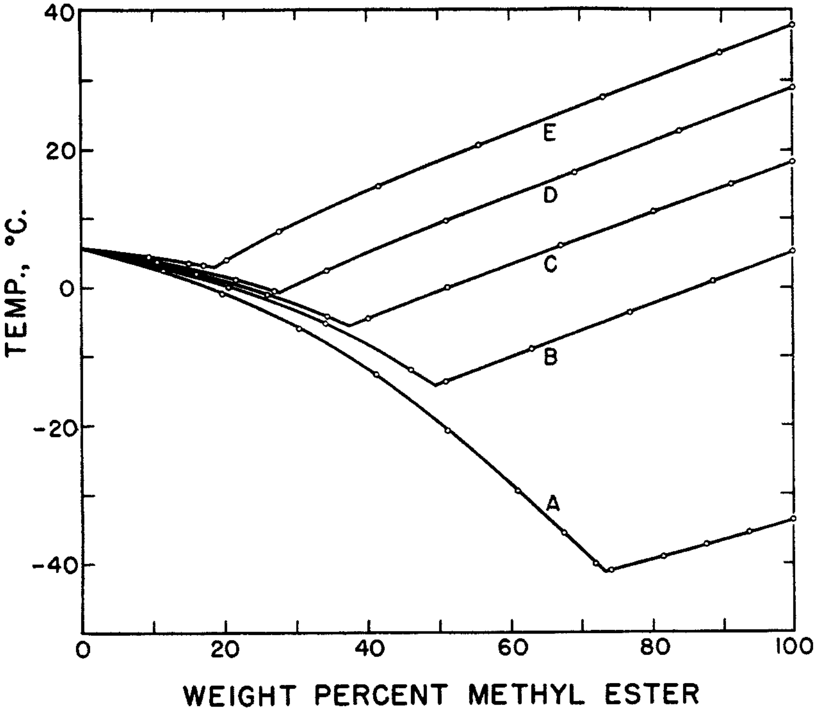

FIG. 1. LIQUIDUS CURVES OF METHYL ESTERS IN BENZENE. A, methyl caprylate; B methyl laurate; C, methyl myristate; D, methyl palmitate; and E, methyl stearate.

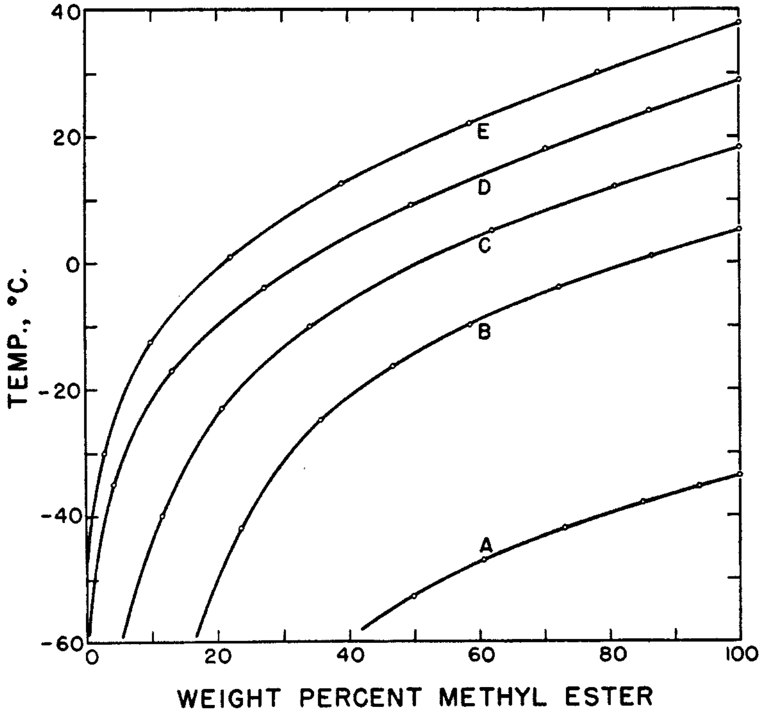

FIG. 2. SOLUBILITIES OF METHYL ESTERS IN CHLOROFORM. A, methyl caprylate; B, methyl laurate; C, methyl myristate; D, methyl palmitate; and E, methyl stearate.

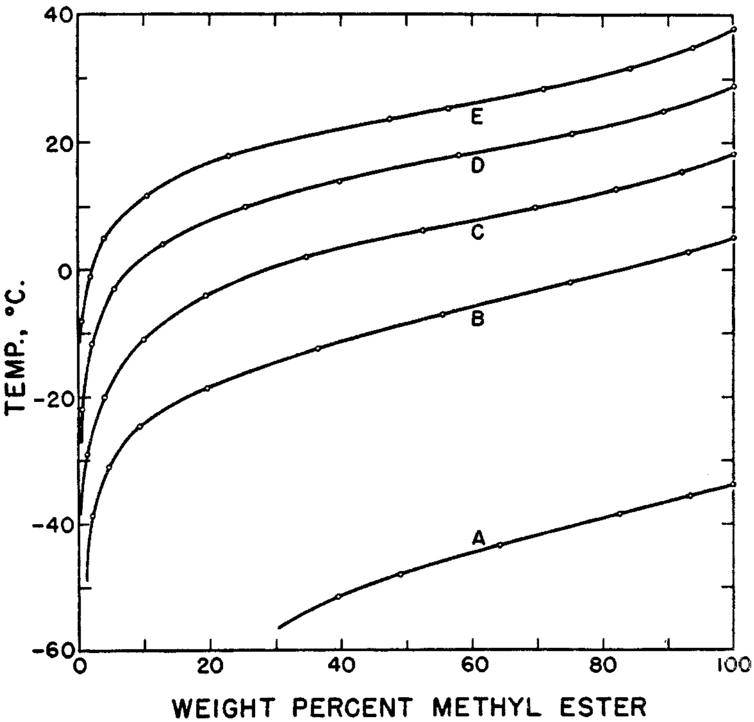

Fig. 3. Solubilities of Methyl Esters in Ethyl Acetate. A, methyl caprylate; B, methyl laurate; C, methyl myristate; D, methyl palmitate; and E, methyl stearate.

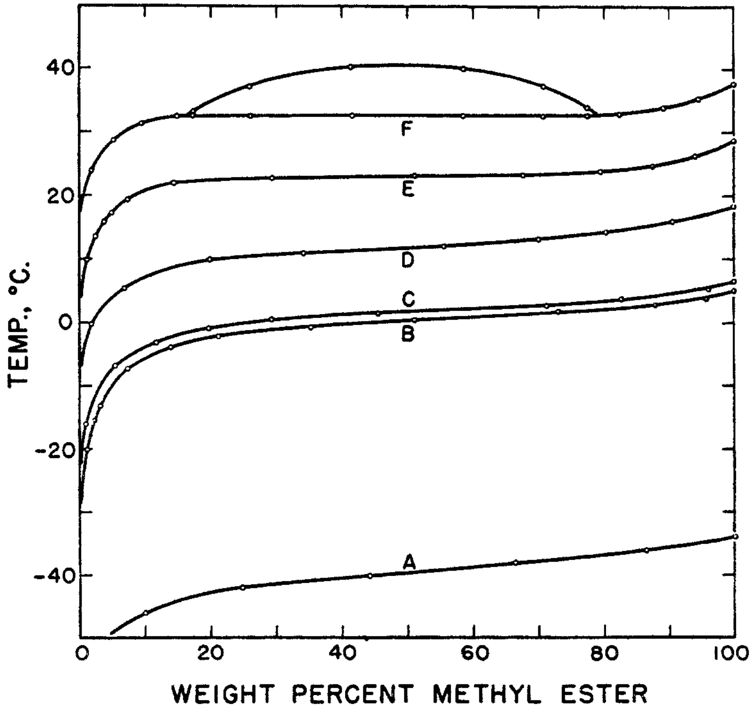

Fig. 4. Solubilities of Methyl Esters in Methanol. A, methyl caprylate; B, methyl laurate; C, methyl tridecanoate; D, methyl myristate; E, methyl palmitate; and F, methyl stearate.

acetonitrile the curve of methyl laurate approximates that of caprylic acid in the same solvent.

It is to be noted that, of the esters investigated, only ethyl stearate exhibits more than one crystalline modification, as demonstrated by the difference in freezing and melting points and by the existence of two solubility curves for this compound. Upon freezing the pure ethyl ester or upon precipitation from solution, a lower-melting, transparent, crystalline modification is obtained. This form is unstable and transforms shortly to a higher-melting, opaque modification. The solubility of both forms is readily determined in non-polar and slightly polar solvents. In the more highly polar solvents, the transformation to the higher-melting form is so rapid that the solubility of the unstable form can be determined with accuracy only in more concentrated solutions. From the most highly polar solvents, the ethyl ester crystallizes only in its higher-melting, opaque modification.

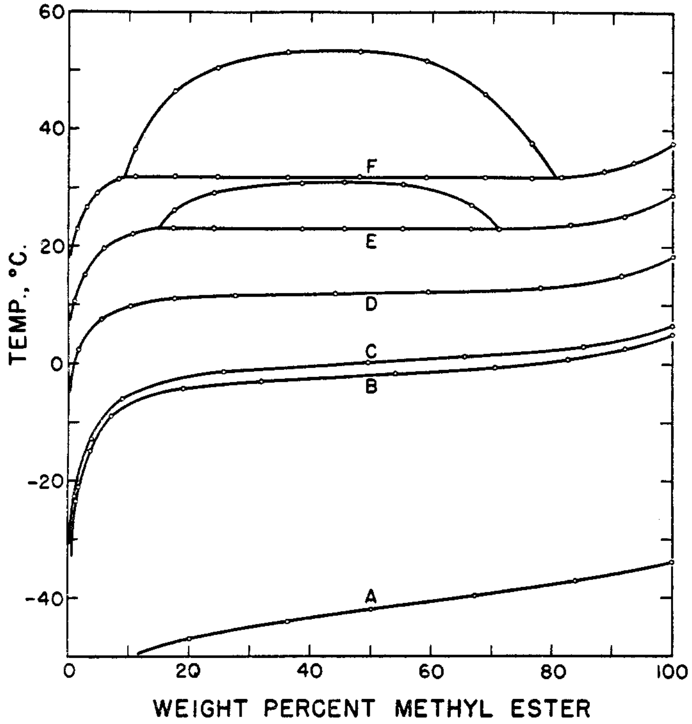

Fig. 5. Solubilities of Methyl Esters in Acetonitrile. A, methyl caprylate; B, methyl laurate; C, methyl tridecanoate; D, methyl myristate; E, methyl palmitate; and F, methyl stearate.

Logical evaluation of solubility behavior requires that the systems under consideration be compared on an equivalent basis. A suitable and convenient method has been used extensively by Hildebrand (7) in studying the behavior of a wide variety of solutes, and has been applied by Bailey (8) to the correlation of the solubilities of the fatty acids. In this method, the logarithm of the mole fraction of solute is plotted against the reciprocal of the absolute temperature. The advantage of such a plot lies in the fact that not only are the solutes comparable on a molecularly equivalent basis, but the ideal solubility yields a straight line. The behavior of the solute can be interpreted by the pattern of its solubility curves for various solvents and the extent to which they deviate from the ideal.

For purposes of comparison, the solubilities of methyl palmitate and of lauric acid (4, 5) on the mole-fraction basis (log *N*. *vs*. $\frac{1}{T}$) are shown in Figs. 6 and 7, respectively. Lauric acid was chosen for this comparison because its ideal solubility curve is almost identical with the estimated ideal curve of methyl palmitate. Thus, the heat of fusion of this ester must approximate that of lauric acid despite the differences in melting points and chain length.

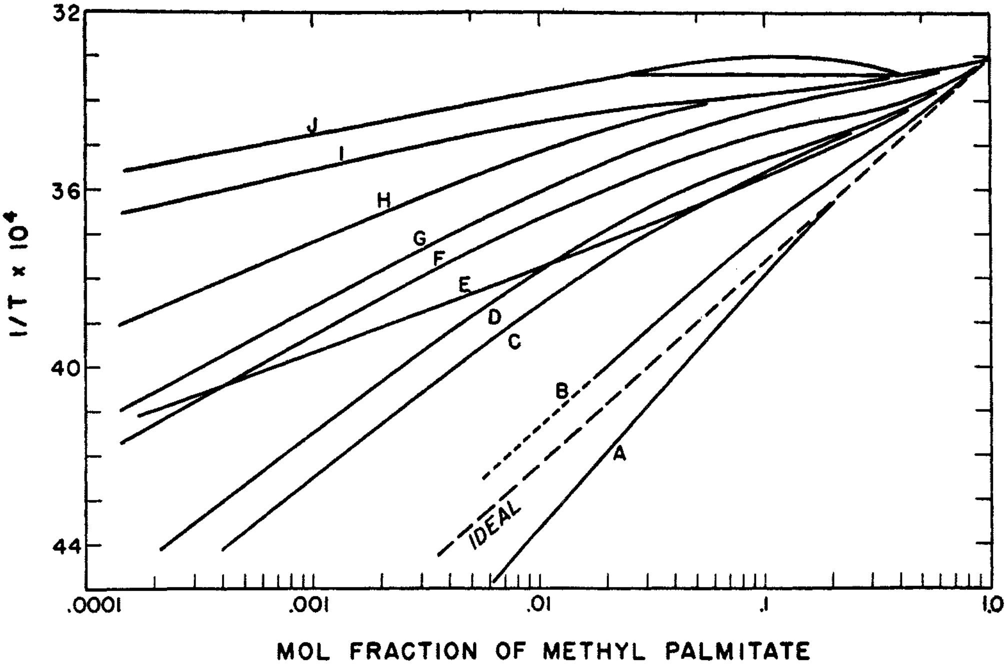

FIG. 6. SOLUBILITY OF METHYL PALMITATE IN VARIOUS ORGANIC SOLVENTS. A, chloroform; B, carbon tetrachloride; C, butyl acetate; D, ethyl acetate; E, hexane; F, acetone; G, butanol; H, 95% ethanol; I, methanol; and J, acetonitrile.

Comparison of the curves in Figs. 6 and 7 reveals that the behavior of the esters is not so similar to that of the fatty acids as appears on the basis of weight per cent plots, methyl palmitate showing a pattern of much greater deviations from solvent to solvent than lauric acid. In view of the fact that the ester deviations correspond in almost direct proportion to the relative internal pressures and polarities of the solvents (7), it would appear that there is little, if any, solubilizing interaction between ester and solvent molecules. In contrast, the relatively narrower range of deviations of the acids, *i.e.*, generally greater solubility, in solvents containing hydroxyl, carbonyl, and ester groups, demonstrates the well-known tendency of the fatty acid molecules to associate with the molecules of these solvents through the formation of hydrogen bonds. It can be concluded from this comparison that the esters present no definite indications of possessing any hydrogen atoms which are sufficiently active to bond with even strongly attracting electron-acceptor atoms.

With respect to the association of the ester molecules with each other, the literature is contradictory. The X-ray studies of Malkin (9) indicate that the methyl esters crystallize as double molecules, whereas the ethyl esters exist in the solid state as single molecules. Such behavior suggests that the methyl esters crystallize, as do the fatty acids, in molecular layers with the ester groups adjacent, *i.e.*, in a "head to head" arrangement. In order to explain Malkin's conclusions regarding the structure of the ethyl esters, it would be necessary to assume that these compounds, which differ but little from the methyl esters, crystallize in the opposite arrangement with the ester groups adjacent to the terminal methyl groups of the contiguous molecules. The investigations by King and Garner (10) of the heats of crystallization of the esters did not reveal any unusual thermal effects which they assumed should accompany a dissociation from double to single molecules.

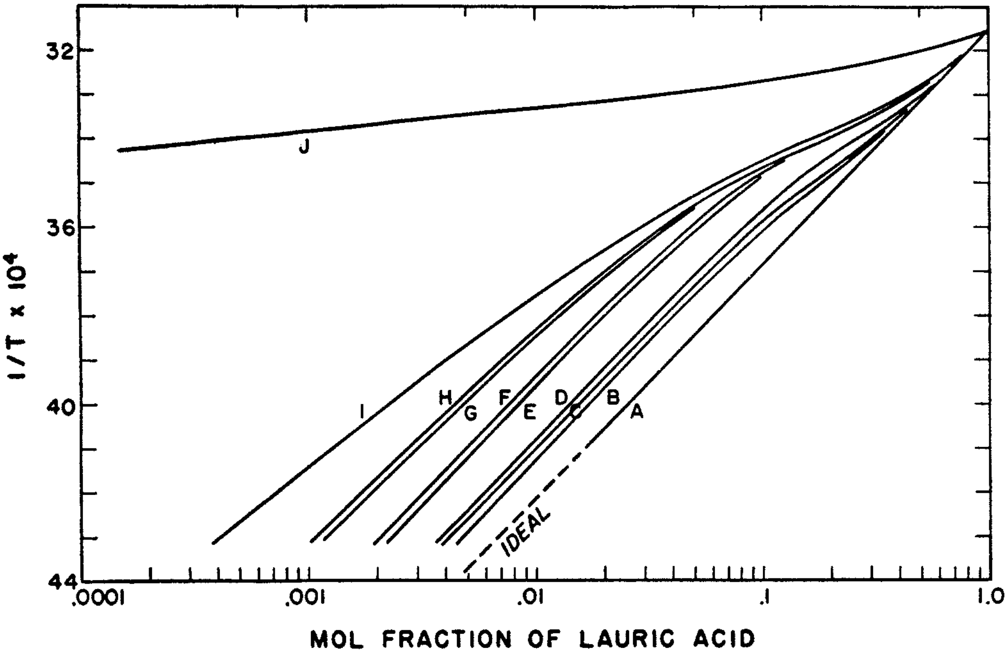

FIG. 7. SOLUBILITY OF LAURIC ACID IN VARIOUS ORGANIC SOLVENTS. A, chloroform; B, carbon tetrachloride; C, butyl acetate; D, butanol; E, ethyl acetate; F, 95% ethanol; G, methanol; H, acetone; I, hexane; and J, acetonitrile.

That there is but little difference between the behavior of methyl, ethyl, *n*-propyl, and *n*-butyl esters is demonstrated by the solubility curves shown in Fig. 8. The pronounced regularity of these series of curves indicates identical behavior of the solutes. Any phenomenon such as molecular association of one of the solutes would be reflected as a divergence of its solubility curve from those of the other solutes. Since no such divergence occurs, it can be deduced that the physical nature of the solutes is essentially identical. Thus, if the higher esters exist as single molecules, then the methyl esters must also. If, on the other hand, the methyl ester molecules associate despite the evidence at hand, then the higher esters must behave similarly.

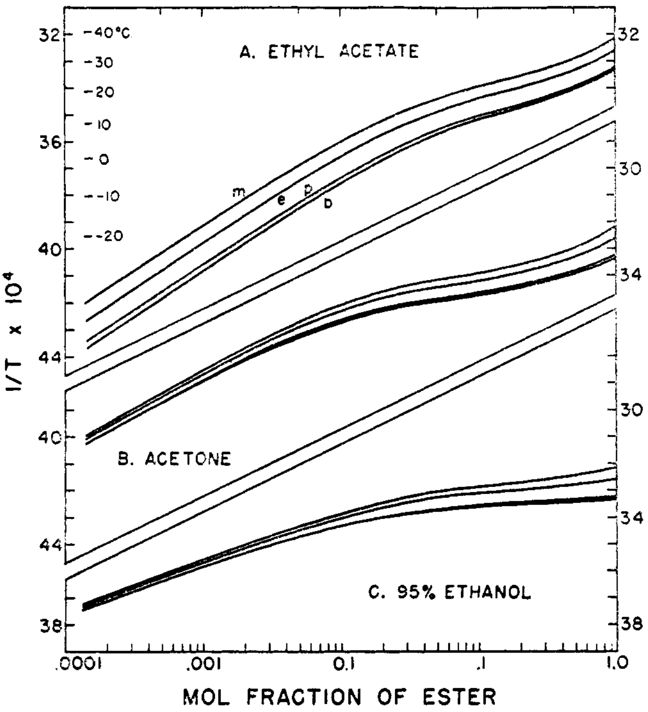

FIG. 8. SOLUBILITIES OF STEARIC ACID ESTERS IN ETHYL ACETATE (A), ACETONE (B), AND 95% ETHANOL (C). Each set of curves duplicates the order of those labeled m, e, p, and b, representing the methyl, ethyl, propyl, and butyl stearates, respectively.

The limited solubilities of both the esters and the fatty acids in acetonitrile (and also in the nitroparaffins) are attributable to the extremely high internal pressure and polarity of the solvent. Apparently some interaction occurs between the fatty acid and solvent molecules since this solute shows liquid-liquid miscibility, whereas the esters exist as two-phase liquid systems with the solvent over a part of the concentration-temperature diagram.

SUMMARY

The solubilities of the methyl esters of caprylic, lauric, myristic, palmitic, and stearic acids have been determined in benzene, cyclohexane, carbon tetrachloride, chloroform, ethyl acetate, butyl acetate, methanol, 95% ethanol, *n*-butanol, acetone, and acetonitrile. The solubilities of methyl tridecanoate and of ethyl, *n*-propyl, and *n*-butyl stearates have been determined in several of these solvents. The behavior of the esters has been compared on a molecularly equivalent basis with that of the corresponding fatty acids. It is indicated that the esters, at least in solution, do not exhibit the tendency toward intermolecular association that is evidenced by the acids.

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REFERENCES

(1) RALSTON, *Fatty Acids and Their Derivatives*, Wiley and Sons, Inc., New York, 1948, pp. 361–363, 500–521.
(2) HOERR AND HARWOOD, *J. Org. Chem.*, **16**, 779 (1951).
(3) HOERR, BINKERD, POOL, AND RALSTON, *J. Org. Chem.*, **9**, 68 (1944).
(4) RALSTON AND HOERR, *J. Org. Chem.*, **7**, 546 (1942).
(5) HOERR AND RALSTON, *J. Org. Chem.*, **9**, 329 (1944).
(6) HOERR, SEDGWICK, AND RALSTON, *J. Org. Chem.*, **11**, 603 (1946).
(7) HILDEBRAND AND SCOTT, *The Solubility of Non-Electrolytes*, 3rd Ed., Reinhold Publishing Co., New York, 1950.
(8) BAILEY, *Melting and Solidification of Fats*, Interscience Publishers, Inc., New York, 1950.
(9) MALKIN, *J. Chem. Soc.*, 2796 (1931).
(10) KING AND GARNER, *J. Chem. Soc.*, 1372 (1936).