Subscripts

1 = first component
2 = second component
12 = mixture of 1 and 2
c = critical constants
g = gas phase
L = liquid phase

Superscripts

E = excess function

LITERATURE CITED

(1) Altenberg, K., *Z. Physik. Chem.*, **216**, 139 (1961).
(2) Bass, K. C., *J. Chem. Soc.*, **1964**, p 3498.
(3) Bhatgadde, L. G., PhD thesis, Indian Institute of Technology, Bombay, India, 1969.
(4) Deshpande, D. D., Bhatgadde, L. G., *Aust. J. Chem.*, in press (1971).
(5) Deshpande, D. D., Bhatgadde, L. G , *J. Phys. Chem.*, **72**, 261 (1968).
(6) Deshpande, D. D., Pandya, M. V., *Trans. Faraday Soc.*, **61**, 1858 (1965).
(7) Deshpande, D. D., Pandya, M. V., *ibid.*, **63**, 2149 (1967).
(8) Deshpande, D. D., Pandya, M. V., *ibid.*, p 2346.
(9) Deshpande, D. D., Pandya, M. V., *ibid.*, **65**, 1456 (1969).
(10) Dobratz, C. S., *Ind. Eng. Chem.*, **33**, 759 (1941).
(11) Eyring, H., Hirschfelder, J. O., *J. Phys. Chem.*, **41**, 249 (1937).
(12) Fort, R. J., Moore, W. R., *Trans. Faraday Soc.*, **61**, 2102 (1965).
(13) Guecker, F. T., Chernick, C. L., Chowdhury, P. R., *Proc. Nat. Acad. Sci.* (U.S.), **55**, 12 (1966).
(14) Hiedemann, E., Bachem, Ch., *Z. Physik.*, **91**, 418 (1934).
(15) Hiedemann, E., Bachem, Ch., *ibid.*, **94**, 68 (1935).
(16) Hougen, O. A., Watson, K. H., Ragatz, R. A., "Chemical Progress Principles," Vol 1, Wiley, New York, N.Y., 1959.
(17) Jatkar, S. K. K., Laxminarayanan, O., *J. Ind. Inst. Sci.* (Bangalore), **A-28**, 1 (1946).
(18) Kuhnkies, R., Schaaffs, W., *Acustica*, **13**, 408 (1963).
(19) Lipkin, M. R., Davison, J. T., Harvey, W. T., Kurtz, S. S., *Ind. Eng. Chem., Anal. Ed.*, **16**, 55 (1944).
(20) Sannigrahi, A. B., Chandra, A. K., *J. Phys. Chem.*, **67**, 1105 (1963).
(21) Timmermans, J., "Physico-Chemical Constants of Pure Organic Compounds," Vol 1, Elsevier, Amsterdam, The Netherlands, 1950.
(22) Timmermans, J., *ibid.*, Vol 2, 1965.
(23) Weissberger, A., "Techniques of Organic Chemistry," Vol 7, Interscience, New York, N.Y., 1959, pp 333, 349, 424, 441, 445.

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Binary Freezing-Point Behavior of Methyl and Ethyl Esters of Positional and Geometric Isomers of Octadecenoic Acid

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Mutual solubilities have been obtained on both the methyl and ethyl esters of geometric isomers of two octadecenoic acids. Binary systems investigated were methyl petroselinate–methyl petroselaidate, methyl oleate–ethyl elaidate, ethyl petroselinate–ethyl petroselaidate, ethyl oleate–ethyl elaidate, methyl oleate–methyl petroselinate, methyl elaidate–methyl petroselaidate, ethyl oleate–ethyl petroselaidate, and ethyl oleate–ethyl petroselinate. Simple eutectic systems were obtained for all combinations of the cis, trans, and positional isomers investigated. No polymorphism was observed in either the pure compounds or the binary mixtures.

Recently, special interest has been attached to the preparation and purification of closely related mono and dienoic acids and esters in biological studies. Whereas the mutual solubilities of the methyl and ethyl esters of the saturated acids have been studied by numerous investigators, little information is available on the unsaturated acids and esters. In our continuing investigations of the solubilities of fatty acids and fatty acid derivatives (*1-5*, *7*), we have prepared geometric isomers of the Δ6 and Δ9 octadecenoic acids. Binary freezing-point behavior of the methyl and ethyl esters of these acids is reported.

EXPERIMENTAL

The pure acids used in the preparation of the esters were recrystallized materials prepared from the fractionally distilled methyl esters. The trans isomers of the acids were prepared by the procedure of Mack and Bickford (*8*) which involves shaking the acid in a separatory funnel in the presence of a mixture of sodium nitrite and dilute nitric acid followed by solvent crystallization of the isomerized acid. The methyl or ethyl ester was prepared by refluxing the pure acid in an excess of the anhydrous alcohol in the presence of catalytic amounts of toluene sulfonic acid followed by solvent crystallization.

The purity of the esters and their freezing points were determined using the method of heating curves and apparatus described by Skau (*10*). The heating curves were run on approximately 0.5-gram samples in a sealed glass tube fitted with a thermocouple well. The sample tube was suspended in a copper block also fitted with a thermocouple well. The entire assembly was cradled in an unsilvered Dewar flask using liquid nitrogen as a coolant. The temperature of the solidified sample was risen at a rate of approximately 0.2°C/min. Both the block and sample temperatures were moni-

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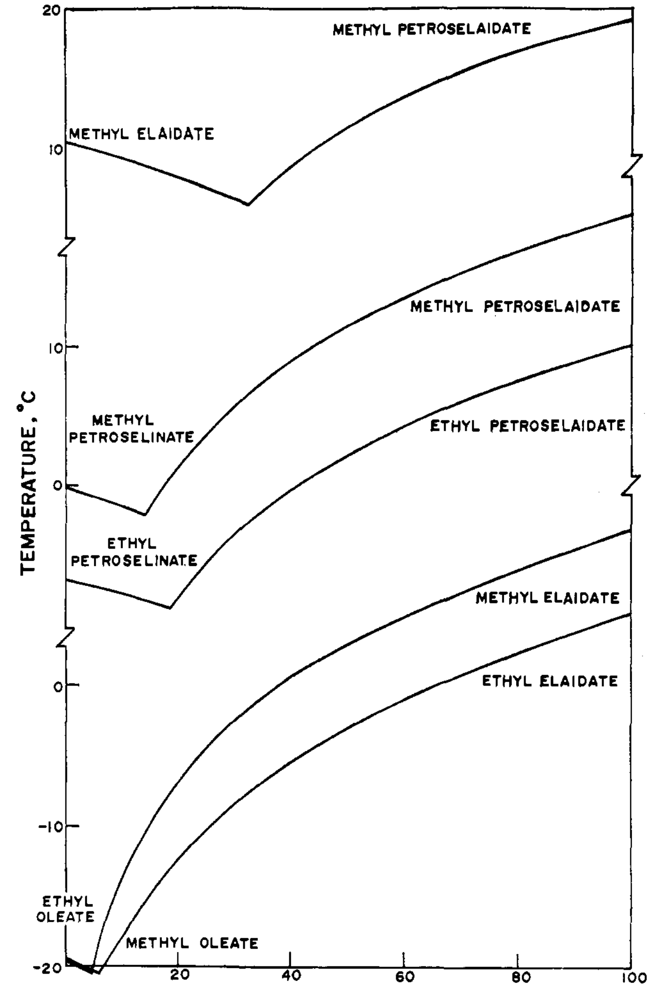

Figure 1. Binary freezing point diagrams of methyl and ethyl esters of some positional and geometric isomers of octadecenoic acid

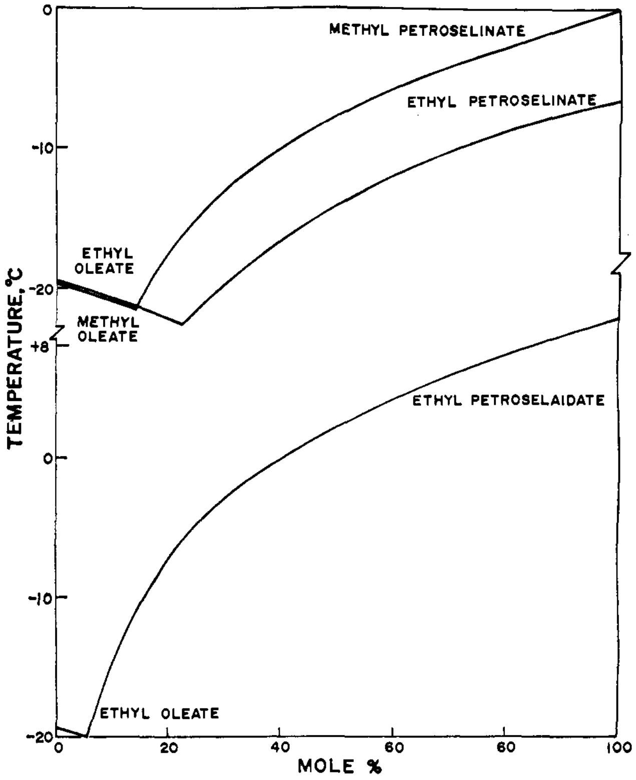

Figure 2. Binary freezing point diagrams of methyl and ethyl esters of some positional and geometric isomers of octadecenoic acid

tored on a strip chart recorder. For pure samples the block and sample temperatures assume a parallel rise wherein the sample temperature does not deviate until the block temperature has reached the melting point of the sample. Impure sample temperatures will assume a less parallel rise depending upon the amount and kind of impurities present. The thermocouples used were calibrated at the freezing points of benzoic acid, naphthalene, and mercury using thermometric cells, and at the equilibrium sublimation temperature of carbon dioxide (*9*).

The freezing points obtained were: methyl oleate, −19.69; methyl elaidate, 10.27; methyl petroselinate, −0.15; methyl petroselaidate, 19.60; ethyl oleate, −19.48; ethyl petroselinate, −6.66; ethyl elaidate, 5.14; and ethyl petroselaidate, 10.07°C.

The binary freezing points were determined by the thermostatic sealed-tube method. Weighed amounts of the two materials were placed in sealed glass tubes along with two glass tubes to ensure good agitation. The tube was rotated end-over-end in a constant-temperature bath. Two temperatures were determined at which the last crystal either disappears or remains undissolved after prolonged agitation. The mean of these two temperatures was the true equilibrium

Table I. Binary Freezing Point Data

Methyl petroselinate in methyl petroselaidate		Methyl oleate in methyl elaidate		Ethyl petroselinate in ethyl petroselaidate		Ethyl oleate in ethyl elaidate	
Mol %, *trans*-ester	Temp, °C	Mol %, *trans*-ester	Temp, °C	Mol %, *trans*-ester	Temp, °C	Mol %, *trans*-ester	Temp, °C
0.00	−0.15	0.00	−19.69	0.00	−6.66	0.00	−19.48
4.43	−0.8	3.00	−20.1	6.03	−7.2	1.03	−19.7
9.28	−1.5	5.0[a]	−20.3[a]	11.93	−8.0	2.06	−19.9
14.3[a]	−2.3[a]	5.02	−20.2	18.7[a]	−8.7[a]	3.23	−20.1
14.59	−2.0	6.26	−18.6	19.54	−8.2	6.0[a]	−20.6[a]
19.68	1.3	10.06	−14.1	25.21	−5.5	7.97	−19.4
39.64	8.7	14.76	−10.2	32.60	−2.7	20.41	−12.5
59.94	13.5	19.68	−7.1	48.02	1.6	38.30	−6.0
80.79	17.0	40.46	0.5	63.93	4.8	61.73	−0.8
100.00	19.60	60.20	4.8	70.43	6.0	78.55	2.0
		79.62	8.0	74.56	6.7	100.00	5.14
		100.00	10.53	80.01	7.4		
				100.00	10.07		

(Continued)

Table I. *(Continued)*

Methyl oleate in methyl petroselinate		Methyl elaidate in methyl petroselaidate		Ethyl oleate in ethyl petroselaidate		Ethyl oleate in ethyl petroselinate	
Mol %, Δ6-ester	Temp, °C	Mol %, Δ6-ester	Temp, °C	Mol %, Δ6-ester	Temp, °C	Mol %, Δ6-ester	Temp, °C
0.00	−19.69	0.00	10.53	0.00	−19.48	0.00	−19.48
4.81	−20.4	19.97	8.0	2.01	−19.6	9.19	−20.7
9.49	−21.0	27.95	6.8	3.71	−19.9	20.49	−22.3
14.2[a]	−21.6[a]	32.4[a]	6.1[a]	8.4[a]	−20.1[a]	22.7[a]	−22.6[a]
14.61	−21.8	33.92	6.7	9.87	−15.4	24.65	−21.8
20.00	−17.8	39.86	8.6	18.09	−8.8	36.53	−17.5
40.13	−10.2	59.09	13.5	36.93	−1.0	51.15	−13.9
59.91	−5.9	69.55	15.3	55.12	3.1	65.76	−11.2
79.55	−2.8	80.24	16.9	74.53	6.6	82.77	−8.6
100.00	−0.15	90.58	18.3	81.13	7.9	100.00	−6.66
		100.00	19.60	91.69	9.1		
				100.00	10.07		

[a] Eutectic point by interpolation.

temperature between the crystals and the liquid. The freezing point thus determined corrected for thermometer calibration and emergent stem was considered accurate to within ±0.2°C. The apparatus and complete procedure were described previously (*6*).

RESULTS AND DISCUSSION

The freezing points would seem to have special significance when the effects of the ester moiety, the double bond position, and geometric configuration are considered. The freezing points of the esters of saturated acids decrease to a minimum with the butyl ester and thereafter increase with increasing carbon chain length of the ester moiety. For the unsaturated acid esters, the freezing points vary as a result of the location of the site of unsaturation as well as the geometric configuration. Of the esters investigated, larger differences were noted between the methyl and ethyl esters of the trans acids than between the esters of the corresponding cis acids. Likewise, greater differences were exhibited as a result of the unsaturation site in the Δ6 position as opposed to the Δ9 position. Ethyl oleate actually has a higher melting point than methyl oleate. Dimorphism, reported for the esters of the saturated acids, was not observed in the pure esters or in the binary mixtures.

The data for complete binary freezing point diagrams of eight combinations of the aforementioned methyl and ethyl esters are given in Table I. Represented graphically in Figure 1 are binary freezing point diagrams for the *cis*-6–*trans*-6 and *cis*-9–*trans*-9 methyl and ethyl octadecenoate systems. Also illustrated is the *trans*-9–*trans*-6 methyl octadecenoate system. In each system, simple eutectic points were exhibited.

In Figure 2 are illustrated binary freezing point diagrams for *cis*-6–*cis*-9 methyl octadecenoate, *cis*-6–*cis*-9 ethyl octadecenoate, and *trans*-6–*cis*-9 ethyl octadecenoate. Again, simple eutectic points were exhibited. The experimental points not shown were coincidental with the smooth curves illustrated in Figures 1 and 2.

Since simple eutectic systems result from binary mixtures of both the positional and geometric isomers of methyl and ethyl octadecenoates, and none of the esters, either pure or in mixtures, exhibited polymorphic behavior, these esters should be readily amenable to separation and purification by crystallization techniques.

LITERATURE CITED

(1) Bailey, A. V., Harris, J. A., Skau, E. L., *J. Amer. Oil Chem. Soc.*, **45**, 183 (1967).
(2) Bailey, A. V., Harris, J. A., Skau, E. L., *ibid.*, **46**, 583 (1969).
(3) Bailey, A. V., Harris, J. A., Skau, E. L., *ibid.*, **48**, 170 (1971).
(4) Bailey, A. V., Harris, J. A., Skau, E. L., *J. Chem. Eng. Data*, **15**, 583 (1970).
(5) Bailey, A. V., Mitcham, D., Skau, E. L., *ibid.*, 542 (1970).
(6) Harris, J. A., Bailey, A. V., Skau, E. L., *J. Amer. Oil Chem. Soc.*, **45**, 639 (1968).
(7) Harris, J. A., Bailey, A. V., Skau, E. L., *J. Chem. Eng. Data*, **13**, 265 (1968).
(8) Mack, C. H., Bickford, W. G., *J. Org. Chem.*, **18**, 686 (1953).
(9) Scott, R. B., *J. Res. Nat. Bur. Stand.*, **25**, 459 (1940).
(10) Skau, E. L., *Proc. Amer. Acad. Arts Sci.*, **67**, 551 (1933).

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