Solid-Liquid Phase Relations of Some Normal Long-Chain Fatty Acids in N,N-Dimethylacetamide and N,N-Dimethylformamide

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Abstract

Solubility data are reported for capric, lauric, myristic, palmitic, stearic, and arachidic acids in N,N-dimethylacetamide (DMA) and N,N-dimethylformamide (DMF). Complete binary freezing-point diagrams were constructed for the capric, myristic, and stearic acid systems. A solid, incongruently melting 1:1 molecular compound formed in all except the stearic acid-DMF system. Calculated solubility data for lauric, palmitic, and arachidic acids in both solvents were in good agreement with experimental determinations on selected compositions.

Introduction

A KNOWLEDGE OF THE SOLUBILITY characteristics of long-chain fatty acids in organic solvents is important to fats and oils technology and research. Extensive solubility data have already been published (1), but new processes with new solvents require these data to be constantly supplemented. In recent years considerable interest has been shown in N,N-dimethylacetamide (DMA) and N,N-dimethylformamide (DMF) as solvents. These are highly aprotic solvents (2–4). They dissolve both organic compounds and inorganic salts and, because of their excellent solvating and ionizing powers, they act as catalysts in many chemical reactions. The present report deals with the solid-liquid phase relations of capric, lauric, myristic, palmitic, stearic, and arachidic acids in these two solvents.

Experimental Procedures

The pure fatty acids were prepared by the procedures previously described (5). White Label Eastman DMA and Fisher Reagent Grade DMF were used without further purification.

The freezing-point or solubility determinations were made by the thermostatic sealed-tube method (6), which gives the temperature of true equilibrium between the crystals and the liquid to within 0.1 to 0.2C.

Results and Discussion

The freezing-point data are given in Table I and are represented graphically in the figures.

It is evident from Fig. 1 that solid 1:1 acid·DMA compounds are present in all the DMA systems. These

TABLE I

Freezing Points of Binary Mixtures of DMA and DMF with Long-Chain Fatty Acids[a]
(Composition in Mole % Acid)

C_{10}			C_{12}		C_{14}		C_{16}		C_{18}			C_{20}	
%	°C	°C	%	°C	%	°C	%	°C	%	°C	°C	%	°C
					DMA Systems								
100.00	31.6		100.00	43.8	100.00	54.4	100.00	62.5	100.00	69.5		*100.00*	*75.3*
74.17	23.6		*80.00*	*40.2*	69.42	47.0	*80.00*	*59.0*	75.63	65.2		*80.00*	*72.2*
65.23	18.8		70.58	35.9	53.00	38.1	71.71	56.3	62.01	61.4		*70.00*	*70.1*
60.55	15.0		*70.00*	*35.9*	48.26	34.0	*70.00*	*56.2*	47.10	54.3		*60.00*	*67.6*
53.74	8.2		*60.00*	*30.1*	41.56	27.4	*60.00*	*52.7*	30.29	41.4		*50.00*	*63.6*
45.3[b]	− 2.2[b]		*50.00*	*21.7*	39.71	25.3	53.32	48.6	27.8[b]	38.6[b]			
45.14	− 2.2				38.7[b]	24.2[b]	*50.00*	*46.6*	25.05	37.6			
42.54	− 2.9				30.92	21.2			16.88	34.1			
25.24	−10.8				22.18	17.2			15.51	33.4			
12.54	−20.0				9.45	9.4			14.46	33.0			
7.7[c]	−27.8[c]				2.83	0.4			10.44	30.8			
6.7[c]		−30.0[c]			0.58	−12.9			7.88	29.0			
4.35	−25.2	−28.0							6.71	28.2			
0.00	−22.3	−25.3							4.09	25.4			
									1.79	20.4			
									0.384	9.4			
									0.188	4.2			
					DMF Systems								
100.00	31.6		100.00	43.8	100.00	54.4	100.00	62.5	100.00	69.5		*100.00*	*75.3*
74.26	25.4		*80.00*	*39.5*	75.41	48.8	*80.00*	*58.8*	81.27	66.3		*80.00*	*71.5*
57.83	14.2		*70.00*	*35.7*	50.86	38.5	71.24	56.4	60.70	61.4		*70.00*	*69.7*
40.37	− 3.8		68.17	35.1	35.88	28.7	*70.00*	*56.2*	47.34	55.8	56.1	*60.00*	*67.4*
37.35	− 5.8	− 7.3	*60.00*	*31.1*	27.38	21.6	*60.00*	*52.7*	25.88	42.5	43.7	*50.00*	*64.3*
38.8[b]	− 7.5[b]		51.42	26.4	21.2[b]	13.7[b]	51.02	48.8	19.98	38.5	40.0		
35.37	− 8.6		*50.00*	*25.2*	17.13	12.2	*50.00*	*48.4*	17.46	36.8	38.4		
33.34	− 9.6		21.53	1.5	16.60	12.0	16.84	24.8	14.03	34.4	36.1		
21.54	−15.6		1.47	−22.2	9.31	7.5	0.094	−13.7	10.84	32.4	34.0		
18.91	−17.6				6.54	5.2			6.75	29.3	30.8		
9.48	−24.6				3.68	1.2			3.80	26.4	28.0		
5.76	−29.8				1.86	− 3.6			2.68	23.1			
3.22	−35.2				0.89	− 9.2			1.09	17.7			
0.89	−48.4				0.287	−19.0			0.46	11.2			
					0.152	−24.7			0.146	2.7			
									0.048	− 5.8			
									0.014	−16.0			

[a] Values in italics obtained by isopleth interpolation and extrapolation method (7).
[b] Incongruent mp (by extrapolation).
[c] Eutectic (by extrapolation).

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[1] So. Utiliz. Res. Dev. Div., ARS, USDA.

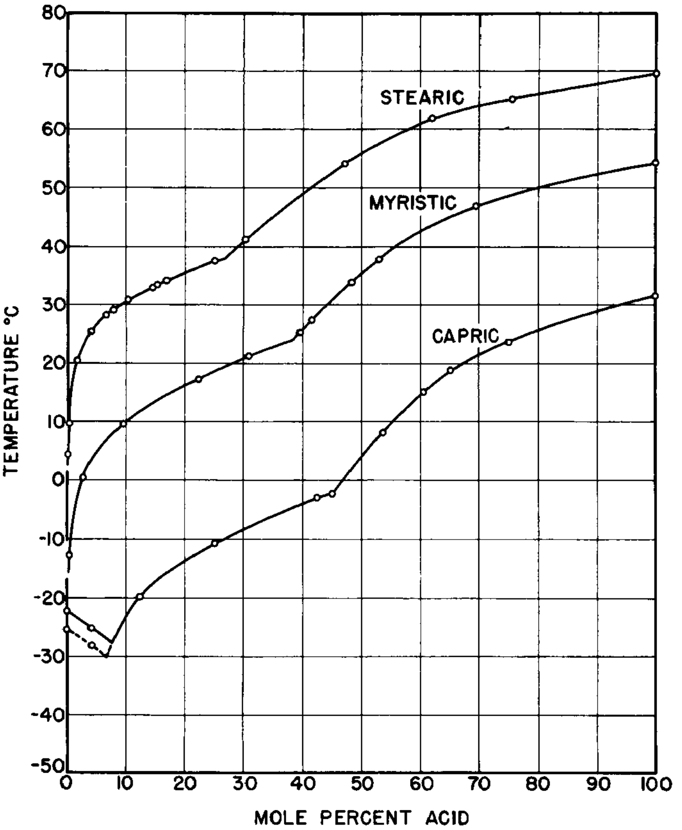

Fig. 1. Binary freezing-point diagram for DMA with capric, myristic, and stearic acids.

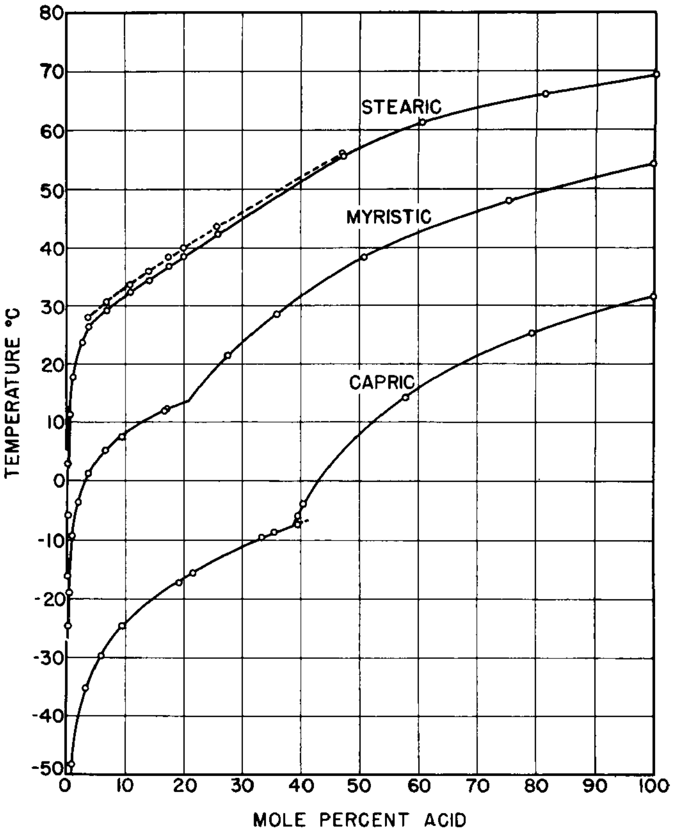

Fig. 2. Binary freezing-point diagram for DMF with capric, myristic, and stearic acids.

melt incongruently at the invariant points: 27.8%, 38.6C in the stearic acid systems; 38.7%, 24.2C in the myristic acid system; and 45.3%, −2.2C in the capric acid system. The eutectic point for the 1:1 capric acid compound is at 7.7%, −27.8C. In the other two DMA systems the eutectic is close to the DMA axis and was not determined. Two freezing points were observed for DMA and for the 4.35% capric acid composition. These double freezing-points represent solid-liquid equilibrium with two polymorphic forms of DMA: a stable modification, f.p. −22.3C, and a metastable modification, f.p. −25.3C. They indicate the existence of a metastable eutectic at 6.7% and −30.0C.

Solid 1:1 compounds with incongruent melting points were also formed in the DMF-capric acid and DMF-myristic acid systems, as indicated by the invariant points 38.8%, −7.5C and 21.2%, 13.7C respectively (Fig. 2). Two freezing points were observed for the sample containing 39.35% capric acid. At the upper temperature, −5.8C, the liquid is in stable equilibrium with crystals of capric acid and, at the lower temperature, −7.5C, it is in metastable equilibrium with the 1:1 compound. The DMF-stearic acid system showed no signs of solid 1:1 compound formation. However compositions which contained from about 4 to 47% of acid gave two freezing points. These can be attributed to the formation of two different polymorphic modifications of the acid.

Solubility data for lauric, palmitic, and arachidic acids, given in italics in Table I, were calculated from the data for capric, myristic, and stearic acids by the isopleth method of interpolation and extrapolation (7). Freezing points which were determined for selected compositions of lauric and palmitic acid were in good agreement with the calculated data.

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REFERENCES

1. Singleton, W. S., in "Fatty Acids," Part I, K. S. Markley, ed., Interscience Publishers Inc., New York, 1960, pp. 609–678.
2. Parker, A. J., Quart. Rev. (London) *16*, 163 (1962).
3. Agami, C., Bull. Soc. Chim. France *1965*, 1029.
4. Martin, D., A. Weise and H.-J. Niclas, Angew. Chem. Intern. Ed. Engl. *6*, 318 (1967).
5. Mod, R. R., and E. L. Skau, J. Phys. Chem. *60*, 963 (1956).
6. Magne, F. C., and E. L. Skau, J. Am. Chem. Soc. *74*, 2628 (1952).
7. Skau, E. L., and A. V. Bailey, J. Phys. Chem. *63*, 2047 (1959).

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