straight line (line DG in Fig. 1) instead of the curve previously reported.[8] However, if one estimates the values of the points on the curve given by Ramsdell and Webb[8] and then assumes that the values for glucose are the initial concentrations of glucose and that the sum of values for glucose and galactose at each point is the percentage of solids in the corresponding solution saturated with galactose, one may calculate a series of results, using equations 4 and 5 above, that agrees much more closely with the values obtained in this work. Equations 1–6 take into account the fact that the concentrations of the initial sugars in the solution decrease percentagewise when the solid sugar dissolves, although the ratios between the initial sugars and the water present initially remain constant. The values in parentheses in Table II, given for comparison, were calculated in this manner. A plot of these points gave a straight line which is close to the line plotted from the points determined in this work.

There was no indication of curved lines or surfaces in the representation of any of the data reported in Tables II and III. As mentioned above, the deviations of the experimental points from those calculated were small and, moreover, the deviations appeared to be completely random; neither the positive nor the negative deviations could be associated with adjacent points in any way. The data as worked up present a consistent picture in every respect, and check determinations on points which could not be determined directly and easily by experiment showed that the methods were correct. Therefore, the results reported are believed to be correct within the limits indicated by the standard errors of estimate listed above. The methods given will be useful for similar studies.

Acknowledgment.—The authors are indebted to Dr. E. Yanovsky for his valuable advice and criticism in connection with this work.

PHILADELPHIA 18, PENNA.

[FROM THE SOUTHERN REGIONAL RESEARCH LABORATORY[1]]

Binary Freezing Point Diagrams for Palmitic Acid with Substituted Acetamides and Other Amides[2]

BY FRANK C. MAGNE, EDWIN J. HUGHES, ROBERT R. MOD AND EVALD L. SKAU

RECEIVED JANUARY 2, 1952

In a search for other amides which, like acetamide, would form stable crystalline molecular compounds with long-chain, saturated fatty acids, complete binary freezing point data have been obtained for palmitic acid with the following amides: formamide, propionamide, *n*-butyramide, isobutyramide, chloroacetamide, phenoxyacetamide, phenylacetamide, stearamide and benzamide. All of these systems proved to be of the simple eutectic type except that with formamide, which showed a region of immiscibility in the liquid state. Binary systems of palmitic acid with malonamide, succinimide, cyanoacetamide and urea were also found to show regions of immiscibility in the liquid state. In none of the thirteen systems investigated was there evidence of a molecular compound of palmitic acid with the amide, such as was found with acetamide.

It was demonstrated in a previous publication that acetamide forms stable 1:1 molecular compounds with long-chain saturated fatty acids such as palmitic acid.[3] These compounds can be used as a basis for a method of purification of the acids.[4] In a search for other amides which might form similar molecular compounds and which might be more effective than acetamide in this method of purification, complete binary freezing point data have been obtained for palmitic acid with nine other amides, including homologs and derivatives of acetamide. Sufficient data have also been obtained for four additional amides to show that they do not behave like acetamide. In none of these thirteen binary systems was there evidence of compound formation.

Experimental

The palmitic acid was a recrystallized sample obtained through the usual fractional vacuum distillation of the methyl ester. Its freezing point by the Francis and Collins cooling curve method[5] was 62.51°. The amides were the best Eastman Kodak products.[6] The formamide was purified by fractional vacuum distillation,[7] f.p. 2.4°. The propionamide was recrystallized repeatedly from benzene and then from acetone, f.p. 79.8°; the *n*-butyramide, from water and from 20% ethanol, f.p. 115.0°; the isobutyramide, from water followed by vacuum sublimation, f.p. 127.6°; the chloroacetamide, from acetone, f.p. 118°; the phenylacetamide, from absolute methanol, f.p. 158.5°; and the cyanoacetamide, from 6:4 methanol–dioxane mixture and from water, f.p. 119.4°. The other amides were used without further purification. All samples were dried in vacuum over phosphorus pentoxide before use.

The freezing points were determined by the sealed tube, static method previously described.[3] Precautions were taken to exclude moisture in making up the mixtures. In the case of formamide all transfers were made in a moisture-free atmosphere and the samples were sealed off in vacuum after chilling to −78°. The freezing point determinations were made with an accuracy and precision of ±0.2° with the exception of a few points on the chloroacetamide curve, as mentioned later.

Results and Discussion

The freezing point data for binary mixtures of palmitic acid with nine different amides are given in Table I and are represented graphically in Fig. 1. All of these binary systems are of the simple eutectic type except that with formamide.

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[1] One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture.

[2] Article not copyrighted.

[3] F. C. Magne and E. L. Skau, THIS JOURNAL, **74**, 2628 (1952).

[4] E. L. Skau, unpublished.

[5] F. Francis and F. J. E. Collins, *J. Chem. Soc.*, 137 (1936).

[6] The mention of names of firms or trade products does not imply that they are endorsed or recommended by the Department of Agriculture over other firms or similar products not mentioned.

[7] H. H. Sisler, C. A. VanderWerf and S. Stephanou, THIS JOURNAL, **68**, 2538 (1946).

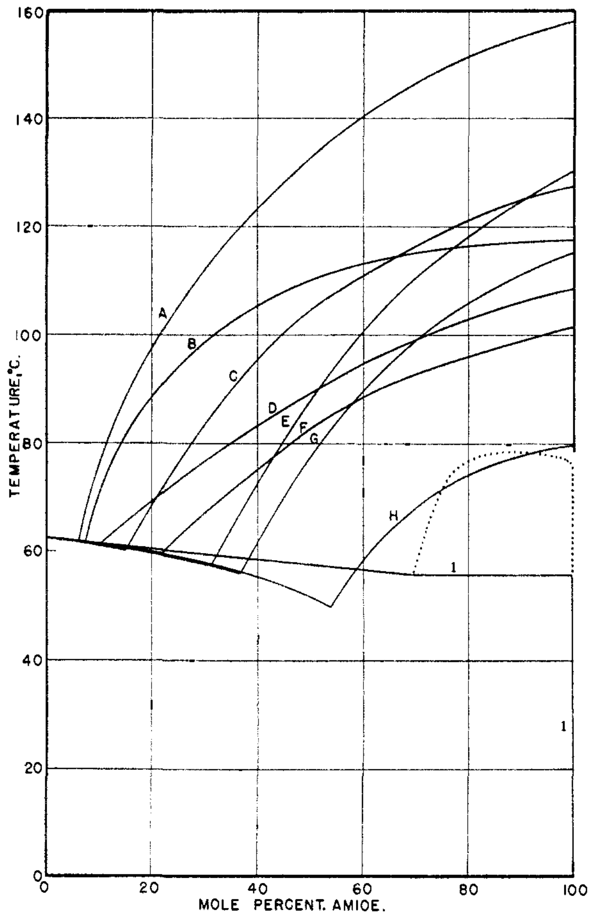

Fig. 1.—Binary freezing point diagrams for palmitic acid with: A, phenylacetamide; B, chloroacetamide; C, benzamide; D, stearamide; E, isobutyramide; F, phenoxyacetamide; G, *n*-butyramide; H, propionamide; and I, formamide.

Table I

Binary Freezing Point Data for Palmitic Acid with Various Amides[a]

Mole % amide	Freezing point, °C.	Mole % amide	Freezing point, °C.	Mole % amide	Freezing point, °C.
Formamide		Propionamide		*n*-Butyramide	
0.00	62.5	0.00	62.5	0.00	62.5
11.76	61.1	11.98	60.8	10.42	61.2
21.43	60.3	20.02	59.5	20.39	59.6
38.96	58.7	25.05	58.8	30.31	57.5
41.52	58.5	32.05	57.4	(37.0)[c]	(56.0)[c]
45.50	58.1	40.42	55.4	37.27	56.5
48.13	58.0	47.95	52.7	44.34	68.7
55.37	57.2	50.68	51.4	50.02	77.4
62.59	56.5	(54.0)[c]	(50.1)[c]	60.22	90.0
65.45	56.3	54.04	50.1	69.94	99.3
67.46	56.1	55.06	51.5	84.97	108.6
71.94	56.0[b]	58.74	56.7	100.00	115.3
77.83	55.9[b]	59.98	58.6		
88.62	55.8[b]	60.07	58.5		
96.44	55.7[b]	63.00	61.8		
99.68	55.9[b]	71.41	69.5		
100.00	2.4	80.01	74.5		
		89.92	77.7		
		100.00	79.8		
Isobutyramide		Chloroacetamide		Phenoxyacetamide	
0.00	62.5	0.00	62.5	0.00	62.5
20.26	59.4	3.23	62.3	9.92	61.2
30.08	57.5	(7.5)[c]	(61.8)[c]	20.14	59.6
(31.0)[c]	(57.4)[c]	8.30	64.6	(21.6)[c]	(59.4)[c]
35.77	65.4	13.87	79.2	30.53	67.4
40.06	72.2	23.57	92.8	40.17	75.4
50.16	88.2	31.21	99.8	49.95	82.6
59.51	99.2	40.81	105.7	60.11	88.6
69.95	110.9	50.70	110.4[d]	69.74	92.8
79.94	117.8	60.52	112.4[d]	85.31	97.5
100.00	127.6	69.89	115.0[d]	100.00	101.6
		79.69	115.9[d]		
		90.15	116.5[d]		
		100.0	117.6[d]		
Phenylacetamide		Stearamide		Benzamide	
0.00	62.5	0.00	62.5	0.00	62.5
3.13	62.2	5.43	61.9	4.98	61.9
(6.2)[c]	(61.9)[c]	(10.2)[c]	(61.4)[c]	11.44	60.9
6.83	64.0	10.67	61.8	13.99	60.2
20.16	98.0	15.08	64.2	(15.2)[c]	(60.0)[c]
35.88	119.1	19.88	69.3	21.86	71.4
49.91	132.3	31.65	77.8	35.86	90.5
66.95	144.2	48.52	88.2	49.52	104.4
79.84	150.3	66.61	97.6	67.89	115.3
100.00	158.5	100.00	108.6	100.00	126.6

[a] Corrected for thermometer calibration and emergent stem. [b] Two liquid layers at the freezing point, changing to one homogeneous phase at the following temperatures: 77.83% at 75.4°; 96.44% between 76.2 and 77.1°; and 99.68% between 76.4 and 76.9°. [c] Eutectic composition and temperature obtained by graphical extrapolation. [d] Slight discoloration during freezing point determination.

In the formamide system there is a region of immiscibility, in the range between roughly 69 and 99.8 mole % of formamide, within which two liquid phases are present at the freezing point. No attempt was made to define the exact boundaries of the region of immiscibility but they are shown approximately by the dotted curve. Since the solubility of palmitic acid in formamide is extremely small the depression of the freezing point of the formamide to the probable eutectic point below 2.4° was not observed; at a concentration of 0.32 mole % of the acid, the freezing point had risen to 55.9° and two liquid layers were present.

In the chloroacetamide system the compositions containing from 50.70 to 100% of amide showed signs of incipient decomposition, as evidenced by a slight discoloration during the determinations. These freezing points were therefore probably slightly below the true values. That the system is of the simple eutectic type as drawn in Fig. 1 was confirmed by microscopic examination which showed that the crystals forming in the 50.70% mixture were identical with those in the pure amide sample.

The palmitic acid branches of the propionamide, *n*-butyramide and isobutyramide diagrams in Fig. 1 almost coincide and lie very considerably below that of the formamide diagram. The corresponding curve for the acetamide system would fall in between, and the ideal curve for palmitic acid calculated from its heat of fusion would be the lowest by a small amount. Deviation from ideality in this direction can be explained by association of the amide molecules. Thus the data are consistent with the idea that the degree of association is greatest for formamide, less for acetamide, and least for the next higher homologs.

A few binary mixtures of palmitic acid with malonamide, succinimide, cyanoacetamide and urea were investigated and found to form two liquid layers. The compositions studied were 40 and 70% of malonamide, 50% of succinimide, 10.5, 20, 50, and 80% of cyanoacetamide, and 15, 22, 30, 40, 50, 60, 70 and 80% of urea. No freezing point data were obtained for these systems.

In none of the thirteen systems investigated was there separation of a crystalline molecular compound of palmitic acid with the amide, such as was previously found for acetamide. In this respect, therefore, acetamide seems to be unique.

NEW ORLEANS 19, LOUISIANA

[CONTRIBUTION NO. 24 FROM THE THERMODYNAMICS LABORATORY, PETROLEUM EXPERIMENT STATION, BUREAU OF MINES]

Thiacyclopropane (Ethylene Sulfide): Infrared Spectrum, Vapor Pressure and Some Thermodynamic Properties[1]

BY G. B. GUTHRIE, JR., D. W. SCOTT AND GUY WADDINGTON

RECEIVED OCTOBER 27, 1951

The infrared spectrum of liquid thiacyclopropane (ethylene sulfide) was observed between 2 and 15μ. Interpretation of the infrared data and other available spectroscopic data with the aid of normal coördinate calculations resulted in the following vibrational assignment: 625, 660, 824, 875, 943, 1025, 1051, 1100, 1112, 1427, 1446, 3000 (2) and 3080 (2). This assignment and moments of inertia from microwave measurements (ref. 13) were used to compute thermodynamic functions to 1000°K. The vapor pressure of thiacyclopropane was measured from 18 to 88° and the following equation was selected to represent the data: $\log_{10} p(\text{mm.}) = 7.03725 - 1194.37/(t + 232.42)$. The heat of vaporization at 25° calculated from this equation is 7240 ± 50 cal. mole^{-1}. The heat, free energy and equilibrium constant of formation of thiacyclopropane at selected temperatures to 1000°K. were computed using heat of combustion data for the liquid (ref. 2), the heat of vaporization and the thermodynamic functions.

The series of thiacycloalkanes (saturated cyclic sulfides) constitute one group of compounds in the thermodynamic research program of American Petroleum Institute Research Project 48A. Several members of this series and their derivatives have been identified in petroleum and others may be of interest to petroleum refiners and the chemical industry at large.

This paper presents the results of a study of the first member of the series, thiacyclopropane (ethylene sulfide). Since thiacyclopropane polymerizes readily, the experimental determination of its entropy and vapor heat capacity would have presented great practical difficulties and such measurements were not undertaken. However the relative simplicity of the molecule made it possible to obtain a reliable vibrational assignment and to circumvent these calorimetric measurements by calculating the thermodynamic functions from spectroscopic and molecular structure data alone. A value of the heat of formation of liquid thiacyclopropane was available from the work of Sunner,[2] but an accurate value of the heat of vaporization was necessary for extending this datum to the vapor state. The present investigation therefore included: (a) obtaining certain spectroscopic data not available in the literature and making a vibrational assignment, (b) obtaining a value of the heat of vaporization from a study of the vapor pressure as a function of temperature and (c) using the results of these studies and other available data to calculate the thermodynamic functions and the heat, free energy and equilibrium constant of formation of thiacyclopropane for selected temperatures up to 1000°K.

When the present research was undertaken, the only spectroscopic data available for making a vibrational assignment were those of Thompson and Dupré,[3] who had studied the Raman spectrum of the liquid and the infrared spectrum of the vapor, and had proposed a nearly complete vibrational assignment. Examination of these spectroscopic data and the proposed assignment suggested that some of the reported infrared bands may have been spurious and that other bands were obscured by the rotational structure of adjacent bands. For this reason, the infrared spectrum of thiacyclopropane was studied over the range 2–15 μ in the liquid state so that the bands would be sharpened and the conditions for resolving adjacent bands would be improved. The infrared spectrum of the polymerized material also was measured so that weak bands resulting from traces of polymer in the sample of thiacyclopropane could be identified. These studies revealed two previously unresolved bands in the region of fundamental frequencies and many new overtone and combination bands, and also confirmed the surmise that some of the bands observed by Thompson and Dupré were not characteristic of the pure substance. Shortly after these studies had been carried out in this Laboratory, Thompson and Cave[4] published the results of a reinvestigation of the infrared spectrum of the vapor and the Raman spectrum of the liquid. They found that one of the strong bands reported by Thompson and Dupré had been due to hydrogen cyanide impurity. Also, by using infrared spectrometers of greater resolving power,

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(1) This investigation was performed as part of the work of American Petroleum Institute Research Project 48A on "The Production, Isolation and Purification of Sulfur Compounds and Measurement of their Properties" which the Bureau of Mines conducts at Bartlesville, Okla., and Laramie, Wyo.

(2) S. Sunner, Dissertation, University of Lund, 1949, "Studies in Combustion Calorimetry Applied to Organo-sulfur Compounds," Carl Bloms Boktryckerie, Lund, Sweden, 1949, p. 76.

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(4) H. W. Thompson and W. T. Cave, *ibid.*, **47**, 951 (1951).