If the above Hirschfelder activation energies are used, k_4/k_2 is 29.6.

Assuming a value of 0.038 for the quantum yield at a pressure ratio of 20 (Fig. 3), the constant $k = k_1I_a$ becomes 0.094 and the quantum yield is given by

$$\Phi = \frac{(0.094\ (H_2))/(ICl)}{(H_2)/((ICl) + 29.6)}$$

Points calculated from this equation are plotted in Fig. 3 as the dashed line. Agreement between the experimental values and the calculated curve is surprisingly good.

There are several possible sources of differences between this and the earlier work, *viz.*, impurities, adsorption on the cell walls, moisture and quality and purity of the light. The work of Ashley and West[8] shows that the presence of impurities, such as stopcock grease, increases the yield. In the present work, fluorocarbon stopcock grease was used, but only occasional streaking was encountered; and since Hofer and Wiig used all-glass valves, the effect of impurities may be largely discounted.

The runs with a sodium chloride coating in the reaction cell clearly indicate that the nature of the surface may be an important factor. A sixfold increase in quantum yield was observed (Run 37), although the effect decreased in successive runs, indicating some kind of poisoning effect. Part of the difference between the flow and static methods might be accounted for by adsorption effects, since in a flow system little adsorption of products would take place.

The effect of moisture is largely unknown, but hydrogen chloride would be produced from iodine monochloride and water, increasing the quantum yield. Certainly the effect would be more serious in a flow system. In the present research no measurable amount of hydrogen chloride was found in the dark reaction. However, in a flow system a liquid air trap is not a very efficient drying method when the total pressure is one atmosphere, and the effect would be in the right direction to explain the difference in yields.

If the light used by Hofer and Wiig were not strictly monochromatic, a considerable error might have been introduced. Two blue glass plates and a solution of quinine sulfate were used as filters. The latter cuts off very sharply on the low wavelength side of 3800 Å. This allows a few lines below 4358 Å. to pass. Although the blue glass plates used in their work were not available, a spectrophotometer test of similar ones showed definitely that some light as high as 5100 Å. is transmitted. Since the uranyl oxalate actinometer is unaffected by some of these lines, the number of quanta would be in error and the quantum yields would be too high.

It is clear that no essential conflict exists between the present research and that of Hofer and Wiig. Their proposed mechanism agrees with the facts found in this work within the limits of experimental error. Possibly, the values of the quantum yield of hydrogen chloride found here are slightly low as a result of adsorption effects, which were doubtless smaller in the previous work. The value of 9.0 kcal. for the energy of activation may be somewhat high as it would include any effect of temperature on adsorption. Since the quantum yield found earlier may be too high and the present values may be too low, the true value may lie somewhere between the limits set by the different methods.

ROCHESTER, NEW YORK

[CONTRIBUTION FROM THE EASTERN REGIONAL RESEARCH LABORATORY][1]

Solubility of Lactose and its Hydrolytic Products

BY EUGENE A. TALLEY AND ANN S. HUNTER

RECEIVED NOVEMBER 2, 1951

The solubility in water at 25° of various mixtures of lactose, D-glucose and D-galactose has been determined. First order, empirical equations have been derived which express the solubility relationships of the three sugars.

Lactose might be utilized in the form of a sirup if the solids content could be increased without danger of crystallization. Partial or complete hydrolysis of lactose into its constituent hexoses would be expected to make a sirup of high solids content possible. The present work was undertaken to determine the solubility relationships of various mixtures of lactose and its hydrolytic products in water at ordinary temperatures.

The solubility of lactose itself in water has been studied thoroughly,[2] and solubility studies have been made in the presence of other materials, such as sucrose,[3] whole and skim milk,[3b] alcohol[4] and pyridine,[5] but not in the presence of D-glucose and D-galactose. The solubility of D-glucose[6] and D-galactose[5b,7] individually, as well as mixtures of the two sugars,[8] has been determined in water.

Experimental

Lactose and glucose hydrates obtained from commercial sources were recrystallized until they gave the correct constant optical rotations. Galactose was recrystallized from

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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. Article not copyrighted.

[2] (a) E. O. Erdmann, *Ber.*, **13**, 2180 (1880); (b) C. S. Hudson, THIS JOURNAL, **30**, 1767 (1908); (c) E. Saillard, *Chimie & industrie*, **2**, 1035 (1919); (d) J. Gillis, *Rec. trav. chim.*, **39**, 88, 677 (1920); and (e) A. Leighton and P. N. Peter, *Proc. World's Dairy Congress*, **1**, 477 (1923).

[3] (a) P. N. Peter, *J. Phys. Chem.*, **32**, 1856 (1928); (b) O. F. Hunziker and B. H. Nissen, *J. Dairy Science*, **9**, 517 (1926).

[4] C. S. Hudson and E. Yanovsky, THIS JOURNAL, **39**, 1013 (1917).

[5] (a) J. G. Holty, *J. Phys. Chem.*, **9**, 764 (1905); (b) W. M. Dehn, THIS JOURNAL, **39**, 1399 (1917).

[6] R. F. Jackson and C. G. Silsbee, *Bur. Standards Sci. Papers*, **17**, No. 437, 715 (1922).

[7] Stephen P. Gould, *J. Dairy Science*, **23**, 227 (1940).

[8] G. A. Ramsdell and B. H. Webb, *ibid.*, **28**, 677 (1945).

commercial sources; some was prepared from lactose.[9] The materials had the following equilibrium rotations and moisture constants: α-Lactose hydrate $[\alpha]^{25}\text{D}$ +52.5° (c 5, H_2O) (calculated from Browne and Zerban,[10] $[\alpha]^{25}\text{D}$ +52.2°) and 5.1% water of crystallization (theory, 5.0). α-D-Glucose hydrate, $[\alpha]^{25}\text{D}$ +48.0° (c 5, H_2O) (calculated from Browne and Zerban,[11] $[\alpha]^{25}\text{D}$ +47.9°) and 9.2% water of crystallization (theory 9.1). α-D-Galactose, $[\alpha]^{25}\text{D}$ +79.1° (calculated from Browne and Zerban,[12] $[\alpha]^{25}\text{D}$ +79.0°) and 99.9% solids (theory, 100.0%).

For the determination of solubility, samples of known sugar concentration were made by weighing the sugar or sugars into small conical flasks and then running in the calculated amount of water from a buret. After the sugar or sugars were dissolved to give the initial solution, an excess of the solid sugar, the solubility of which was to be determined, was added. A few drops of toluene were used as an antiseptic. The flasks were stoppered with rubber stoppers and placed in a bath held at 25°. The flasks were shaken from time to time. After two or three weeks, 5 to 6 g. of the clear supernatant liquid (the final sugar solution) was weighed into a 50-ml. volumetric flask and made up to volume. This solution could be analyzed for the sugars by the method of Ramsdell,[13] but the following method was deemed simpler and more direct. The optical rotation was determined in a 4-dm. tube. An aliquot was measured into a large weighed aluminum moisture dish, evaporated to apparent dryness in an oven at atmospheric pressure at 60°, and then dried to constant weight at 100° in a vacuum oven (the sugars dried to the anhydrous form under these conditions). This sampling and analysis procedure was repeated at approximately weekly intervals until the rotation and moisture values were constant. Little change occurred after the first determination. Reducing power determinations did not give useful results. A test set of ten solutions in which the concentrations of the three sugars varied over the ranges studied showed that the optical rotations of the sugars in solution were additive within the limits of error of this work; the root mean square deviation for the ten samples was 0.1% of the calculated value.

Since the initial sugar concentrations were known and since neither the ratio of the concentrations of these sugars nor the ratios of the concentrations to that of the water initially present changed when the solid sugar was added, the final sugar concentrations could be calculated from either the optical rotation or the moisture of the weighed sample (W) taken. The sets of simultaneous equations for each method may be solved as follows: For the equations based on optical rotation: Let

W = wt. of final sugar solution taken for analysis
x = wt. of X sugar (soln. saturated with respect to X only) in sample W
y = wt. of Y sugar in sample W
z = wt. of Z sugar in sample W
D = length of polarimeter tube in decimeters
e = wt. ratio of Y sugar to Z sugar in the initial solution
f = wt. ratio of water to Z sugar in the initial solution
g = 50/D
α = observed rotation (sample W diluted to 50 ml.)
A = $[\alpha]^{25}\text{D}$ of X (for the hydrates in the case of glucose and lactose)
B = $[\alpha]^{25}\text{D}$ of Y
C = $[\alpha]^{25}\text{D}$ of Z

Since the ratio of Y to Z is the same in the initial and final solutions

$$y/z = e \text{ and } y = ez$$

$$\alpha = \frac{ADx}{50} + \frac{BDy}{50} + \frac{CDz}{50} = \frac{Ax + By + Cz}{g}$$

Substituting $y = ez$ and solving for z

$$z = \frac{\alpha g - Ax}{eB + C}$$

If the concentration of X sugar is expressed in terms of the hydrate for glucose and lactose and of the anhydrous form for galactose, then the ratio of water to Z sugar may be taken as the same in the initial and the final solutions, *i.e.*

$$f = \frac{W - (x + y + z)}{z}$$

Then

$$W = x + y + z + [W - (x + y + z)] = x + y + z + fz$$

Substituting $y = ez$ and solving for z

$$z = \frac{W - x}{e + 1 + f}$$

Equating the two expressions for z and solving for x

$$x = \frac{\alpha g(e + 1 + f) - (eB + C)W}{A(e + 1 + f) - (eB + C)} \quad \% X = \frac{100x}{W} \qquad (1)$$

$$z = \frac{W - x}{e + 1 + f} = \frac{\alpha g - Ax}{eB + C} \quad \% Z = \frac{100z}{W} \qquad (2)$$

$$y = ez \quad \% Y = \frac{100y}{W} \qquad (3)$$

For the equations based on moisture (in addition to the symbols listed for optical rotation): Let

M = wt. of moisture in sample (W) taken
h = wt. ratio of Y sugar to the water initially present
i = wt. ratio of Z sugar to the water initially present
n = number of moles of water per mole of sugar hydrate

$$j = \frac{n(H_2O)}{\text{mol. wt. of } X} = \frac{n(18.02)}{\text{mol. wt. of } X}$$

And for ease in solving equations

M_x = wt. of moisture added to Sample W when the X sugar hydrate dissolved

Then

$$y/(M - M_x) = h \qquad y = h(M - M_x)$$

$$z/(M - M_x) = i \qquad z = i(M - M_x)$$

$$M_x = \left[\frac{n(H_2O)}{\text{mol. wt. of X}}\right] x = jx$$

$$x + y + z + M = W$$

Substituting and solving for x

$$x + h(M - M_x) + i(M - M_x) + M = W$$

$$x + hM + iM + M - jx(h + i) = W$$

$$x = \frac{W - M(h + i + 1)}{1 - (h + i)j} \qquad (4)$$

$$y = h(M - jx) \qquad (5)$$

$$z = i(M - jx) \qquad (6)$$

If $W = 100$ and M = % moisture in the final sample, then x, y and z are obtained directly as percentages by using the equations based on moisture. These results are on the anhydrous basis if the initial values and the molecular weight of X are on the anhydrous basis. The equations for optical rotation, however, do not take into account the water added when a hydrated sugar is dissolved to saturate the final solution. Then the value for x must be corrected after it is calculated from equation 1, if results are to be on the anhydrous basis.

A sample calculation is given to illustrate the method. A solution was prepared which contained 10% lactose and 7.5% galactose on the anhydrous basis. Analysis of a sample of this solution after saturation with glucose hydrate gave a moisture content of 46.0% and an observed rotation of 14.60° when a sample weighing 6.156 g. was diluted to 50 ml. and observed in a four decimeter tube. Substituting the appropriate values in equation (1), we have

$$x = \frac{(14.60)(12.5)(1.333 + 1 + 11.00) - [(1.333)(55.3) + 79.1][6.156]}{(48.0)(1.333 + 1 + 11.00) - [(1.333)(55.3) + 79.1]}$$

x = 3.064 g. of glucose hydrate in sample W = 2.785 g. of anhydrous glucose or 45.2%.

Substituting in equation (2)

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(9) Frederick J. Bates and Associates, "Polarimetry, Saccharimetry and the Sugars," Circular C440 of National Bureau of Standards, 1942, p. 462.

(10) C. A. Browne and F. W. Zerban, "Physical and Chemical Methods of Sugar Analysis," 3rd ed., John Wiley and Sons, Inc., New York, N. Y., 1941, p. 196.

(11) Ref. 10, p. 270.

(12) Reference 10, p. 272.

(13) G. A. Ramsdell, *J. Dairy Science*, **28**, 671 (1945).

$$z = \frac{6.156 - 3.064}{1.333 + 1 + 11.00} =$$

0.232 g. of anhydrous galactose or 3.76%.

Substituting in equation (3)

$$y = (1.333)(0.232) = 0.309 \text{ g. anhydrous lactose or } 5.02\%$$

Using values based on moisture and substituting in equation (4), we have

$$x = \frac{(100 - 46.0)(0.1212 + 0.0909 + 1)}{1 - (0.1212 + 0.0909)(0.1000)} =$$

45.2% anhydrous glucose

Substituting in equation (5)

$$y = [0.1212][46.0 - (45.2)(0.1000)] = 5.03\% \text{ anhydrous lactose}$$

Substituting in equation (6)

$$z = [0.0909][46.0 - (45.2)(0.1000)] = 3.77\% \text{ anhydrous galactose}$$

Results and Discussion

Good agreement was obtained between the results based on optical rotation determinations and those based on moisture determinations. This is indicated by the results listed in Table I.

TABLE I

SOLUBILITY DATA[a]

Glucose, %		Galactose, %		Lactose, %	
O	S	O	S	O	S
46.47	46.16	3.67	3.69	2.44	2.46
45.25	45.20	3.77	3.77	5.03	5.03
43.41	43.49	3.92	3.91	7.83	7.82
44.70	44.99	7.62	7.58	2.54	2.53
42.85	42.61	7.93	7.97	5.29	5.32
42.25	43.31	12.05	12.03	2.72	2.68
40.33	40.44	12.52	12.49	5.56	5.55
37.82	37.64	16.06	16.12	5.84	5.86
39.38	39.49	17.00	16.97	2.84	2.83

[a] Under O are results based on optical rotation. Under S are results based on solids or moisture.

Tables II and III list the final concentrations of all the samples tested, where equilibrium was approached from unsaturation, along with the initial sugar concentration. These are averaged values based on both moisture and optical rotation. In a few cases, solution of the added sugar caused the solution to become supersaturated with respect to one of the initial sugars. No indication was found, however, that any of the initial sugar came out of the solution when the solid form of that sugar was not present. These points were included in the correlations given below since their deviations were in the normal range. A few cases (not listed) were tested in which equilibrium was approached from supersaturation and only one sugar was used. The rate was much slower than that from unsaturation, even with the solid phase present.[3a]

The equations representing the solubility relationships of the three sugars were calculated by the method of least squares[14] using the values from Tables II and III. The equations are

$$La = 17.50 - 0.2452Gl - 0.2477Ga \quad (7)$$

$$Gl = 50.38 - 0.6305La - 0.5550Ga \quad (8)$$

$$Ga = 32.09 - 0.3898Gl - 0.3973La \quad (9)$$

where La, Gl and Ga represent the number of grams (anhydrous basis) of lactose, glucose and galactose, respectively, per 100 g. of solution. The standard deviations[14] of the experimentally determined values from the values estimated by the equations given above were 0.269, 0.219 and 0.180, respectively. The standard errors of estimate[14] were calculated to be 0.288, 0.240 and 0.196, respectively. The limiting final solubility of the three sugars in water at 25°, saturated with respect to all three, was calculated from the equations 7 to 9 to be 4.10% lactose, 39.42% glucose and 15.10% galactose.

From these equations (7 to 9) were derived pairs of equations, which represent the limiting solubilities of two of the sugars in varying concentrations of the third (none of the experimental points in Tables II and III should fit these derived equations)

For varying concentrations of galactose	$Gl = 46.54 - 0.4718Ga$	(10)
	$La = 6.09 - 0.1320Ga$	(11)
For varying concentrations of lactose	$Ga = 15.89 - 0.1934La$	(12)
	$Gl = 41.56 - 0.5231La$	(13)
For varying concentrations of glucose	$Ga = 27.88 - 0.3243Gl$	(14)
	$La = 10.60 - 0.1648Gl$	(15)

A plot of the orthographic projections of the points in Tables II and III, made by the methods of descriptive geometry,[15] showed that the final solubilities of the sugars could be represented graphically by three plane surfaces in a three-coördinate system, as indicated in Fig. 1. In this figure, plane BCFE represents the limiting solubility of lactose in the presence of glucose and galac-

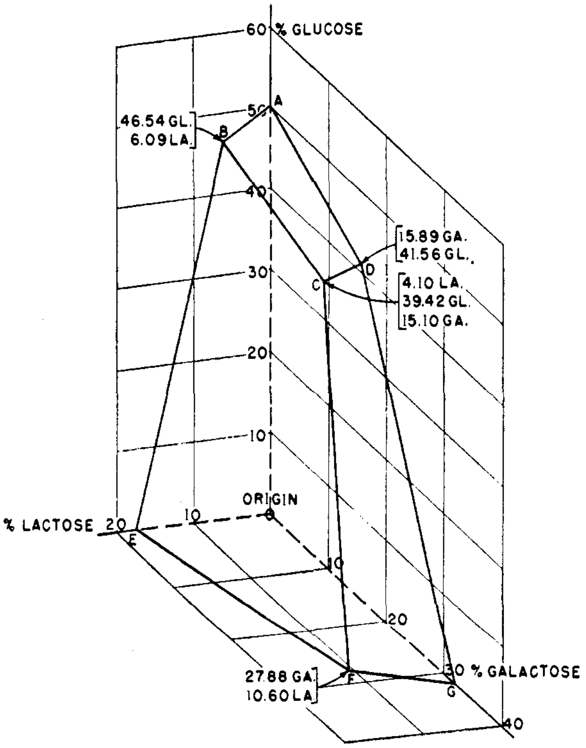

Fig. 1.—Solubility relationships of lactose, D-glucose and D-galactose in water at 25°.

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[14] Mordecai Ezekiel, "Methods of Correlation Analysis," John Wiley and Sons, Inc., New York, N. Y., 2nd ed., 1941.

[15] (a) A. V. Millar, E. S. Maclin, L. J. Markwardt and K. G. Shiels, "Descriptive Geometry," Kilgore Printing Company, Madison, Wisconsin, 1930. (b) G. C. Anthony, "Elements of Mechanical Drawing," D. C. Heath and Co., New York, N. Y., 1904.

TABLE II

SOLUBILITY OF D-GLUCOSE, LACTOSE AND D-GALACTOSE (GRAMS ANHYDROUS SUGAR PER 100 G. OF SOLUTION)

Two-sugar component systems

Initial sugar content			Final sugar content		
Glucose	Lactose	Galactose	Glucose	Lactose	Galactose
		Saturated with glucose			
	0		50.2	0	
	5.2		48.6	2.43	
	10.5		47.3	5.01	
	15.7		45.6	7.82	
		0	50.5		0
		7.5	48.7		3.48
		15.0	46.5		7.32
		22.5	44.2		11.6
		30.0	41.4		16.4
		Saturated with lactose			
0			0	17.6	
10.0			8.4	15.4	
20.0			17.2	13.4	
30.0			26.5	11.0	
40.0			36.3	8.75	
50.0			47.2	5.39	
		0		17.6	0
		5.0		16.5	4.1
		10.0		15.5	8.4
		15.0		14.6	12.7
		20.0		13.2	17.2
		25.0		11.9	21.9
		30.0		11.1	26.5
		Saturated with galactose			
	0			0	32.0
	5.0			3.46	30.8
	10.0			7.40	29.7
	15.0			10.8	27.7
0 (0)[a]			0 (0)[a]		32.1 (32.1)[a]
10.0 (10.0)			7.1 (7.1)		29.5 (30.1)
20.0 (20.0)			14.8 (14.6)		26.1 (26.9)
30.0 (30.2)			23.1 (23.0)		23.0 (23.8)
40.0 (40.3)			32.1 (32.0)		19.7 (20.6)
50.0 (49.1)			42.2 (40.6)		15.7 (17.3)
(50.0)			(41.7)		(16.6)

[a] The values in parentheses are calculated from Ramsdell and Webb.[8] (See the text for method of calculation.)

TABLE III

SOLUBILITY OF D-GLUCOSE, LACTOSE AND D-GALACTOSE (GRAMS ANHYDROUS SUGAR PER 100 G. OF SOLUTION)

Three-sugar component systems

Initial sugar content			Final sugar content		
Glucose	Lactose	Galactose	Glucose	Lactose	Galactose
		Saturated with lactose			
10.0		7.5	8.6	13.7	6.4
10.0		14.9	8.7	12.0	13.1
10.0		22.5	8.9	10.2	20.1
20.0		7.6	17.6	11.4	6.7
20.0		15.0	17.9	9.80	13.4
20.0		22.5	18.4	7.64	20.7
30.0		7.5	27.1	9.17	6.8
30.0		15.0	27.9	6.82	13.9
40.0		7.5	37.1	6.89	7.0
40.0		14.9	37.6	5.69	14.1
		Saturated with glucose			
	5.0	7.5	46.5	2.44	3.7
	10.0	7.5	45.2	5.03	3.8
	15.0	7.5	43.4	7.83	3.9
	5.0	15.0	43.9	2.58	7.8
	10.0	15.0	42.4	5.35	8.0
	5.0	22.5	41.6	2.72	12.2
	10.0	22.5	39.8	5.61	12.6
	10.0	27.5	37.8	5.84	16.1
	5.0	30.0	39.2	2.85	17.1
		Saturated with galactose			
10.0	5.0		7.2	3.61	27.8
10.0	10.0		7.4	7.35	26.3
10.0	15.0		7.6	11.3	24.3
20.0	5.0		15.1	3.78	24.4
20.0	10.0		15.4	7.70	23.1
30.0	5.0		23.6	3.94	21.4
25.0	7.2		19.5	5.56	22.2
35.0	5.0		28.1	4.02	19.7
40.0	5.0		32.9	4.10	17.7
25.0	10.0		19.7	7.82	21.4

tose in water at 25°. Similarly, plane ADCB represents the solubility of glucose, and plane CDGF represents the solubility of galactose. Equations 7, 8 and 9, respectively, are the equations of these planes. The line of intersection, BC, represents the solubility of both glucose and lactose in the presence of varying concentrations of galactose. Similarly, line CD represents the solubility of glucose and galactose, and line CF represents the solubility of lactose and galactose. The pairs of equations, 10 and 11, 12 and 13, and 14 and 15, respectively, are the equations of these lines. Point C is the triple point representing the limiting solubilities when the solution is saturated with all three sugars. (The values in the figure were calculated from the equations. The values for this point estimated from the original plot were: 4.5% lactose, 39.6% glucose and 14.8% galactose.) Points B, D and F represent double points where the third sugar is not present. Points A, E and G, respectively, represent the solubilities of the individual sugars: glucose, 50.4%; lactose, 17.5%; and galactose, 32.09%.

The concentrations of the sugars were estimated from the original plot for nine points where the solutions would be saturated with respect to two of the sugars as well as the point where the solution would be saturated with respect to all three. Solutions having the concentrations thus determined then were made up, and the rotations and solids values were checked experimentally. The solid forms of the sugars with which the solutions were supposed to be saturated, were added, and the solutions were kept in the bath at 25° as before. The maximum change observed was 3.5% of the original value for rotation and 4.4% of the solids value. The root mean square deviations were 2.25 and 2.4%, respectively.

The value 17.5% for the solubility of lactose from equation 7 agrees fairly well with the literature value[2b] of 17.8%; the value 50.38% for the solubility of glucose from equation 8 agrees with the value, 50.81%, interpolated from the data of Jackson and Silsbee.[6] The value for galactose, 32.09%, agrees exactly with those previously reported,[7,8] but the values for mixtures of galactose and glucose are different from those previously reported.[8] The final solubilities of galactose and glucose together were found to be 15.89 and 41.56%, respectively, instead of the previously reported values of 8.5 and 49.8%. The locus of the final solubility of galactose in the presence of varying concentrations of glucose also was found to be a 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.

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[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).