J. Chem. Eng. Data 1980, 25, 305-307

Dobry and Keller reported the vapor pressures of bicyclohexyl represented by the Clapeyron equation at the temperature range up to 240 °C, but values calculated from this equation are in serious disagreement with ours.

Acknowledgment

We acknowledge the leave of absence granted by the Institute of Physical Chemistry of the Polish Academy of Sciences, to the first author, Electric Power Research Institute, for providing the financial support of this investigation, and the Monsanto Chemical Company for providing the bath fluid, Therminol 88, gratis. Personal acknowledgments to Dr. Pervaiz Nasir for helpful discusssions and R. J. Martin for extensive assistance with the experimental apparatus are due.

Literature Cited

(1) Ambrose, D.; Counsell, J. F.; Davenport, A. J. *J. Chem. Thermodyn.* **1970**, *2*, 283.
(2) Crafts, J. M. *Ber.* **1875**, *13*, 105.
(3) Dobry, A.; Keller, R. *J. Phys. Chem.* **1957**, *61*, 1448.
(4) Glasser, F.; Ruland, H. *Chem.-Ing.-Tech.* **1957**, *29*, 772.
(5) Glasgow, A. R.; Streiff, A. J.; Rossini, F. D. *J. Res. Natl. Bur. Stand. (U.S.)* **1945**, *35*, 355.
(6) Sebastian, H. M.; Simnick, J. J.; Lin, H. M.; Chao, K. C. *Can. J. Chem. Eng.* **1978**, *56*, 743.
(7) Simnick, J. J.; Liu, K. D.; Lin, H. M.; Chao, K. C. *Ind. Eng. Chem. Process Des. Dev.* **1978**, *17*, 204.
(8) Nasir, P.; Hwang, S. C.; Kobayashi, R., preceding paper.

Received for review January 25, 1980. Accepted June 26, 1980.

X-ray Diffraction Data for Some Amine Salts of Long-Chain Fatty Acids and Related Compounds

E. L. Skau,* R. R. Mod, and Donald Mitcham

Southern Regional Research Center, Science and Education Administration, U.S. Department of Agriculture, New Orleans, Louisiana 70179

X-ray long and short spacings of 48 amine salts of long-chain fatty acids and of some related compounds and mixtures are presented. Included are data on four homologous series of amine salts, those of piperazine, morpholine, cyclohexylamine, and tris(hydroxyethyl)aminomethane. The long-spacing data are used to calculate the angles of tilt for these four series. Studies on the polymorphic forms of palmitamide are presented, along with a calculation of the angle of tilt of long-chain fatty amides from data derived mainly from the literature. X-ray long and short spacings of four methyl ketones (2-tridecanone, 2-pentadecanone, 2-heptadecanone, and 2-nonadecanone) are presented, along with a calculation of the angle of tilt of these compounds.

Introduction

During our investigations of the solid–liquid phase relations between long-chain fatty acid derivatives, many highly pure crystalline compounds were prepared and characterized. The present report deals with the X-ray diffraction measurements of the "long" and "short" spacings for a few homologous series of amine salts, for a number of individual amine salts, amides, and N-substituted amides of long-chain saturated and unsaturated fatty acids, and for a few related compounds.

Experimental Section

Unless otherwise indicated, the compounds were prepared and purified by the procedures previously described for the amine salts (*1*), the acid-free amides (*2*), the N-substituted amides (*3*), the octadecenoic acids (*4*), and the various aminopyridine salts (*5,6*). The A form of palmitamide was obtained by recrystallization of the B form from a dilute methanol solution. The mixture of morpholine stearate and cyclohexylamine palmitate was prepared from equimolar amounts of the pure salts. The mixture was melted and the melt was allowed to cool slowly until it crystallized.

The X-ray long- and short-spacing measurements were made by the powder method of O'Connor et al. (*7*). A General Electric XRD-5 diffractometer or a Phillips Electronics diffractometer was used to obtain X-ray diffraction patterns by the direct-measurement technique with a chart recorder. The instrument was equipped with a copper-target X-ray tube and a 0.018-mm nickel filter. Divergence and antiscattering slits were used. The X-rays were generated at 30 kVp and 15 mA from 0 to 12.5°, 2θ, and 36 kVp and 16 mA from 12.5 to 50°, 2θ.

Results and Discussion

Table I shows X-ray long and short spacings on 48 amine salts of long-chain fatty acids and on some related compounds and mixtures, including four homologous series of amine salts. The long spacings, L, for each of these homologous series show a linear relationship to n, the number of carbon atoms in the fatty acid molecule. This relationship can be represented by eq 1, where m is the number of long-chain molecules contributing

$$L = (md)n + k \qquad (1)$$

to the length of the repeating unit, d is the increase in long spacing per additional carbon atom per molecule measured along a line perpendicular to the 001 planes of the crystal lattice, n is the number of carbons in the acid residue, and k is a constant.

The method of least squares was used to determine the equation of the best straight line through the L vs. n data for each of the homologous series. A digital computer gave the values for md and k of the equation, as well as the standard error of estimate of the individual values of L.

The equation for the piperazine salts, items 1–7 in Table I, was

$$L = 2.270n + 5.022 \qquad (2)$$

with an average deviation of 0.02 Å. The calculated angle of tilt is therefore $\sin^{-1} 2.270/2.54 = 63° \, 20'$ (*8*). The angles of tilt for the other three homologous series, calculated in a similar manner, were the following: for the morpholine salts, items 8–11, 74° 41′; for the cyclohexylamine salts, items 12–20, 42° 39′; and for the tris(hydroxyethyl)aminomethane salts, items 22–26, 47° 23′.

Table I. X-ray Diffraction Data for Some Amine Salts of Long-Chain Fatty Acids and Related Compounds

no.	amine	acid[a]	acid-amine mole ratio	long spacing,[b] A	short spacings, A	
					no. obsd	selected values[c]
1	piperazine	L	2:1	18.66^5	17	4.53 ms, 4.11 ms, 3.87 w, 3.68 m
2		M	2:1	20.90^8	23	4.53 vs, 4.18 m, 4.08 vs, 3.85 s, 3.68 vs
3		P	2:1	23.20^7	17	4.54 vs, 4.18 s, 4.05 s, 3.85 s, 3.69 s
4		S	2:1	25.45^6	15	4.54 s, 4.18 m, 4.03 m, 3.84 ms, 3.69 ms
5		A	2:1	27.74^7	7	4.53 w, 4.18 s, 3.93 m, 3.46 w
6		E	2:1	25.10^{10}	17	4.55 vs, 4.09 vs, 3.88 s, 3.72 vs
7		O	2:1	26.31^9	6	4.38 vs, 4.14 vs, 3.74 w, 3.29 w
8	morpholine	L	1:1	24.25^6		
9		M	1:1	26.64^9	14	4.58 ms, 4.39 ms, 4.05 m, 3.71 s, 2.39 m
10		P	1:1	29.33^8	12	4.57 s, 4.39 vs, 4.06 m, 3.70 vs, 2.40 m, 2.13 m
11		S	1:1	31.52^6	11	4.56 vs, 4.39 s, 4.07 m, 3.69 vs, 2.40 m, 2.13 m
12	cyclohexylamine	C	1:1	15.71^5	26	5.25 s, 4.78 vs, 4.58 m, 4.10 vs, 3.97 s, 3.89 m, 3.62 m
13		L	1:1	17.27^5	15	5.26 w, 4.89 s, 4.61 vs, 4.31 s, 4.09 vs, 3.80 ms, 3.61 m
14		M	1:1	18.93^6	19	5.20 m, 4.76 s, 4.47 ms, 4.07 s, 3.91 ms, 3.77 w, 3.63 m
15		P	1:1	20.88^7	12	5.15 w, 4.84 m, 4.60 vs, 4.05 vs, 3.79 ms, 3.56 m
16		S	1:1	22.51^7	13	5.15 m, 4.69 s, 4.48 ms, 4.19 m, 4.01 vs
17		E	1:1	22.60^7	14	5.25 m, 4.76 m, 4.55 m, 4.32 vs, 4.07 s, 3.85 ms
18		P′	1:1	22.22^9	7	5.05 m, 4.67 m, 4.25 vs, 3.98 m, 3.86 ms
19		P″	1:1	22.40^9	7	5.31 m, 4.69 m, 4.23 s, 4.16 m, 4.07 vs, 3.93 m
20		H	1:1	20.64^{10}	10	5.15 s, 4.75 m, 4.21 ms, 4.09 vs, 3.93 s, 3.41 vs
21	equimolar mixture of 11 and 15			22.45^6	9	5.30 w, 4.86 w, 4.61 s, 4.41 ms, 4.10 s, 3.71 s
22	tris(hydroxyethyl)aminomethane	L	1:1	19.46^7	21	4.45 vs, 4.12 s, 3.87 vs
23		P	1:1	23.07^6	23	4.55 w, 4.39 vs, 4.11 s, 3.81 s
24		S	1:1	25.10^5	18	4.61 ms, 4.38 m, 4.05 vs, 3.80 w
25		E	1:1	24.86^9	17	4.59 m, 4.39 vs, 4.16 s, 3.85 vs
26		O	1:1	23.43^6	13	4.99 m, 4.54 w, 4.31 vs, 3.86 w
27	2,2′-dipyridylamine	P	1:1	30.56^5	20	4.90 m, 4.25 m, 4.05 vs, 3.78 s, 3.48 s
28	2,2′-dipyridylamine	S	1:1	32.82^7	11	5.04 w, 4.26 m, 4.08 s, 3.79 ms, 3.50 ms
29	ethylamine	P	1:1	27.68^8	23	4.16 vs, 3.65 s, 3.43 s, 2.52 ms
30	diethylamine	P	2:1	23.58^4	10	4.30 vs, 4.02 vs, 3.71 vs
31	dibutylamine	P	2:1	24.0^3	13	4.66 ms, 4.41 vs, 4.09 vs, 3.71 s
32	diisobutylamine	P	2:1	24.8^4	13	4.23 vs, 3.75 s
33	di-*sec*-butylamine	P	2:1	24.3^5	15	4.51 vs, 4.02 vs, 3.83 vs, 3.71 s
34	ethylenediamine	P	2:1	36.3^7	13	4.64 s, 4.42 s, 3.83 s, 3.63 s
35	ethanolamine	P	1:1	24.5^8	22	4.29 s, 4.05 vs, 3.71 vs, 3.47 s
36	ethanolamine	P	2:1	46.0^{14}	11	4.58 s, 4.47 ms, 3.89 ms, 3.50 s
37	triethanolamine	P	1:1	29.5^{10}	22	4.36 vs, 4.20 vs, 3.74 s, 3.54 s
38	4-aminopyridine	P	2:1	25.6^6	19	4.61 vs, 3.89 vs, 3.59 m, 3.46 vs
39	4-aminopyridine	P	4:1	40.8^8	27	4.25 vs, 4.08 vs, 3.87 vs, 3.73 m, 3.43 m
40	2-amino-3-methylpyridine	P	1:1	21.9^3	18	5.07 ms, 4.21 ms, 4.06 m, 3.85 s, 3.59 s
41	2-amino-3-methylpyridine	P	2:1	23.7^8	15	5.11 ms, 4.32 vs, 4.18 s, 4.04 vs, 3.84 s
42	2-amino-4-methylpyridine	P	1:1	20.6^4	15	5.54 s, 4.75 ms, 4.63 s, 4.07 s, 3.57 s
43	2-amino-4-methylpyridine	O	1:1	22.6^4	15	5.55 s, 4.47 ms, 4.22 s, 3.98 s, 3.55 ms
44	2-amino-5-methylpyridine	P	1:1	21.6^7	23	5.61 s, 5.39 s, 4.45 s, 4.14 s, 3.81 s, 3.62 s
45	2-amino-4,6-dimethylpyridine	P	1:1	20.9^5	26	4.92 w, 4.43 vs, 3.81 vs, 3.59 s, 3.41 ms
46	2-amino-4,6-dimethylpyridine[d]	P	1:1	22.5^4	27	4.83 ms, 4.61 m, 4.47 s, 3.78 vs, 3.49 s, 3.40 m
47	2,6-dimethylpiperidine	P	1:1	29.1^6	21	4.70 m, 4.42 s, 4.09 vs, 3.81 ms, 3.67 m
48	2-phenylethylamine	P	1:1	28.0^8	13	4.71 m, 4.24 vs, 4.10 s, 3.82 vs, 3.59 m
49	palmitamide A			31.4^{12}	16	4.91 vs, 4.74 s, 4.55 vs, 4.05 m, 2.78 vs
50	palmitamide B			32.8^{13}	9	4.46 s, 4.08 w, 3.73 s, 3.25 w, 2.56 w
51	palmitamide A + B			31.4^{11} 32.6^6		4.90 s, 4.79 s, 4.56 s, 4.07 m, 3.79 vs, 3.74 vs
52	stearamide B			36.6^{15}	6	4.47 vs, 3.74 vs, 3.29 w, 2.57 w, 2.34 w
53	petroselaidamide			49.3^{19}	12	4.93 s, 4.10 s, 3.79 m, 3.52 s, 3.08 ms
54	*N*-butylcapramide			34.9^{13}	4	4.13 s, 3.70 s, 3.07 ms
55	petroselinic acid			41.4^{15}	5	4.48 ms, 4.04 s, 3.90 s, 3.67 ms, 3.14 m
56	petroselaidic acid			45.6^9	10	4.61 m, 4.44 s, 4.11 m, 3.86 vs, 3.71 s
57	2-tridecanone			36.81^{10}	25	4.08 vs, 3.85 ms, 3.01 m, 2.42 ms, 2.24 m, 2.05 m
58	2-pentadecanone			42.60^7	6	4.11 vs, 3.84 s, 3.01 w, 2.43 w, 2.26 w, 2.06 w
59	2-heptadecanone			47.39^{10}	13	4.09 vs, 3.90 s, 2.99 w, 2.44 w, 2.25 w, 2.05 w
60	2-nonadecanone			52.22^{14}	9	4.11 vs, 3.80 s, 2.99 w, 2.44 w, 2.25 w, 2.06 w
61	2-amino-4-methylpyridine			27.3^7	18	4.61 s, 4.41 vs, 3.74 vs, 3.54 ms, 3.16 vs
62	2-amino-5-methylpyridine			9.3^3	10	5.05 vs, 4.06 ms, 3.68 vs, 3.12 s
63	2-amino-4,6-dimethylpyridine			12.4^3	16	4.14 m, 3.98 m, 3.74 s, 3.45 m

[a] C, Capric; L, lauric; M, myristic; P, palmitic; H, heptadecanoic; S, stearic; O, oleic, E, elaidic; P′, petroselinic; P″, petroselaidic. [b] Superscript shows number of orders observed. [c] vs, very strong; s, strong; ms, medium strong; m, medium; w, weak. [d] Metastable form.

The polymorphic forms of palmitamide and stearamide (items 49, 50, and 52) were identified by their long spacings as Sakurai's (*9, 10*) palmitamide A (31.52 Å), palmitamide B (32.47 Å), and stearamide B (36.16 Å). The short spacings indicate that these values correspond to Kurokawa's (*11*) palmitamide types I and II′ and stearamide type II, for which he reported the long spacings as 30.62, 32.46, and 36.2 Å, respectively.

The A form of palmitamide (item 49) was obtained by crystallization of the B form from dilute methanol solution. In one instance this process resulted, for some unknown reason, in crystals (item 51) that gave two long spacings, one for the A form (10 orders) and the other for the B form (4 orders), but the short-spacing pattern differed from the A pattern only by an additional strong spacing at 3.74 Å. Therefore, a strong short spacing at 3.74 Å can be taken as characteristic of the B form.

A review of the long-spacing data based on the X-ray powder-diffraction data of Kurokawa (*11*), five values, and those calculated ($c \sin \beta$) from the single-crystal data of Turner and Lingafelter (*12*), six values, and of Sakurai (*9*), three values, indicates that the A modification has been the only form observed for even-carbon amides up to myristamide. When plotted against n, these data were satisfied by eq 3 with an average deviation

$$L = 1.755n + 3.263 \qquad (3)$$

of 0.16 Å. The calculated angle of tilt is therefore $\sin^{-1} 1.755/2.54 = 43° 42'$.

Because only limited X-ray data were published on four long-chain methyl ketones reported in a previous publication (*13*), these four compounds (2-tridecanone, 2-pentadecanone, 2-heptadecanone, and 2-nonadecanone) are listed in Table I with complete X-ray data. When the long spacings of these compounds are plotted vs. number of carbons, the three longer compounds fall squarely on a straight line (the C_{13} compound is slightly off the line) represented by eq 4. The calculated angle

$$L = 2.40n + 6.60 \qquad (4)$$

of tilt of these long-chain methyl ketones is therefore $\sin^{-1} 2.40/2.54 = 70° 53'$.

Item 21 in Table I, prepared by melting an equimolar mixture of morpholine stearate and cyclohexylamine palmitate and allowing it to crystallize from the melt, gave a long spacing characteristic of cyclohexylamine stearate (item 16) and none for the other combination possible from the four ions present. Mod et al. (*14*) have studied the ternary reciprocal salt pair system involving the cyclohexylamine and morpholine salts of stearic and palmitic acids and prepared a freezing-point diagram for this system. A study of this diagram indicates that the first crystals to form from the melt of a 50:50 mixture would be cyclohexylamine stearate. The first crystals would tend to grow and be larger and better formed than those coming out later when components of eutectic mixtures were crystallizing. It is therefore not surprising that the long spacing for only cyclohexylamine stearate was observed in the X-ray data for the mixture.

Acknowledgment

We thank Gene Sumrell for assistance with the manuscript.

Literature Cited

(1) Mod, R. R.; Magne, F. C.; Skau, E. L. *J. Am. Oil Chem. Soc.* **1959**, *36*, 616.
(2) Mod, R. R.; Magne, F. C.; Skau, E. L. *J. Chem. Eng. Data* **1960**, *5*, 478.
(3) Mod, R. R.; Magne, F. C.; Skau, E. L. *J. Chem. Eng. Data* **1962**, *7*, 31.
(4) Mod, R. R.; Harris, J. A.; Skau, E. L. *J. Chem. Eng. Data* **1968**, *13*, 115.
(5) Mod, R. R.; Magne, F. C.; Skau, E. L. *J. Phys. Chem.* **1956**, *60*, 1651.
(6) Mod, R. R.; Magne, F. C.; Skau, E. L. *J. Am. Oil Chem. Soc.* **1959**, *36*, 102.
(7) O'Connor, R. T.; Mod, R. R.; Murray, M. D.; Skau, E. L. *J. Am. Chem. Soc.* **1955**, *77*, 892.
(8) Skau, E. L. *J. Am. Oil Chem. Soc.* **1973**, *50*, 245.
(9) Sakurai, T. *J. Phys. Soc. Jpn.* **1955**, *10*, 1040.
(10) Sakurai, T.; Yabe, M. *J. Phys. Soc. Jpn.* **1958**, *13*, 5.
(11) Kurokawa, S. *Bull. Chem. Soc. Jpn.* **1955**, *28*, 660.
(12) Turner, J. D.; Lingafelter, E. C. *Acta Crystallogr.* **1955**, *8*, 549.
(13) Bailey, A. V.; Mitcham, D.; Skau, E. L. *J. Chem. Eng. Data* **1970**, *15*, 542.
(14) Mod, R. R.; Magne, F. C.; Skau, E. L. *J. Am. Oil Chem. Soc.* **1958**, *35*, 688.

Received for review March 21, 1980. Accepted June 17, 1980.

Densities of NaCl, $MgCl_2$, Na_2SO_4, and $MgSO_4$ Aqueous Solutions at 1 atm from 0 to 50 °C and from 0.001 to 1.5 *m*

Chen-Tung A. Chen and Joanne Hwa Chen
School of Oceanography, Oregon State University, Corvallis, Oregon 97331

Frank J. Millero*
Rosenstiel School of Marine and Atmospheric Science, University of Miami, Miami, Florida 33149

The relative densities ($d - d_0$) of NaCl, $MgCl_2$, Na_2SO_4, and $MgSO_4$ aqueous solutions have been determined at 1 atm with a vibrating flow densimeter from 0.001 to 1.5 *m* and from 0 to 35 °C. The data have been combined with our earlier measurements at temperatures up to 55 °C and fitted to equations of the following form (precisions better than 15×10^{-6} g cm^{-3}): $d - d_0 = Am + Bm^{3/2} + Cm^2 + Dm^{5/2}$, where d and d_0 are the densities of solution and pure water, respectively, m is the molality, and A, B, C, and D are temperature-dependent parameters. The equations agree well with the results of other workers.

Introduction

The basic pressure–volume–temperature–concentration properties of NaCl, $MgCl_2$, Na_2SO_4, and $MgSO_4$ aqueous solutions are of prime importance for various thermodynamic calculations in solution chemistry, geochemistry, and oceanography. They are also important in the engineering calculations such as those concerning the process of converting salty water to potable water and the process of assessing salty water intrusion in the freshwater aquifers. A survey of the literature (*14*) reveals the scarcity of reliable experimental 1-atm density data for these solutions at temperatures other than 25 °C. The present paper provides precise 1-atm density data from 0 to 55 °C and from 0 to 1.5 *m* for the major sea salts. The results have been fitted to equations that are simple polynomial functions of t(°C) and $m^{1/2}$ (molality).

Experimental Section

Densities of NaCl, $MgCl_2$, Na_2SO_4, and $MgSO_4$ aqueous solutions have been measured at various temperatures and concentrations on a high-precision digital readout flow densimeter

0021-9568/80/1725-0307$01.00/0