The Solubilities of Sodium and Calcium Sulfates in Aqueous Glycerine

H. R. TILL JR., J. B. SEGUR, and C. S. MINER JR., The Miner Laboratories,[1] Chicago, Illinois

SODIUM AND CALCIUM SULFATES are commonly present in certain glycerine sweet waters and may precipitate during concentration of the sweet waters to crude glycerine. A knowledge of their solubilities in aqueous glycerine would therefore be helpful in the design of processing equipment. Solubilities have been determined at 20°, 40°, 60°, 80°, and 100°C. with glycerine concentrations of approximately 40%, 70%, and 95% by weight in water.

Materials

Sodium sulfate, anhydrous. Reagent grade.
Calcium sulfate, anhydrous. Reagent grade.
Glycerine. U.S.P. grade.
Water. Distilled.

Apparatus and Procedure

The saturated solutions were prepared in 100-ml. serum bottles (No. 14,200 Kimble Brand, Owens-Illinois Glass Company) fitted with rubber sleeve stoppers (No. 17 rubber sleeve stoppers, No. 73 red; West Company Inc., Phoenixville, Pa.). For saturation at 20°, 40°, and 60°C., the bottles were held on a reel with rubber bands, and the reel was immersed in a constant temperature water bath and rotated at about 12 r.p.m. with a small gear-head motor and chain drive. The bath temperatures were constant within ± 0.05°C. Saturation experiments at 80° and 100°C. were carried out in constant temperature air baths. The air-bath temperatures were constant within ± 1.0°C.

A solution was considered saturated when its refractive index remained constant for at least three days. The amount of dissolved salt was measured by sulfated ash determinations.

TABLE I

Solubility Data and Physical Properties of Aqueous Glycerine Saturated with Sodium Sulfate

Temp. °C.	% wt. glyc. in solvent	n_D^{25}	Sp. gr. 25/25	Na_2SO_4 % by wt.	Na_2SO_4 g./100 ml. at 25°C.
20	0	....	....	31.13(2)	....
20	40.0	1.4012	1.2320	14.44	17.79
20	69.9	1.4316	1.2202	4.55	5.55
20	94.7	1.4660	1.2610	1.54	1.94
40	0	....	....	32.79(3)	....
40	40.0	1.3999	1.2232	13.46	16.46
40	69.8	1.4312	1.2188	4.40	5.36
40	94.5	1.4660	1.2600	1.41	1.78
60	0	....	....	31.18(3)	....
60	40.0	1.3993	1.2181	12.93	15.75
60	69.7	1.4310	1.2172	4.26	5.19
60	94.8	1.4658	1.2584	1.26	1.59
80	0	....	....	30.41(3)	....
80	39.3	1.3980	1.2164	12.79	15.56
80	69.9	1.4312	1.2169	4.16	5.06
80	94.6	1.4657	1.2572	1.15	1.45
100	0	....	....	29.82(3)	....
100	40.0	1.3984	1.2134	12.37	15.01
100	69.8	1.4310	1.2164	4.07	4.95
100	94.7	1.4655	1.2567	1.02	1.28

NOTE: Below 23.7°C. the solid phase in the system sodium sulfate-water is $Na_2SO_4 \cdot 7H_2O$, and solubility increases with temperature. Above this temperature the solid phase is Na_2SO_4. At this temperature the Na_2SO_4 concentration in saturated solution is 34.4% (2).

TABLE II

Solubility Data and Physical Properties of Aqueous Glycerine Saturated with Calcium Sulfate

Temp. °C.	% wt. glyc. in solvent	n_D^{25}	Sp. gr. 25/25	$CaSO_4$ % by wt.	$CaSO_4$ g./100 ml. at 25°C.
20	0	....	....	0.30(4)	......
20	40.1	1.3850	1.1039	0.22	0.24
20	69.7	1.4280	1.1824	0.10	0.12
20	94.6	1.4651	1.2486	0.08	0.10
40	0	....	....	0.22(4)	......
40	39.8	1.3845	1.1014	0.16	0.18
40	69.6	1.4275	1.1819	0.08	0.09
40	94.3	1.4646	1.2473	0.05	0.06
60	0	....	....	0.15(4)	....
60	39.8	1.3850	1.1020	0.11	0.12
60	69.6	1.4281	1.1820	0.04	0.05
60	94.3	1.4649	1.2472	0.03	0.04
80	0	....	....	0.10(4)	....
80	40.9	1.3854	1.1038	0.08	0.09
80	69.6	1.4280	1.1816	0.03	0.04
80	94.4	1.4641	1.2474	0.02	0.02
100	0	....	....	0.07(4)	....
100	40.9	1.3856	1.1041	0.04	0.04
100	69.6	1.4271	1.1820	0.02	0.02
100	94.4	1.4641	1.2471	0.01	0.01

Discussion

Both sodium sulfate and calcium sulfate have negative coefficients of solubility in aqueous glycerine, *i.e.*, for any given glycerine concentration they become less soluble as the temperature increases. At constant temperature their individual solubilities also decrease, in a non-linear manner, as the glycerine concentration of the solvents is increased.

Although both sodium sulfate and calcium sulfate have negative coefficients of solubility in aqueous glycerine, the solubility becomes less temperature-dependent as the glycerine concentration of the solvent is increased.

Experimental

Solutions containing approximately 40, 70, and 95% glycerine by weight were prepared by adding the calculated amounts of water to given quantities of U.S.P. glycerine. Their exact concentrations were then determined from their specific gravity, using the tables of Bosart and Snoddy (1).

In preparing the saturated salt solutions, 70 g. of the desired aqueous glycerine solution and a moderate excess of the salt were placed in a serum bottle containing three short pieces of glass rod which aided in stirring the mixture. Each solution was prepared in duplicate. After the mixtures had been agitated at constant temperature for five days, they were allowed to settle, and the refractive index of each solution was measured. Agitation of the mixtures was resumed, and after three days the refractive index was again measured. When the refractive index remained constant for at least three days, a solution was considered saturated. The refractive index at 25°C. and specific gravity at 25°C. are reported for each saturated solution.

Concentrations of dissolved salt were calculated from sulfated ash determinations. Duplicate analyses were made on each of the duplicate solutions of sodium sulfate, giving a total of four determinations

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for each solution composition. The average deviation in the groups of four was 0.01%. Single analyses were made on each of the duplicate solutions of calcium sulfate. The average difference between these determinations was 0.009%. The solubility data for sodium and calcium sulfates are given in Tables I and II.

Specific gravity at 25°C. and refractive index at 25°C. were also determined for each saturated solution. It was possible to make these determinations at 25°C. on solutions saturated at higher temperatures because of the negative coefficient of solubility of both salts. None of the solutions saturated at 20°C. showed signs of precipitation during the time required to make these physical measurements at 25°C.

Acknowledgment

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2. Seidell, A., "Solubilities of Inorganic and Metal Organic Compounds," Supplement to the Third Edition, p. 482, New York, O. van Nostrand Co. Inc. (1952).
3. Seidell, A., *ibid.*, Third Edition, vol. I, p. 1301 (1940).
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Letter to Editor

Johnson, Hunt, Neustadt, and Zeleny report that the Stein mill is an efficient dry grinding mill for soybeans, flax, and safflower seeds but not for sunflower seeds. In our laboratory we have been successfully using this instrument for several years in the grinding of sunflower seed samples. Our technique differs in several particulars from that of the above authors. We grind a 50-g. sample for one minute, then transfer the contents to a 5-in. hemispherical, 16-mesh household type of sieve and work the meats through the mesh. This completely breaks up the cake. Hulls remain on top of the wire. If there are only a few whole seeds, they are picked out and discarded. If a substantial amount remains unground, the coarse fraction is reground for 30 seconds and rescreened. Then the two fractions are blended together. By this technique we are able to use a 1-g. sample for the extraction, otherwise following AF 3-54 method for oil content of flax seed.

MAX C. MARKLEY
The Markley Laboratories
Minneapolis, Minn.

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ABSTRACTS . . . . R. A. Reiners, Editor

• Oils and Fats

S. S. Chang, Abstractor
Sin'itiro Kawamura, Abstractor
Dorothy M. Rathmann, Abstractor

The detection of chemical reactions in complex mixtures of food antioxidants by infrared spectrometry. L. A. Hall (The Griffith Labs., Inc., Chicago, Ill.) and G. L. Clark. *Food Tech.* **10**, 384–6 (1956). Infrared spectrometry has been used as a modern instrumental technique of characterizing complex mixtures of as many as seven constituents in effective food antioxidants with comparison of data for three typical blends with the absorption band frequencies for the individual constituents. It is demonstrated that the infrared spectrum is highly characteristic for each blend and that there is clear evidence of reactions among the constituents such as the formation of lecithin citrate.

Which antioxidants for your fat-containing foods. B. N. Stuckey (Res. Div., Eastman Chemical Products, Inc., Kingsport, Tenn.). *Food Eng.* **28**(7), 76, 78 and 198. There are many fat-soluble antioxidants with which the shelf life of animal fats, vegetable oils, dry cereals, essential oils, vitamins, nuts and confections can be extended. Most complaints arising from the use of antioxidants in fats and oils are due to inadequate mixing of the antioxidants into the fat. It is well known that it is not practical to attempt to stabilize a fat that has already started to show substantial peroxide formation.

The sterol and carbohydrate constituents of the walnut (Juglans regis). L. Jurd (Western Utilization Res. Branch, Agr. Res. Service, U. S. Dept. of Agr., Pasadena, Calif.). *J. Org. Chem.* 21, 759–60 (1956). The sterol and carbohydrate constituents of the walnut have been isolated and identified as β-sitosterol, β-sitosteryl-D-glucoside, and sucrose.

Contributions to the study of marine products. XL. Waxes and triglycerides of sea anemones. W. Bergmann, S. S. Creighton and W. M. Stokes (Sterling Chem. Lab. and the Bingham Oceanographic Lab., Yale Univ.). *J. Org. Chem.* 21, 721–28 (1956). Certain lipid fractions from three sea anemones have been investigated. The warm water anemone *Condylactis gigantea* has been shown to contain substantial quantities of solid lipides. These were found to consist of a mixture of myristyl myristate and myristyl palmitate and symmetrical palmityldimyristin. Two cold-water anemones *Bolocera iuediae* and *Actinostola collosa* have been shown to contain substantial quantities of liquid lipides. These were found to consist mainly of esters of unsaturated alcohols and acids of the order C_{20} and C_{22} and triglycerides of acids of the same order. Two new alcohols, 11-eicosenol and 11-docosenol, have been isolated. Cholesterol has been shown to be the principal sterol of the cold-water anemones.

An improved procedure for the isolation of neoabietic acid from pine oleoresin and rosin. Virginia M. Loeblich and R. V. Lawrence (Naval Stores Res. Sec., U. S. Dept. of Agr., Olustee, Florida). *J. Org. Chem.* 21, 610–11 (1956). A method is described for isolating neoabietic acid from pine oleoresin or rosin in 8–12% yield by recrystallization of the 2-amino-2-methyl-1,3-propanediol salt of the resin acids from methyl ethyl ketone.

A note on component fatty acids of the oil from the seeds of Momordica charantia, Linn. J. P. Verma and J. S. Aggarwal (Natl. Chem. Lab. of India, Poona). *J. Indian Chem. Soc.* 33, 357–8 (1956). The fatty acid composition of the oils from the seeds of *Momordica charantia*, Linn. as obtained by the present analysis is α-elaeostearic acid, 46.7%; linoleic acid, 7.7%; oleic acid, 15.8%; and stearic acid, 29.8%.

Fat absorption studies. IV. Polyunsaturated fatty acids in the feces of infants. L. Söderhjelm. *Acta Soc. Med. Upsaliensis* **57**, 438–47 (1952). In the feces of breast-fed infants 1.8–7.1% of the fatty acids contained more than one double bond, compared with 0.4–2.0% in the feces of infants fed with cow milk; the value for meconium was about 3%.

V. Polyunsaturated fatty acids in fetal organs. *Ibid.* 448–54. Polyunsaturated fatty acids were estimated in brain, heart, muscle, liver, lung, kidney, and subcutaneous fatty tissue of fetuses obtained from surgical abortions and premature infants. In all the organs examined appreciable amounts of tetra- and hexaenoic acids were always present, but dienoic acids were not always found and occurred rarely in brain tissue. (*C. A.* **50**, 7973)

The chemistry of branch-chain fatty acids. II. K. E. Schulte, W. Weisskopf, and J. Kirschner (Deut. Forsch. Lebensmitt,