Part II

PHYSICAL PROPERTIES

EVALUATION OF COMPOUNDS AND MATERIALS

Nonaqueous Solvents for Sucrose

OLEG K. KONONENKO AND KARL M. HERSTEIN
Herstein Laboratories, Inc., New York, N. Y.

Sugar has the highest potentiality as a raw material for the chemical industry both because of its enormous availability, and because the field of industrial applications is almost unexplored.

Reaction media for sugar are required which will not react with themselves or interfere with the desired reaction. Almost no suitable solvents for sugar were known. The literature of sugar solubilities in nonaqueous solvents has been surveyed and summarized. Determinations of solubility of sugar in 14 solvents at various temperatures have been made. A relationship involving the melting point of sugar and the dielectric strength of the solvents has been determined.

The rapid emergence of sucrochemistry as a new field of research and industrial application requires information on possible reaction media. Water has been the most studied sugar solvent. For many applications water is unsuitable since it may itself react, it may prevent or interfere with the desired reaction, or it may not be a good solvent for the other reactants. Some previous studies of other solvents are recorded, especially for their physicochemical interest. Many of the results found in the literature are in very poor agreement. Often, determinations were made at only one temperature so that comparisons with other results are impossible. Equilibration times have varied with different workers from 5 minutes to 240 hours. In some cases no attempt was made to obtain saturated solutions. Finally, polarimetric measurements, frequently used for determination, are subject to error since the specific rotation of sugar varies with the solvent.

The solubility of sucrose in ethanol and in aqueous ethanol was determined by Scheibler (42), Lindet (30), Schrefeld (45), Pellet (36), Urban (53), Hudson and Yanowski (21), and Reber (40). Grossman and Bloch (11) prepared a solution of sucrose in formic acid. Karcz (24) and Strohmer and Stiff (52) determined the solubility of sugar in glycerol. Other studies in glycerol were made by Browne and Randle (3), Fey, Weil, and Segur (8), and Segur and Miner (48). Methanol was tried by Scheibler (43), Lindet (30), Gunning (13), and Lobry de Bruyn (32). Sherry (50), and Fitzgerald (9) found that sucrose dissolves readily in methylamine. Wilcox (59) made a similar observation for isopropylamine. Vogel (56) reported that sugar is insoluble in piperidine. Schukarew (46) used a dilute solution of sucrose in aqueous propionitrile for critical temperature tests. Fey, Weil, and Segur (8) reported 1.9% by weight for the solubility of sugar in 99% aqueous propylene glycol. Pyridine has been much favored as a solvent. Wilcox (58), Holty (18), Kahlenberg (23), Cohen and Commelin (5), Grossman and Bloch (11), Koenig (27), and Dehn (6) have published determinations of the solubility of sucrose in pyridine.

Sherry (50) found sucrose to be insoluble in sulfur dioxide. Schiff (44) dissolved sugar in both hot and cold acetic acid of 97 to 100% concentration. A French patent (51) claims the separation of sucrose from molasses by its insolubility in acetic acid particularly after adding ethyl acetate or benzene. The solubility of sugar in acetone and in aqueous acetone mixtures is reported by Krug and MacElroy (28), Herz and Knoch (16), and Verhaar (55). Solubility determinations in aqueous and in anhydrous ammonia have been published by Wilcox (59), Sherry (50), and Fitzgerald (9). Wilcox (59) found high solubility for sugar in allylamine and in amylamine. Plato (38) reported that sucrose is insoluble in benzene. Helferich and Masamune (15) found only 0.08% sucrose dissolved in boiling dioxane. Lang (33) prepared a solution containing 40.6% by weight of sucrose in monoethanolamine. The solution did not reach saturation.

Altogether 19 solvents are listed in this literature survey. However, only pyridine has any interest for sucrochemical applications. The remainder are either too poor solvents or enter too readily into competing reactions. Hence, the present data are on a very different group of solvents. Some consideration was also given to a procedure for solubility determination which would yield results of practical accuracy with relatively little consumption of time and effort.

SELECTION OF METHOD

The solubility of sucrose in water has usually been determined by maintaining saturated solution at a given temperature in equilibrium with crystals for a period of time. After separating the saturated liquid from the crystals the concentration of sugar in the solution is determined by polarimetric measurement. Some workers have applied a similar technique to organic solvents for sucrose. In the case of low-boiling solvents, a sample of the saturated solution was taken and the solvent removed by evaporation. Water was added to dissolve the sugar and after dilution to a measured volume the concentration was determined in a polarimeter.

Standard methods were not used because trials were made with new solvents and their effect on the optical properties of sucrose was not known. Hence, the technique developed was to determine, as accurately as possible, the weight of solvent required to dissolve weighed sample of sucrose. The average deviation of the results depended greatly on the solubility observed, and ranged between ±0.24% of the average solubility found in dimethylsulfoxide at 30° C. to 6.5% of the observed solubility in methylpiperazine at 107° to 110° C.

Sugar forms supersaturated solutions most readily. This prevented the authors from approaching saturation both from lower and higher concentrations as would be required for the most precise work.

According to the usually accepted theory of Kukharenko, supersaturated solutions of sucrose in water do not crystallize unless they are seeded. In many articles published by Kukharenko and coworkers (29) the speed of crystallization was expressed as a function of weight and surface of the crystallization centers, and was proved experimentally for different degrees of supersaturation (1). For other solvents no mathematical relationship was found but similar phenomena are well known. For example, Cohen and Commelin (5) reviewed findings that a saturated solution of sucrose in pyridine prepared at reflux temperature did not crystallize on cooling to -16° C. In the authors observation, pyrazine was the only nonaqueous solvent from which sugar crystallized readily. Saturated solutions prepared at 110° to 120° C. solidified in 0.5 hour after cooling to room temperature. The melting point of pyrazine is 52° to 53° C. On rewarming in order to melt the pyrazine, the sucrose remained on the bottom of the flask in well-formed crystals. All other solutions remained in sirup form for many days, even after seeding.

APPARATUS

A 4-liter beaker with white mineral oil was used as the thermostat bath. This bath was placed on an electric hotplate which was used for higher temperature work. Temperature adjustment for both medium and higher temperatures was provided by an open coil of Nichrome wire (approximately 200 watts) which rested on the bottom of the beaker. The coil was controlled by a Fenwal Thermoswitch. The test samples were placed in bulb flasks, approximately 5-ml. capacity, blown on 8-mm. borosilicate glass tubing about 20 cm. long. Eight of these test flasks could be clipped to two sides of a wood block which rocked about 30 cycles per minute. In this way the bath was stirred and the samples were agitated constantly. Temperature regulation was maintained at better than ± 0.5° for the higher temperature and ± 0.1° at 30° C.

In practice a test flask was tared, the sucrose weighed in it, and the tube was placed in the bath. Periodic additions of solvents were made from capillary pipets which were inserted into the bulb of the flark. When complete solution was obtained, the flasks were reweighed to determine the quantity of solvent added. Complete solution was taken as the point at which no crystals were noted when shaking was stopped. Two special precautions were required. The weight of sucrose sample was estimated on the basis of preliminary solubility tests, and the speed of stirring was adjusted to prevent both caking at the bottom of the tiny flask and carrying of sugar up onto the long neck wall. Each determination was repeated sufficient times to give concordant results.

PREPARATION OF REAGENTS

Sucrose was pulverized to 120 mesh and dried at 100° - 110° C.

Pyrazine was prepared by dehydrogenation of piperazine according to the procedure of Kitchen and Hanson (25) for 2-methylpiperazine. Because piperazine is much less soluble in benzene than methylpiperazine, a larger amount of solvent (2 ml. of hot benzene for 1 gram of technical 86 to 91% piperazine) was used. In order to prevent crystallization on cooling, the dropping funnel was provided with a heater and a reflux condenser. The yield of redistilled material (boiling point, 113° to 114.5° C., at 750 mm. Hg) was 22.5%. The high-boiling fractions (unreacted piperazine) were redissolved in benzene and dehydrogenated again, but the amount of undistillable residue was high. The melting point of the pyrazine was 52.5° C.

Methylpyrazine was prepared in the same way as pyrazine (25). It boiled between 63° and 64° C. (78 to 79 mm. Hg).

Mixed pyrazines (containing pyrazine, methylpyrazine, and dimethylpyrazine) were made by dehydrogenation of the piperazine fraction from reductive aminolysis of sucrose. The boiling range was 107° to 140° C., the main portion coming over at 134° to 136° C. The product was dried by azeotropic distillation with benzene and redistilled.

Morpholine, commercial grade, was distilled through a 650-mm. helix-packed, vacuum jacketed column and the center cut of about 20% of the original volume was used.

N-Methylmorpholine, commercial grade, was obtained from Carbide and Carbon Chemicals Co.

Dimethylsulfoxide, commercial grade, 99.9% pure was obtained from the Stepan Chemical Co.

N-Methylpyrrolidone, commercial grade, was purchased from General Aniline & Film Corp.

Dimethylformamide, a Du Pont product, was redistilled and a center cut was collected.

Pyridine was dried by allowing it to stand over sodium hydroxide and redistilled, discarding the forerun and the high-boiling fraction.

TABLE I. SOLUBILITY OF SUCROSE

Solvent	Grams Sucrose per 100 Grams Solution					
	120° C.	110° C.	100° C.	85° C.	60° C.	30° C.
Pyrazine	3.95	3.04[a]	2.23[b]	1.95	. . .	. . .
Methylpyrazine	2.34	1.84	1.25	0.87	. . .	. . .
Mixed pyrazines	. . .	2.73	2.46	2.02	. . .	. . .
Morpholine	50.8	. . .	45.1	39.8	34.7	30.7
N-Methylmorpholine	0.72	0.56	0.38	0.37	. . .	. . .
Dimethylsulfoxide	. . .	61.6	58.7	51.1	49.1	41.6
N-Methyl-2-pyrrolidone	40.4	. . .	33.5	28.0	22.6	17.3
Dimethylformamide	42.8	. . .	29.6	23.6	16.9	14.1
Pyridine	. . .	7.46	5.99	5.00	3.75	3.12
Dioxane	. . .	. . .	0.11	0.11	0.07	. . .
2-Methylpiperazine	30.1[c]	29.6[c]	29.5[c]	26.1	. . .	. . .
Trimethylcyanurate	0.32[d]	. . .	. . .	. . .	. . .	. . .
Tetrahydrofuran	. . .	. . .	. . .	. . .	0.01	. . .
Dimethylsulfolane	0.52[c]	0.50[c]	0.37	0.30	. . .	. . .

[a] At 107° C.
[b] At 97° C.
[c] Solution discolored.
[d] At 140° C.

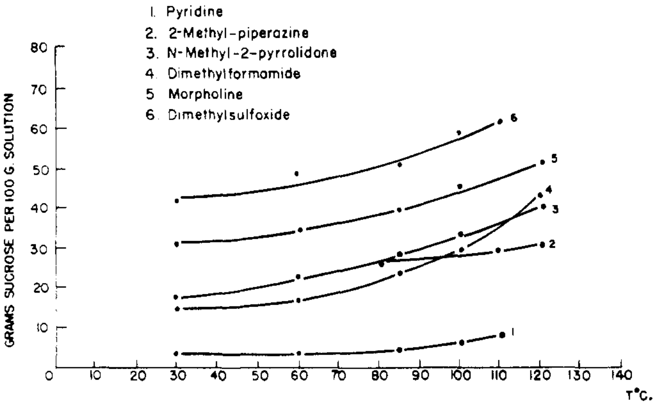

Figure 1. Solubility of sucrose

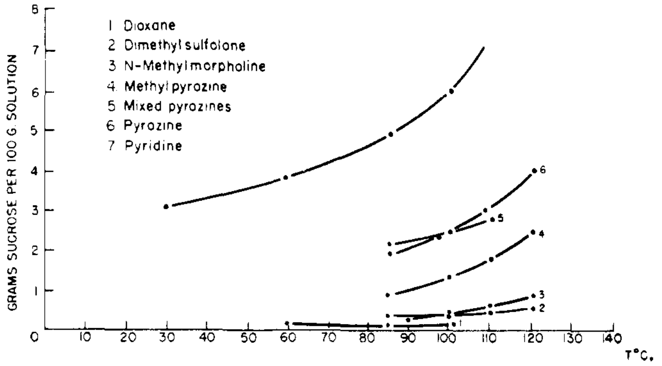

Figure 2. Solubility of sucrose

Dioxane, a commercial product, was refluxed for 4 hours over metallic sodium, filtered from the sodium hydroxide, and aldehyde gum formed. It was refluxed again with fresh sodium for an additional 8 hours and redistilled over metallic sodium, collecting a small median cut.

2-Methylpiperazine was prepared by a modified method of Kitchen and Pollard (26), so that the water formed during cycling was distilled off as it was formed, making the reaction irreversible and giving a higher yield than mere refluxing. Two hundred fifty grams of N-2-hydroxypropylethylene diamine, 250 grams of diethyl carbitol, and 40 grams of sponge nickel catalyst (Davison Chemical Corp.) were heated and gently refluxed for 1 hour in a 2-litter flask with a 40 to 50 cm. Vigreux column. Approximately 55 to 60 ml. of distillate was collected between 95° and 105° C. After a small intermediate cut, 2-methylpiperazine was collected between 150° to 165° C., then the temperature rose to the boiling point of diethylcarbitol (188° C.). After refractionation the yield was 147 to 166 grams (69.4 to 78.4%).

For solubility tests, 2-methylpiperazine was dried by azeotropic distillation with benzene and redistilled. It was kept molten in a small test tube in the same thermostat in which the solubility was determined.

Trimethylcyanurate was prepared from cyanuric chloride, methanol, and sodium hydroxide according to the process given by Dudley and others (7) and recrystallized from water. Because of high melting point (133° to 134° C., Dudley 134° to 135° C.) the solubility determination was made at 140° C. The solvent was added to sucrose molten, in the same manner as methylpiperazine.

Tetrahydrofuran was dried in the same manner as dioxane.

Dimethylsulfolane (2, 4-dimethylcyclotetramethylenesulfone), commercial product from Shell Chemical Corp., was used as received.

DISCUSSION

The results of the author's solubility determinations are summarized in Table I, where the solubility S is expressed in grams of sucrose per 100 grams of saturated solution.

Figures 1 and 2 show the same results graphically. Figure 1 contains the compounds which were found to be very good solvents for sucrose. Figure 2 shows the poor solvents. The solubility in pyridine, which is intermediate between these two groups is plotted on both.

All the curves are quasi parabolic in shape. The first attempt to find an equation representing the solubility of sucrose as the function of temperature was made by Herzfeld (17) using his figures of solubility of sucrose in water. Using the least squares method he found that

$$S = 64.1835 + 0.13477T + 0.0005307T^2$$

where "T" is the temperature in ° C.

Many attempts have been made to simplify this equation or to convert it into a linear function. An excellent review of those is given by Verhaar (54). More recent data on solubility in water are also interesting (1,20).

The formulas of Scott-Macfie (47), Horsin-Deon (19), and the expression of solubility as a logarithmic function (22) did not prove to be sufficiently accurate. Therefore, the formula given by Orth (34) was accepted for the author's work. Orth has shown, using Herzfeld's figures, that if the solubility is expressed in grams of water per 100 grams of sucrose the function becomes linear. Although in a second article (35) his parameters were recalculated on the basis of more recent determinations by Grut (12), he obtained different figures. Verhaar (54) has proved Orth's formula to be remarkably accurate.

The scale of Orth's equation was changed by calculating the weight of solvent required to dissolve 1 gram of sucrose "e" instead of 100 grams ("E," according to Orth) so as to avoid excessively large figures in case of poor solvents. Then the modified equation is as follows: If S equals grams of sucrose and eS equals grams of solvent in 100 grams of saturated solution, then

$$S + eS = 100$$

from which

$$e = \frac{100}{S} - 1$$

The e values calculated from experimental results according to the foregoing given formula are found for different solvents (Table II).

Orth's equation as modified then becomes

$$e = a(b - T)$$

where "a" and "b" are parameters calculated by least squares from the authors' experimental results. The calculated values, except for solvents for which information is insufficient, are given in Table III.

For dioxane, "a" value was calculated as an average for three determinations direct from the Orth's formula, assuming "b" to be 160.

The figures calculated by Orth for water are also included. The "e" values obtained from the formulas are given in Table II together with the difference between the observed and calculated "e" values. These deviations are proportionally larger for technical grade solvents and in cases of higher solubility.

In Figures 3 and 4 the straight lines and experimental "e" values are shown graphically with Orth's line for water for comparison.

TABLE II. SOLUBILITY OF SUCROSE

	"S"	"e"		"e" Difference	
Temp., ° C.	Solubility, %/Wt.	Calc.	Exptl.	Calc. Minus Exptl.	%
		In pyrazine			
120	3.95	24.2	24.3	-0.1	0.4
107	3.04	33.9	31.9	+2.0	5.9
97	2.23	41.5	43.8	-2.3	5.5
85	1.95	50.6	50.3	+0.3	0.6
		In methylpyrazine			
120	2.34	41.9	41.7	+0.2	0.5
110	1.84	60.0	53.4	+6.6	11.0
100	1.25	78.1	79.0	-0.9	1.1
85	0.87	106.0	114.0	-8.0	7.5
		In morpholine			
120	50.8	0.96	0.97	-0.01	1.0
100	45.1	1.26	1.22	+0.04	3.2
85	39.8	1.48	1.51	-0.03	2.0
60	34.7	1.85	1.88	-0.03	1.6
30	30.7	2.29	2.26	+0.03	1.3
		In N-methylmorpholine			
120	0.72	133	138	-5.0	3.8
110	0.56	187	177.5	+9.5	5.1
100	0.38	240	262	-22	9.2
85	0.37	320	299	+21	6.6
		In dimethylsulfoxide			
110	61.6	0.63	0.62	+0.01	1.6
100	58.7	0.73	0.71	+0.02	2.8
85	51.1	0.87	0.96	-0.09	9.3
60	49.1	1.10	1.04	+0.06	5.7
30	41.6	1.38	1.40	-0.02	1.4
		In N-methyl-2-pyrrolidone			
120	40.4	1.35	1.48	-0.13	8.8
100	33.5	2.08	1.99	+0.09	4.5
85	28.0	2.64	2.57	+0.07	2.7
60	22.6	3.56	3.43	+0.13	3.6
30	17.3	4.65	4.78	-0.13	2.7
		In dimethylformamide			
120	42.8	1.36	1.34	+0.02	1.5
100	29.6	2.44	2.38	+0.06	2.5
85	23.6	3.25	3.24	+0.01	0.3
60	16.9	4.60	4.91	-0.31	6.3
30	14.1	6.21	6.09	+0.12	2.0
		In pyridine			
110	7.46	13.1	12.4	+0.7	5.2
100	5.99	15.5	15.7	-0.2	1.3
85	5.00	19.0	19.0	0.0	0.0
60	3.75	24.8	25.7	-0.9	3.5
30	3.12	31.8	31.1	+0.7	2.2
		In 2-methylpiperazine			
120	30.1	2.21	2.32	-0.09	4.1
110	29.6	2.37	2.38	-0.01	0.4
100	29.5	2.52	2.40	+0.12	4.8
85	26.1	2.77	2.83	-0.06	2.2
		In dimethylsulfolane			
120	0.52	172	191	-19	9.9
110	0.50	220	207	+13	6.3
100	0.37	268	269	+1	0.3
85	0.30	340	333	+7	2.1

Having demonstrated that the Orth's law is also applicable to nonaqueous solvents, the authors tried to find some physical meaning for the parameters "a" and "b".

The most notable feature is that "b" values for all solvents, despite their wide diversity, are very close together. With the exception of 2-methylpyrazine (b = 135) and 2-methylpiperazine (b = 259) they all lie between 145 and 185. In Figures 3 and 4 then, "b" can be considered to be the temperature at which e = 0 or, in other words, the temperature at which sucrose can be liquefied without any solvent.

The true melting point of sucrose is not known. It falls between 160° and 186° C. according to different workers (31, 57). With different rates of heating, the melting points of the same sample can vary as much as 25° C. (41). While in case of extreme purity and dryness it can be raised to 188° C. (49), the fusing point of common sugar should be still accepted to be between 160° to 161° C., as was first determined by Berzelius (2) and as

TABLE III. PARAMETERS FOR SOLUBILITY OF SUCROSE

Solvent	a. Solvent factor	b. Sucrose factor
Pyrazine	0.755	152
Methylpyrazine	2.36	135
Mixed pyrazines	. . .	. . .
Morpholine	0.0148	185
N-Methylmorpholine	5.33	145
Dimethylsulfoxide	0.00923	179
N-Methyl-2-pyrrolidone	0.366	157
Dimethylformamide	0.054	145
Pyridine	0.234	166
Dioxane	13.8	160[a]
2-Methylpiperazine	0.0159	259
Trimethylcyanurate	. . .	. . .
Tetrahydrofuran	. . .	. . .
Dimethylsulfolane	4.79	156
Water (Orth based on Herzfeld figures)	0.0035507	157.97
Water (Orth based on Grut's figures)	0.003901	147.7

[a] Assumed value not based on experimental results.

TABLE IV. COMPARISON OF EXPERIMENTAL VALUES WITH THOSE REPORTED IN LITERATURE

Found			Reported in Literature	
Solvent	"b," ° C.	Solvent for Crystallization	Melting point, ° C.	Literature reference
Morpholine	185	Water	182 184-185 185	41 37, 39 4
Dimethylsulfoxide	179	Ethanol	179-180	10
Pyridine	166	Methanol	169-170 170	10 37
N-methylpyrrolidone	157	Aqueous ethanol	160-161	2
Dimethylsulfolane	156	"B" calculated by Orth for water based on Herzfeld's experiments	157.97	34, 35
Pyrazine	152			
Dimethylformamide	145	"B" calculated by Orth based on Grut's experiments	147.7	35
N-methylmorpholine	145			

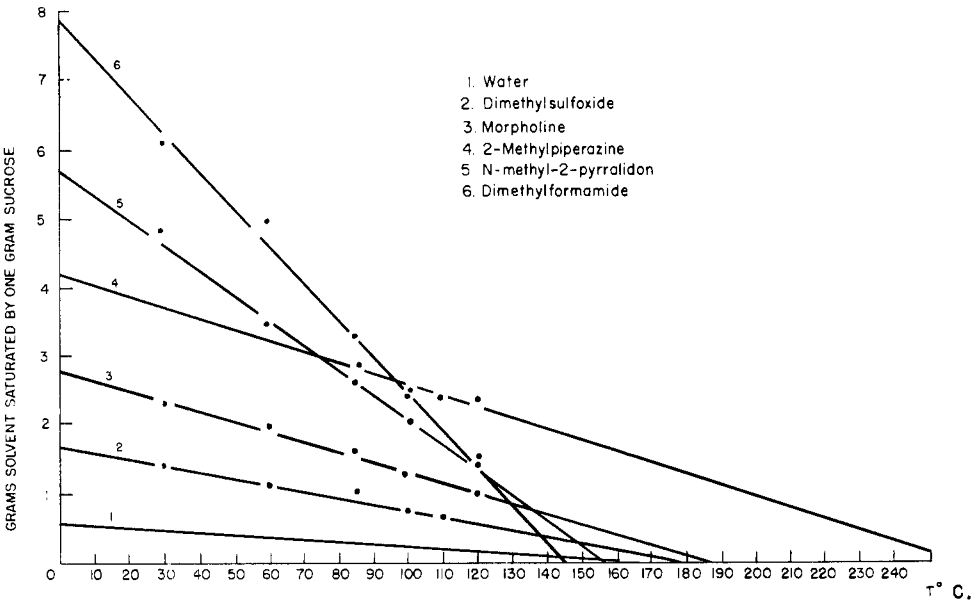

Figure 3. Orth relationships for sucrose

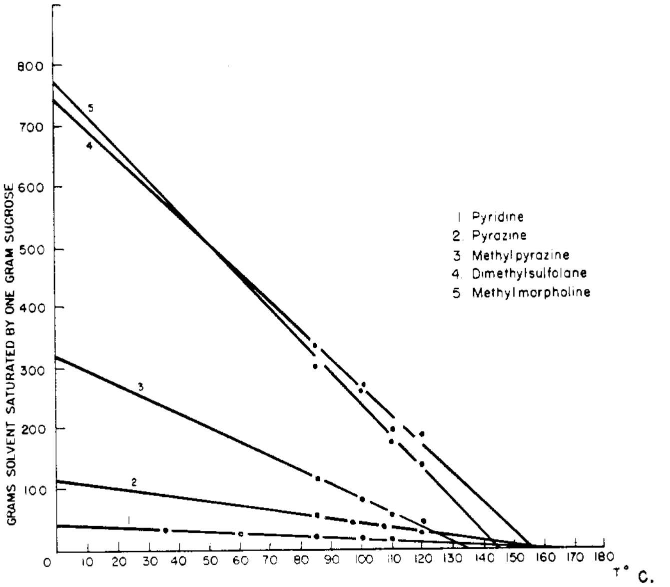

Figure 4. Orth relationships for sucrose

given by many handbooks (Hoolamn, Beilstein, Diels, Weston, and others). The average of the intersections of the authors' lines with the temperature axis is 160.6° C. The deviations from this point can probably be explained by interaction between sucrose and solvent. Observations show that sucrose recrystallized from ethanol melts higher than that crystallized from methanol (10, 37). However, if high-melting sucrose is recrystallized from methanol, the melting point is lowered again.

The "b" value for different solvents in this study are close to melting points found by different authors.

The melting point of sucrose has been reported in three different ranges by various workers. These "b" values also correspond to the three different ranges as illustrated in this table. An explanation of this phenomenon is not yet known.

The sucrose solutions in 2-methylpiperazine were colored yellowish-brown, which may show decomposition or caramelization. The other explanation for the apparent abnormality of 2-methylpiperazine and of 2-methylpyrazine, which was made from it, is the presence of traces of homologs included in this preparation, as was found by infrared analysis. The 2-methylpiperazine was not dried over metallic potassium although Skell claims this is essential for complete drying.

The other parameter "a" should evidently characterize the solvent. When "a" is less than 0.1 the solubility is high, and approaches that of sucrose in water. An attempt to relate the "a" values with the physicochemical properties of solvents is represented on Figure 5 where "a" is plotted in logarithmic scale against the dielectric constant for the few solvents for which dielectric con-

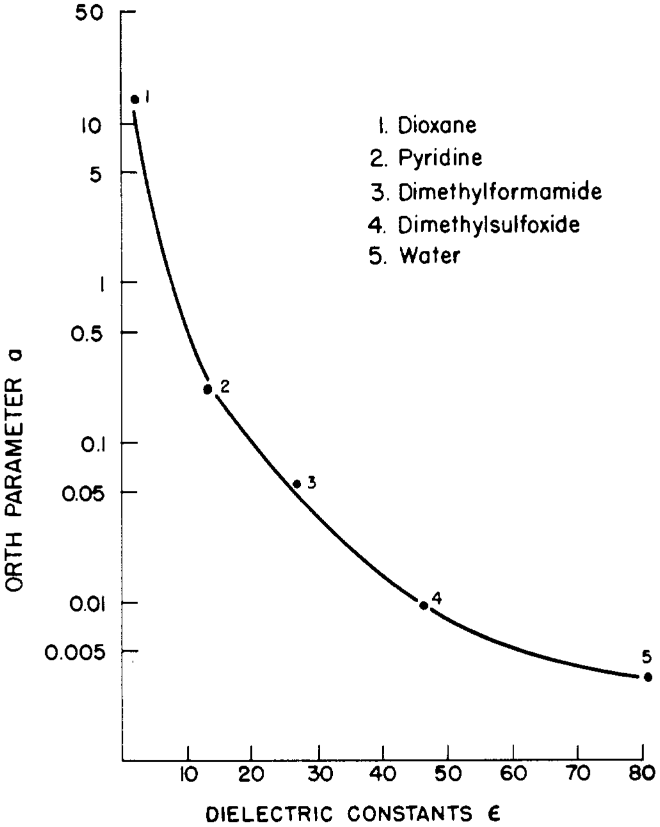

Figure 5. Relationship of parameters a to dielectric constants of sucrose solvents

stants were available. A smooth curve results but the physicochemical significance is not obvious.

CONCLUSIONS

Several nonprotogenic solvents for sucrose have been found.

The solubilities can be expressed by straight lines characterized by two parameters, one depending on the nature of solvent, the other on the nature of dissolved material. Even with the few results given it would appear that only the solubility of sucrose at one temperature and the dielectric constant of the solvent are required to predict the solubility at any other temperature.

Many further measurements are needed in order to determine the parameters more accurately and to find whether this rule can be applied to other substances than sucrose.

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Carbon Dioxide Solubility in Water

W. S. DODDS, L. F. STUTZMAN, AND B. J. SOLLAMI
Chemical Engineering Department, Northwestern University, Evanston, Ill.

All available data on the solubility of carbon dioxide in water have been assembled and converted to a uniform basis. A chart has been prepared which smoothes the normal experimental deviations and thus permits a more accurate determination of solubility and changes in solubility of carbon dioxide in water as a function of temperature and pressure.

Solubilities are properties that are used constantly and therefore solubility data should be available in forms that are both convenient and uniform. Experimental results of any one investigator will not necessarily satisfy the needs of all users, and different investigators will not agree exactly in their results. Often data will be reported in different units or on different bases—e. g., the solubility of gases has been variously defined in coefficients or relationships carrying the names of the originators such as Bunsen, Henry, Kuenen, Ostwald, Raoult, and others. Though the data are sufficiently identified by the investigator to permit accurate interpretation, it is awkward to determine the difference between solubilities under any two conditions. In order to make information on the solubility of carbon dioxide in water more uniform, all the available data have been assembled and correlated on a single basis.

HISTORY

The solubility of carbon dioxide in water has been determined by many investigators (1-8, 11-19, 21, 24-35) and much of their data has been assembled by others (3, 9, 10, 20, 22, 23). The earliest work apparently