Viscosities, Densities, and Related Properties of Solutions of Some Sugars in Dimethyl Sulfoxide

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Viscosities and densities have been determined at 25°, 35°, 45°, and 55° C. for solutions containing up to 40 weight per cent of sucrose, D-glucose, and D-fructose dissolved separately in dimethyl sulfoxide. These data have been fitted to appropriate equations by least squares procedures. Apparent molal volumes and activation energies of viscous flow also have been evaluated.

DIMETHYL SULFOXIDE (DMSO) has been found by Kononenko and Herstein (*6*) to be probably the best nonprotogenic solvent for sucrose. Solubilities of sucrose and other sugars as high as 40 per cent by weight in DMSO solutions can be obtained at 25° C. although total dissolution is slow for the most concentrated solutions. Owing to the increasing importance of sucrochemistry as a field of research and industrial application and to the lack of information other than solubilities for sugars in DMSO, the objective of the present study has been to gain detailed knowledge concerning some physical properties of binary sugar-DMSO systems as a function of both concentration and temperature.

EXPERIMENTAL

Sucrose and D-glucose (both Fisher Certified Reagent Grade) were pulverized and dried overnight at 105° C. prior to use. Fisher Reagent grade D-fructose was pulverized and used without drying or further purification. Commercial, grade DMSO was subjected to several fractional freezing cycles until a final product having a maximum freezing point of 18.50° C. was obtained. The purity of the solvent also was confirmed by the excellent agreement of the values of its density and viscosity at 25° with those reported by other investigators (*3*, *7*).

Solutions in glass-stoppered flasks were prepared on a weight basis using calibrated weights. Densities were determined using 25-ml. Reischauer pycnometers which were calibrated using freshly distilled water. After temperature equilibrium was obtained in each case, excess solution in a pycnometer was removed through a capillary by suction. Appropriate buoyancy corrections were applied prior to the calculation of concentrations and densities. The density data have an estimated accuracy of ±0.02%; in calculations, densities in g./ml. and g./cc. were used interchangeably.

A size 50, 75, 100, 150, or 200 Cannon-Fenske viscometer was used as the case demanded in order to have an efflux time of 200 seconds or greater and thereby eliminate the necessity for making kinetic energy corrections. Calibration constants for the viscometers were provided by the Cannon Instrument Company. Precautions as discussed by Cannon and Fenske (*2*) were observed. Also, to minimize atmospheric contamination, the viscometers were equipped with top adapters vented through tubes filled with calcium chloride and Ascarite. Stopwatches were calibrated against NBS Station WWV time signals. The viscosity data, which have a precision of 0.2%, are reported relative to a viscosity of 1.0019 centipoises for water at 20° C. (*10*). The viscosity values for the most concentrated solutions were found to be independent of the size of viscometer used, indicating the absence of shear effects.

The temperature was controlled within 0.02° C. with a Sargent S-84805 thermostatic water bath assembly. The bath thermometer was compared against one calibrated by the National Bureau of Standards and necessary corrections were applied.

An IBM 1620 digital computer was used for the fitting of data by the method of least squares to various polynomial equations.

RESULTS AND DISCUSSION

The experimental density data are summarized in Table I. For each system at a given temperature, the density as a function of the weight per cent of sugar may be expressed by an equation of the type:

$$d = d_0 + mW + nW^2 \qquad (1)$$

The meanings of these and other symbols are incorporated in a nomenclature section near the end of this article. The least squares values for d_0, m, and n are compiled in Table II. Knowing the corresponding weight per cent

Table I. Experimental Density Data

Wt. %	Densities (Grams/Ml.)			
	25°	35°	45°	55°
		Sucrose		
0.000	1.0955	1.0855	1.0757	1.0657
2.766	1.1056	1.0957	1.0857	1.0760
5.412	1.1156	1.1057	1.0958	1.0864
8.051	1.1256	1.1158	1.1060	1.0970
13.218	1.1452	1.1357	1.1260	1.1167
18.095	1.1650	1.1553	1.1461	1.1368
20.572	1.1749	1.1654	1.1560	1.1469
23.036	1.1849	1.1755	1.1663	1.1573
25.500	1.1947	1.1855	1.1764	1.1676
27.684	1.2035	1.1946	1.1856	1.1769
32.130	1.2223	1.2134	1.2045	1.1957
34.402	1.2320	1.2231	1.2139	1.2055
36.725	1.2419	1.2333	1.2245	1.2158
38.780	1.2507	1.2424	1.2335	1.2250
		D-Glucose		
8.934	1.1291	1.1198	1.1098	1.1002
17.223	1.1614	1.1520	1.1424	1.1331
25.472	1.1946	1.1853	1.1762	1.1669
33.368	1.2259	1.2166	1.2079	1.1987
		D-Fructose		
5.502	1.1151	1.1051	1.0952	1.0853
10.627	1.1340	1.1240	1.1145	1.1046
15.580	1.1517	1.1419	1.1330	1.1228
21.470	1.1742	1.1646	1.1554	1.1459
25.101	1.1883	1.1790	1.1698	1.1602
29.085	1.2035	1.1942	1.1853	1.1760
32.417	1.2167	1.2075	1.1984	1.1891
36.256	1.2319	1.2227	1.2137	1.2043
39.999	1.2467	1.2377	1.2288	1.2195

and density, the concentration of sugar in moles per liter of solution, C, may be calculated readily using the relationship, $C = [(10dW)/(M_2)]$.

For purposes of calculating the apparent molal volume, however, it is advantageous to express densities as a function of molarity as follows:

$$d = d_0 + aC + bC^2 \tag{2}$$

or

$$\frac{d_0 - d}{C} = -(a + bC) \tag{3}$$

The corresponding useful equation for calculating the apparent molal volume, Φ_v, has the following form (*5*):

$$\Phi_v = \frac{1000}{d_0}\left(\frac{d_0 - d}{C}\right) + \frac{M_2}{d_0} \tag{4}$$

Upon combining Equations 3 and 4 and rearranging, one may obtain

$$\Phi_v = \frac{M_2 - 1000\,a}{d_0} - \left(\frac{1000\,b}{d_0}\right) C \tag{5}$$

or

$$\Phi_v = \Phi_v^\circ + kC \tag{6}$$

in which the expressions for the constants Φ_v° and k are obvious from Equation 5. Values obtained for the various constants in the application of Equations 2 and 6 to the three systems may be found in Table III. The theoretical apparent molal volumes, or the ratios of the gram molecular weight to the density of the sugar as a solid, are 112.7, 116.7, and 215.6 ml./mole respectively, for D-fructose, D-glucose and sucrose. These theoretical values are 1, 8, and 4 per cent greater than the corresponding Φ_v° values in Table III.

Table II. Results for Density Data Fitted to Equation 1

°C.	d_0	$m \times 10^3$	$n \times 10^6$	Deviations × 10^4 Std.	Deviations × 10^4 Max.
		Sucrose			
25	1.0954	3.6835	8.280	1.70	3.65
35	1.0855	3.6934	9.044	0.95	1.65
45	1.0755	3.7255	8.952	2.05	3.81
55	1.0657	3.7771	8.481	1.85	3.83
		D-Glucose			
25	1.0954	3.7518	4.915	3.10	4.13
35	1.0855	3.8137	3.602	2.53	3.46
45	1.0756	3.7990	5.121	3.37	4.68
55	1.0656	3.8517	4.234	2.91	3.98
		D-Fructose			
25	1.0955	3.5335	6.244	1.81	3.65
35	1.0854	3.5491	6.525	2.16	4.26
45	1.0756	3.5966	5.907	1.73	3.46
55	1.0656	3.6082	6.132	2.64	4.53

The experimental viscosity data for the sugar solutions are listed in Table IV. For each system at a given temperature, the viscosity increases very rapidly with increasing concentration. At 25°, a 38.8 weight per cent DMSO solution of sucrose is more than 40 times as viscous as a similar aqueous sucrose solution (*1*). The viscosity data have been fitted to an empirical expression of the following type:

$$\log \eta = \log \eta_0 + AC + BC^2 + DC^3 \tag{7}$$

The values for the constants in this equation for each system at the various temperatures may be found in Table V. In general, the data are described very well by Equation 7 as evidenced by the information on deviations.

The logarithm of the viscosity is a linear function of the molal concentration for D-glucose and D-fructose solutions at 25° and for sucrose solutions at 55°. For each system, however, deviations from linearity occur at the other temperatures and become more pronounced as the temperature difference increases.

The viscosity-temperature relationship for each solution in each system is described excellently by the Girifalco equation (*4, 8, 11*):

$$\log \eta = \alpha + \frac{\beta}{T} + \frac{\gamma}{T^2} \tag{8}$$

Also, upon differentiation, it permits the evaluation of the activation energy of viscous flow (*4, 9*):

$$\frac{E_{\text{vis}}}{2.303\,R} = \frac{d(\log \eta)}{d(1/T)} = \beta + \frac{2\gamma}{T} \tag{9}$$

Values for α, β, γ, and E_{vis} (25°) are listed in Table VI.

For each system a linear relation exists between α and β values as noted previously by other investigators for different systems (*8, 12*). Also, it has been observed that the following empirical relation applies to each system at 25°:

$$\log E_{\text{vis}} = 3.5416 + k'\,C \tag{10}$$

Values for k' are 0.1934, 0.2218, and 0.3941 for the D-fructose, D-glucose, and sucrose systems, respectively.

Table III. Results for Density Data Fitted to Equation 2 and for Apparent Molal Volumes

°C.	d_0	$a \times 10^2$	$b \times 10^3$	Deviations × 10^4 Standard	Deviations × 10^4 Maximum	Φ_v°	k
			Sucrose				
25	1.0954	11.495	−3.7694	1.52	3.25	207.6	3.44
35	1.0855	11.640	−3.5162	0.98	1.72	208.1	3.24
45	1.0757	11.726	−2.7186	4.93	12.33	208.3	2.53
55	1.0657	12.124	−4.7046	2.47	4.73	207.4	4.42
			D-Glucose				
25	1.0954	6.1398	−1.7084	2.42	3.22	108.4	1.56
35	1.0855	6.2851	−2.0535	1.97	2.45	108.1	1.89
45	1.0757	6.3299	−1.8408	2.66	3.67	108.6	1.71
55	1.0657	6.4681	−2.1177	2.10	2.88	108.4	1.99
			D-Fructose				
25	1.0955	5.7887	−1.0693	1.73	3.56	111.6	1.07
35	1.0855	5.8720	−1.1944	1.86	3.76	111.9	1.10
45	1.0756	5.9939	−1.3838	1.47	3.07	111.8	1.29
55	1.0656	6.0702	−1.4060	2.31	2.59	112.1	1.32

Table IV. Experimental Viscosity Data

Wt. %	Viscosities (Centipoises) 25°	35°	45°	55°
		Sucrose		
0.000	1.996	1.654	1.396	1.195
2.766	2.400	1.962	1.630	1.388
5.412	2.883	2.319	1.908	1.603
8.051	3.523	2.793	2.266	1.892
13.218	5.532	4.214	3.309	2.669
18.095	9.087	6.615	4.999	3.887
20.572	12.08	8.541	6.292	4.806
23.036	16.40	11.28	8.055	5.989
25.500	22.45	14.86	10.39	7.569
27.684	30.82	19.69	13.36	9.488
32.130	61.59	36.46	23.02	15.45
34.402	90.84	51.59	31.40	20.62
36.725	139.8	75.48	43.98	27.88
38.780	211.4	109.3	61.19	37.04
		D-Glucose		
8.934	3.819	2.988	2.408	1.981
17.223	8.234	5.977	4.525	3.525
25.472	21.23	13.90	9.672	7.001
33.368	62.65	36.04	22.40	14.79
		D-Fructose		
10.627	3.980	3.096	2.480	2.038
15.580	6.037	4.529	3.507	2.799
21.470	10.34	7.330	5.442	4.164
25.101	14.99	10.21	7.283	5.423
29.085	23.48	15.13	10.35	7.440
32.417	35.39	21.64	14.17	9.855
36.256	59.46	34.14	21.19	14.06
39.999	104.7	55.88	32.62	20.58

NOMENCLATURE

d = density of soln. in g./ml. or g./cc.
d_0 = density of solvent
E_{vis} = activation energy of viscous flow in cal./mole
η = viscosity of soln. in centipoises
η_0 = viscosity of solvent
k = constant in Equation 6
k' = constant in Equation 10
log = logarithm to base 10
m, n = constants in Equation 1
M_2 = gram molecular weight of solute
Φ_v = apparent molal volume in ml./mole
Φ_v^0 = limiting apparent molal volume
T = temperature in ° K.
W = wt. %
a, b = constants in Equation 2
A, B, D = constants in Equation 7
α, β, γ = constants in Equation 8
C = conc. in moles/liter of soln.

ACKNOWLEDGMENT

The authors wish to express their appreciation to the University of Kentucky Computing Center for use of the IBM 1620 computer.

LITERATURE CITED

Table V. Results for Viscosity Data Fitted to Equation 7

° C.	log η_0	$A \times 10$	$B \times 10^2$	$D \times 10^3$	100(η calc. − η obs.)/η obs. Av.	Max.
			Sucrose			
25	0.30016	8.4723	32.357	60.771	0.33	0.65
35	0.21854	7.9786	27.430	54.101	0.35	0.96
45	0.14489	7.5144	23.979	43.730	0.39	0.95
55	0.07737	7.1892	19.617	43.234	0.22	0.77
			D-Glucose			
25	0.30016	4.4838	9.8523	−2.4872	0.08	0.10
35	0.21854	4.1471	8.7559	−3.5579	0.05	0.07
45	0.14489	3.8694	8.0560	−5.6674	0.07	0.13
55	0.07737	3.6471	7.0794	−6.0314	0.09	0.14
			D-Fructose			
25	0.30016	4.0842	6.7546	3.2552	0.51	1.15
35	0.21854	3.8272	5.4039	3.2122	0.63	1.46
45	0.14489	3.5675	4.7767	1.8488	0.65	1.43
55	0.07737	3.3668	4.0907	1.1432	0.60	1.26

Table VI. Results for Viscosity Data Fitted to Equation 8

Wt. %	α	$-\beta$	γ	E_{vis} (25° C.)
		Sucrose		
0.000	−0.99882	−14.149	111,256	3,480
2.766	−0.39617	369.054	179,077	3,808
5.412	−0.36183	400.588	192,488	4,075
8.051	0.26214	792.146	261,519	4,402
13.218	0.06192	709.801	272,172	5,106
18.095	0.10100	786.239	310,641	5,937
20.572	0.64496	1164.840	386,173	6,523
23.036	0.11252	880.887	360,646	7,039
25.500	1.44286	1751.440	514,048	7,764
27.682	1.88344	2083.129	586,020	8,455
32.130	2.29241	2471.684	692,260	9,938
34.402	3.59278	3338.005	849,987	10,851
36.725	4.23121	3823.118	954,530	11,804
38.780	2.95579	3111.291	871,607	12,516
		D-Glucose		
8.934	−0.15434	561.338	232,815	4,577
17.223	0.57918	1110.678	361,054	6,000
25.472	1.76661	2002.514	557,953	7,962
33.368	3.05279	3036.402	793,676	10,467
		D-Fructose		
10.627	0.22623	809.421	274,555	4,723
15.580	0.22449	850.264	302,978	5,409
21.470	0.70032	1219.294	391,447	6,436
25.101	1.26535	1641.701	481,540	7,268
29.085	2.27962	2360.515	623,002	8,321
32.417	3.36724	3132.147	772,234	9,370
36.256	3.78839	3508.965	867,171	10,560
39.999	4.70079	4214.660	1,018,305	11,970

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Received for review September 16, 1963. Accepted January 24, 1964. This research was supported in part by the National Science Foundation undergraduate research program.