Density, Viscosity, Refractive Index, and Hygroscopicity of Mixtures of Water and Dimethyl Sulfoxide

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DIMETHYL sulfoxide (DMSO) has been known for over a century, but only recently has it been made on an industrial scale. It is becoming of increasing importance as a versatile solvent and as an intermediate in synthetic processes. Its solvent properties have been demonstrated for a number of gases (*14*), liquids (*1*), certain salts (*1*), and a variety of polymers (*5, 9–12*).

Dimethyl sulfoxide is a colorless, water-soluble, hygroscopic, slightly alkaline organic liquid which boils at 189° C. and freezes at 18.5° C. It has only a slight odor and is nontoxic. Water and DMSO are miscible in all proportions, and like many other solvent-water systems (*13*) the physical properties of the mixtures are not related linearly to those of each constituent.

In a current series of investigations of the physicochemical properties of the hemicelluloses (*7,8*), DMSO was used as a solvent for a variety of hardwood xylans. Under certain conditions, addition of water improved its solvent properties. For such studies, information was required on viscosity, density, refractive index, and hygroscopicity of DMSO-water mixtures. Accordingly, these measurements were undertaken. Very few data on the physical properties of the system DMSO-water are available in the literature; therefore, it was considered worthwhile to report these results.

Considerable care was taken in the distillation of the DMSO to remove as much water as possible. The water content, estimated by an infrared technique, could be reduced to 0.10% by vacuum distillation over Drierite.

Refractive index, viscosity, and density from 0 to 100% water content are given in Table I and plotted in Figure 1. The data were obtained by interpolation from graphs containing 16, 19, and 7 points, respectively, for n_D, η, and ρ. The significant figures given in Table I represent the precision of the graphical data. Differential refractive indices were measured on dilute solutions consisting of DMSO in water, and water in DMSO. Specific refractive increments at λ = 5460 A. were calculated to be 0.134 ml. gram^{-1} for DMSO in water and 0.107 ml. gram^{-1} for water in DMSO. These figures agree within 5% with increments computed from refractive index data over the small initial intervals at 0 and 100% DMSO content.

Table I. Refractive Index, Viscosity, and Density of DMSO-Water System at 25° C.

Water Content, Wt. %	Refractive Index, n_D	Viscosity, Centipoises	Density, G./Ml.
0	1.4768	1.99	1.0956
5	1.4708	2.32	1.0957
10	1.4649	2.70	1.0960
15	1.4589	3.11	1.0961
20	1.4523	3.45	1.0960
25	1.4457	3.68	1.0950
30	1.4385	3.73	1.0926
35	1.4310	3.64	1.0884
40	1.4232	3.42	1.0823
45	1.4150	3.16	1.0753
50	1.4071	2.83	1.0682
55	1.3993	2.51	1.0610
60	1.3913	2.22	1.0535
65	1.3832	1.93	1.0461
70	1.3754	1.69	1.0387
75	1.3677	1.50	1.0314
80	1.3600	1.34	1.0242
85	1.3527	1.18	1.0174
90	1.3458	1.06	1.0105
95	1.3390	0.96	1.0038
100	1.3325	0.89	0.9971

As shown in Figure 1, maximum deviation from ideality in viscosity, density, and (possibly) refractive index occurs at approximately 33% H_2O. This is near the composition (37% H_2O) of a mixture made up in the proportion of 1 mole of DMSO to 2 of water. Such behavior is common. For example, Turner (*15*) has observed maximum deviations in density for mixtures of 1 mole of ether to 1 of alcohol, 2 of benzene to 1 of ether, and 1 of ether to 2 of chloroform. These results support Dolezalek's (*4*) original hypothesis that the deviation of a liquid mixture from the ideality may be connected with the existence of "chemical species" in the mixture. More recent studies (*6*) have confirmed that association compounds of definite composition exist in mixtures of certain liquids.

The uptake of water by DMSO at various relative humidities is shown in Figure 2. Apparently, the solvent has a strong affinity for water, as also shown by the equilibrium vapor pressure isotherm in Figure 3. For comparison, curves for sulfuric acid (*16*) and glycerol (*13*) are included. While DMSO is strongly hygroscopic, its rate of water vapor sorption in absence of stirring (Figure 4) is low enough to allow some work conveniently with open vessels in the laboratory. For example, the data in Figure 4 show that if a 400-ml. beaker containing 200 ml. of dry DMSO was left open in an environment of 75% relative

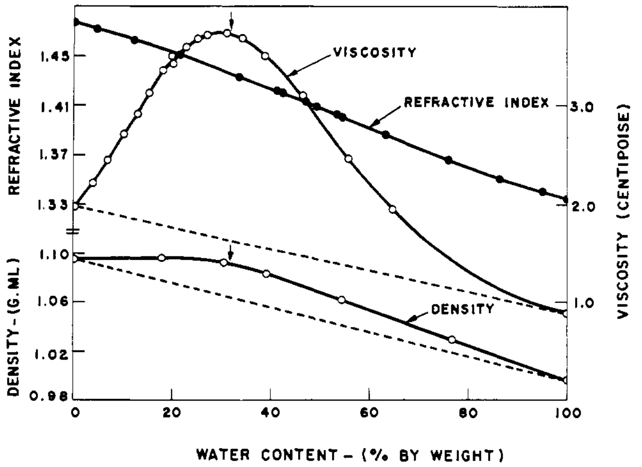

Figure 1. Graphs of n_D, η, and ρ vs. water content

Points of maximum deviation from ideality are indicated by arrows and represent maximum separation of curve from straight line (dashed) joining limiting values

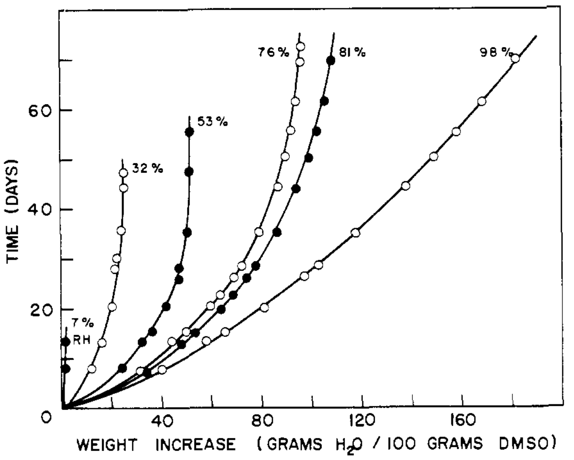

Figure 2. Comparative hygroscopicities of DMSO at various relative humidities

Temp. 22° C.

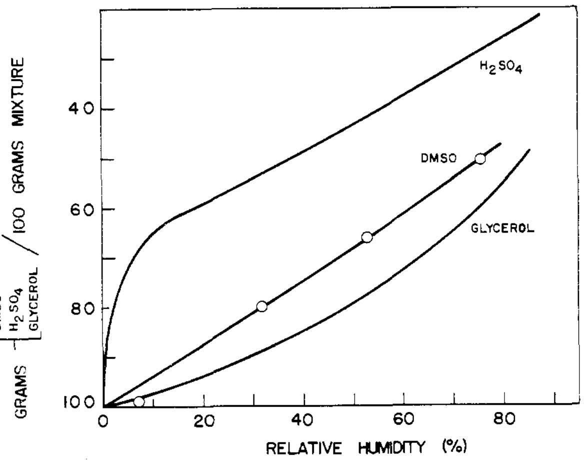

Figure 3. Comparative equilibrium vapor pressure isotherms for DMSO, sulfuric acid, and glycerol at 22° C.

humidity (R.H.) for 1 hour, the solvent would pick up only 0.05% water. However, a slight increase in water content affects viscosity to a marked degree. Consequently, care must be taken to avoid water uptake in the use of DMSO in viscometry.

EXPERIMENTAL

Purification of DMSO. The DMSO used was supplied by Anachemia Chemicals, Ltd. It was purified by distilling under vacuum over Drierite. Barium oxide was equally effective as a drying agent. For maximum dehydration, it was necessary to have the solvent in contact with the drying agent for several days, the whole being shaken vigorously from time to time. Vacuum was applied through water aspiration and the solvent was found to boil near 90° C.

Water Analysis. A Perkin-Elmer Model 21 infrared spectrophotometer was used to estimate the residual water content in the freshly distilled DMSO. NaCl cells equipped with 0.1-mm. spacers were most suitable for the analysis. The concentration of -OH groups was determined quantitatively from the height of the absorption peak at 3500 cm.$^{-1}$ Calibration was achieved by measuring the increase in peak height on addition of small increments of water to dry DMSO. The method gave reproducible results, and was used for water contents of up to 0.5%.

Viscosity. Viscosity (η) was measured in a modified Craig-Henderson viscometer (*3*). A Townson & Mercer water bath was used to maintain 25° C. with a relative temperature control of ±0.02° C. Kinetic energy corrections were assumed to be negligible.

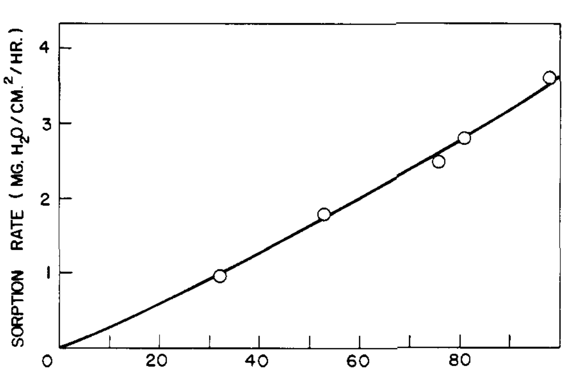

Figure 4. Initial sorption rates of DMSO at various relative humidities

Temp. 22° C.

Density. Density (ρ) was determined by the standard method with a pycnometer of about 10-ml. capacity. Measurements were made at 25° ± 0.02° C.

Refractive Index. Refractive index (n_D) measurements were conducted in an Opton-Zeiss refractometer for λ = 5893 A. (sodium *D* line) at 25° C. Specific refractive increments (dn/dc) were measured with a Brice-Phoenix differential refractometer (*2*) for λ = 5460 A. at 25° C. The instrument was previously calibrated with sucrose solutions.

Hygroscopicity. Saturated aqueous solutions in contact with an excess of NaOH, $CaCl_2$, $Ca(NO_3)_2$, NaCl, $(NH_4)_2SO_4$, and $K_2Cr_2O_7$ in closed jars were used to maintain constant relative humidities of 7, 32, 53, 76, 81, and 98%, respectively. The jars were placed in a room kept at 22° ±1° C. Known amounts of DMSO in open weighing bottles were introduced into the jars and water uptake was recorded by weighing at suitable intervals of time (Figure 2). Initial rates of sorption shown in Figure 4 were computed from the amount of water taken up by the DMSO corresponding to 24 hours of sorption time. The equilibrium composition at a particular relative humidity was obtained in Figure 2 from the abscissal reading at which the uptake no longer increased with time. As shown in Figure 3, this could be done only for the four lowest relative humidity values. At 81 and 98% RH, equilibrium was not reached even after 70 days.

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