Gaylord Chemical Company, L.L.C.

Bulletin 101
June 2014

DIMETHYL SULFOXIDE

PHYSICAL PROPERTIES

DMSO

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Introduction

Dimethyl Sulfoxide (DMSO) is a highly polar and water miscible organic liquid. It is essentially odorless, and has a low level of toxicity. DMSO is a dipolar aprotic solvent, and has a relatively high boiling point.

This bulletin is a compilation of Physical Properties data for this useful solvent.

Contents

Typical DMSO Properties (in Alphabetical order)

Figure 1

Parameter	Value
Auto ignition temp, in air	300-302°C (572-575°)
Boiling point (1 atmosphere)	189°C (372°F)
Coefficient of expansion	0.00088/°C
Conductivity (Electrical), 20°C	3x10-8 (ohm-1 cm-1)
@ 80°C	7x10-8 (ohm-1 cm-1)
Critical heat flux	1.3x105 Btu/hr x ft-2
(4.10x105 J / s / m^2)	
Critical molar volume	2.38x10-4 m^3
Critical Pressure	56.3 atm. abs.
Critical temperature	447°C (837°F)
Density, at 25°C (*see Figure 3*)	1.0955 g / cm^3
Dielectric constant, 1 MHz, @ 20°C	48.9
@ 40°C	45.5
Diffusion coefficient	9.0x104 cm^2 / sec.
Dipole moment, D	4.3
Evaporation rate index @ 25°C	
Relative to n-butyl acetate	0.026
Relative to diethyl ether	0.0005
Flammability limits in air	
lower (100°C)	3 - 3.5% by volume
upper	42 - 63% by volume
Flash point (open cup)	95°C (203°F)
Flash point (closed cup)	89°C (192°F)
Freezing point	18.55°C (65.4°F)
Heat capacity, ideal gas, Cp(T°K)	6.94+5.6x10-2T
-0.227x10-4T2	
Heat capacity (liq.), 25°C	0.47 cal / g / °C
Heat of combustion	6054 cal / g
Heat of fusion	41.3 cal / g
Heat of solution in water at 25°C	-54 cal/g
Heat of vaporization at 70°C	11.3 kcal/mol
Henry's constant @ 21°C	991000
Molar freezing point constant	4.07°C / mol
Molar volume	71.2 cm^3 / g
Molecular weight	78.13
pKa	35.1
pK BH+	-2.7
Refractive index ND@25°C	1.4768

Typical DMSO Properties, continued

Parameter	Value
Solubility parameters	
Hansen's	
- Dispersion	9.0 $(cal / cm^3)^{1/2}$
- Polar	8.0 $(cal / cm^3)^{1/2}$
- Hydrogen bonding	5.0 $(cal / cm^3)^{1/2}$
Hildebrand's	13.0 $(cal / cm^3)^{1/2}$
Specific heat at 29.5°C	0.47± 0.015 cal /g /°C
Surface tension at 20°C	43.53 dynes / cm
Vapor pressure at 25°C (*See Figure 1*)	0.600 mm Hg
Viscosity, cP, at 25°C (*See Figure 4*)	2.0
Log octanol-water partition coefficient	-1.35

Vapor Pressure vs. Temperature Curve for DMSO

Figure 2

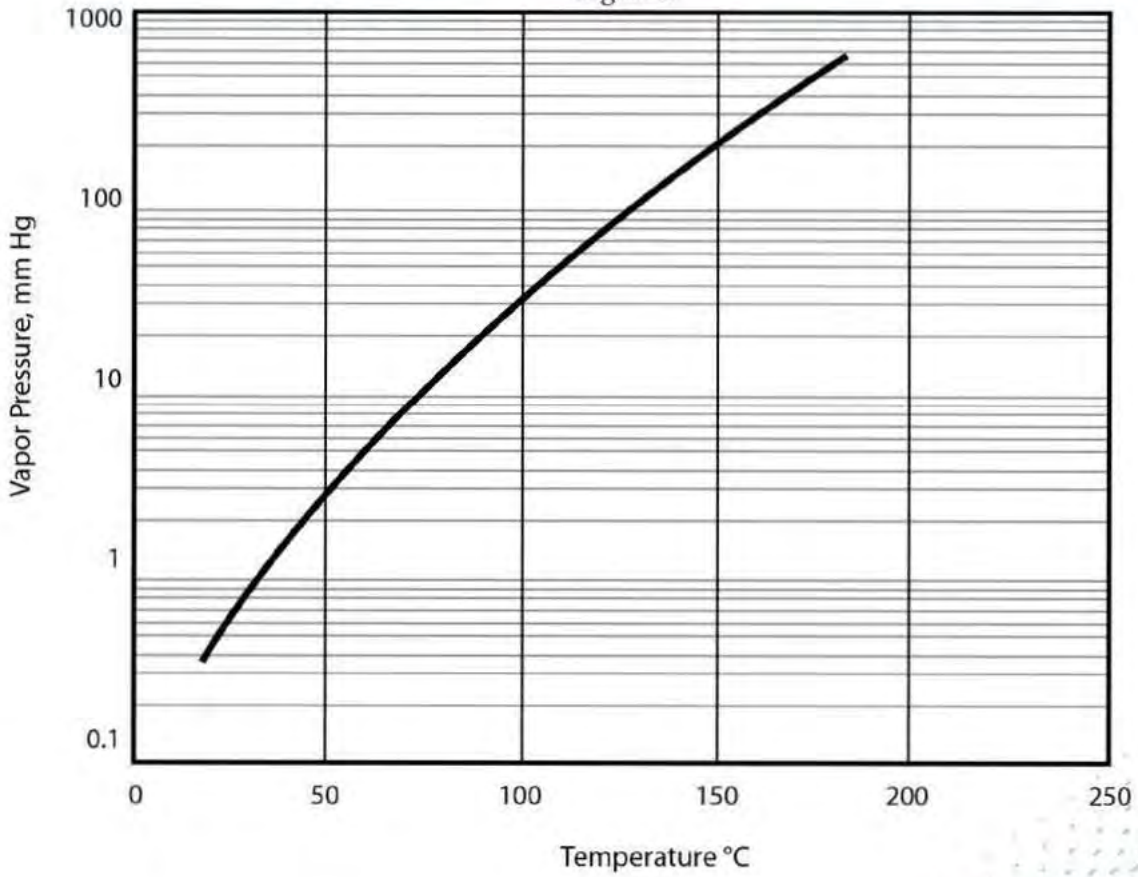


Figure 3

Specific Gravity of DMSO as a Function of Temperature

Temperature (°C)	Specific Gravity (g/cm³)
15.6	1.1047
21	1.0993
25	1.0955
30	1.0904
40	1.0803
50	1.0702
75	1.0454
100	1.0200
125	0.9946
150	0.974

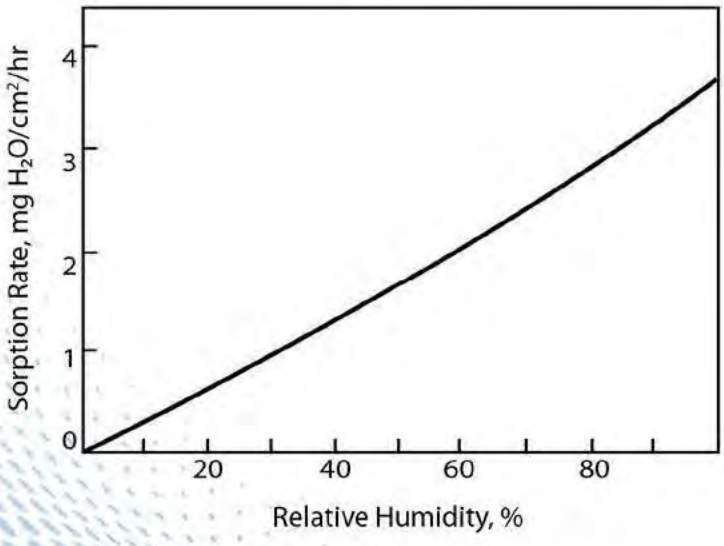
Figure 4

DMSO Viscosity as a Function of Temperature

Temperature (°C)	Viscosity (cP)
25	1.991
30	1.808
40	1.511
50	1.286
75	0.916
100	0.691
125	0.546

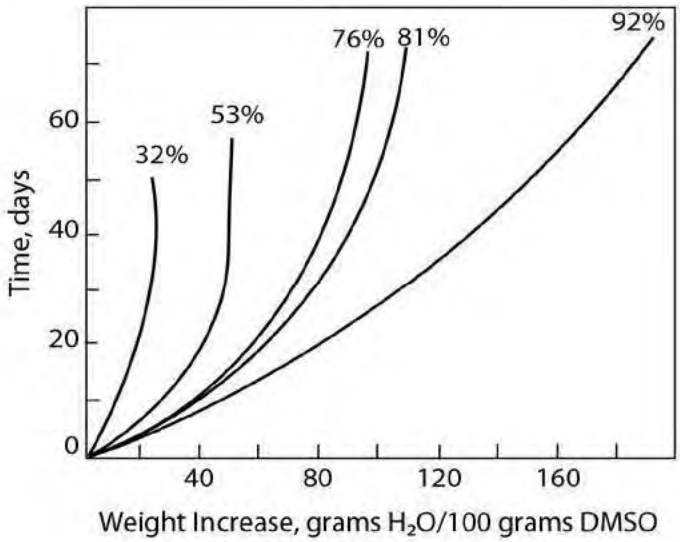
Initial Sorption Rates of DMSO at Various Relative Humidites at 22°C

Figure 5



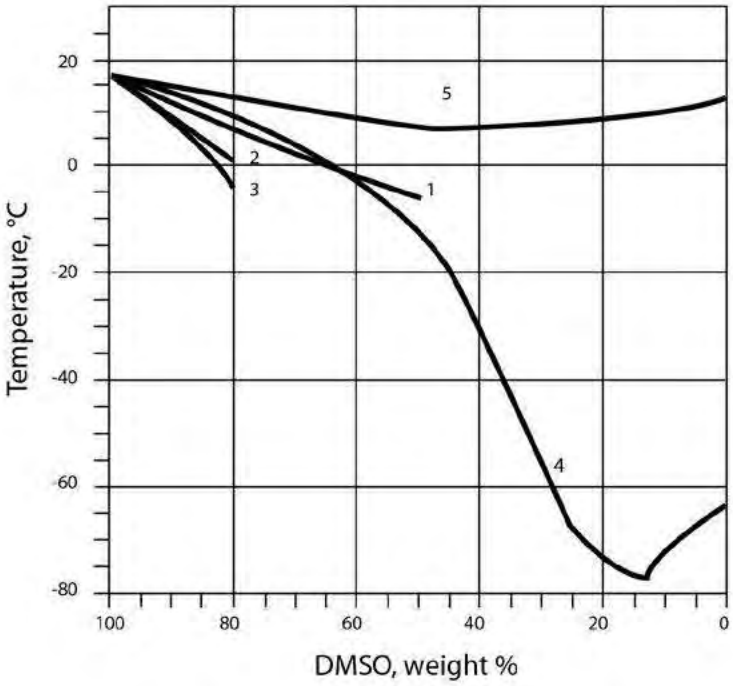
Hygroscopicities of DMSO at Various Relative Humidities at 22°C

Figure 6



Freezing Temperatures for DMSO-Solvent Mixtures

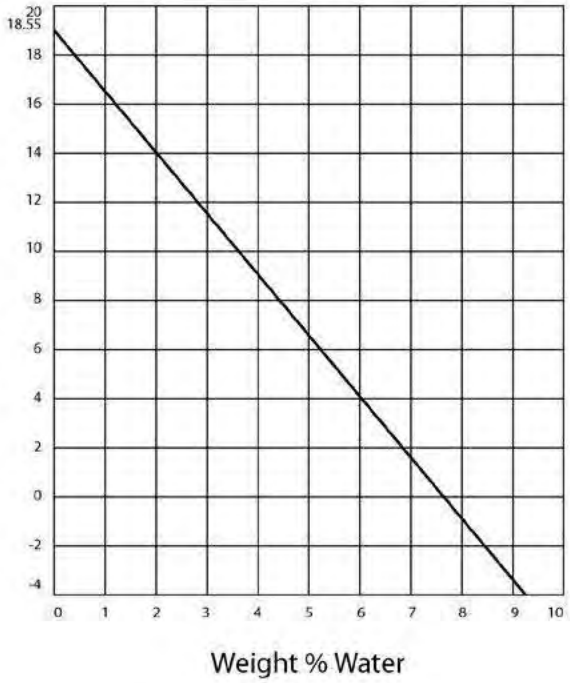
Figure 7



1. DMSO - Methyl ethyl ketone
2. DMSO - Ethanol
3. DMSO -Monoethylene Glycol
4. DMSO - Chloroform
5. DMSO - p-Xylene

Freezing Point Data for DMSO Water Solutions

Figure 8



Freezing Point Data for DMSO Water Solutions

Figure 9

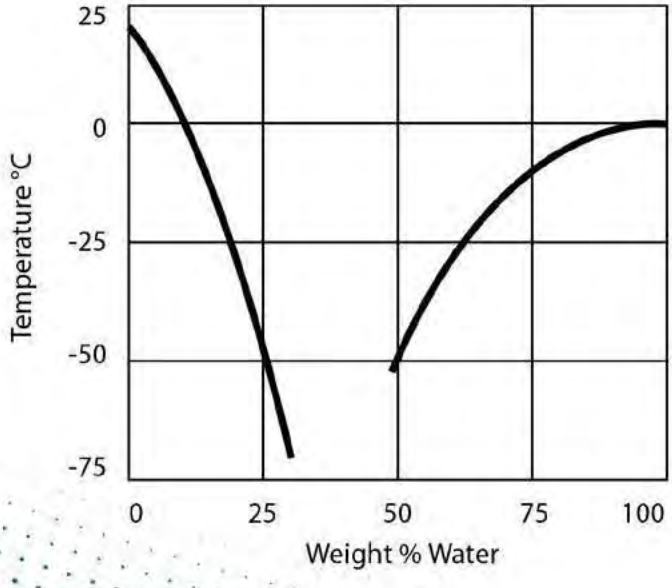
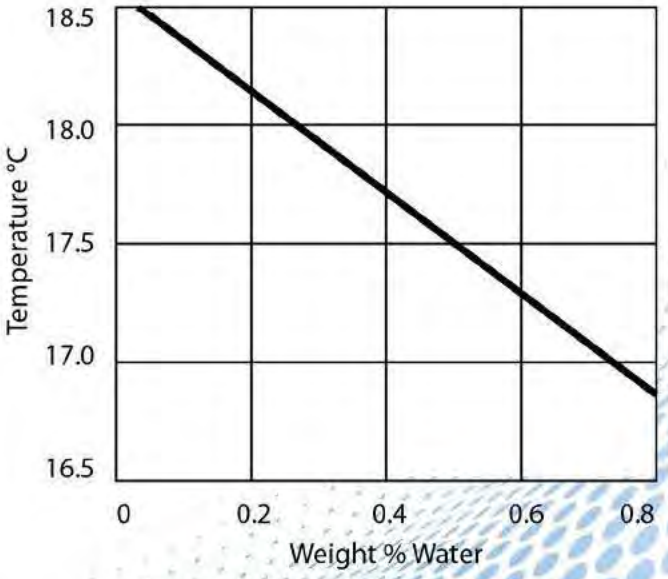


Figure 10



Vapor-liquid Equilibrium for DMSO-Water Solutions
(One atmosphere pressure)

Figure 11

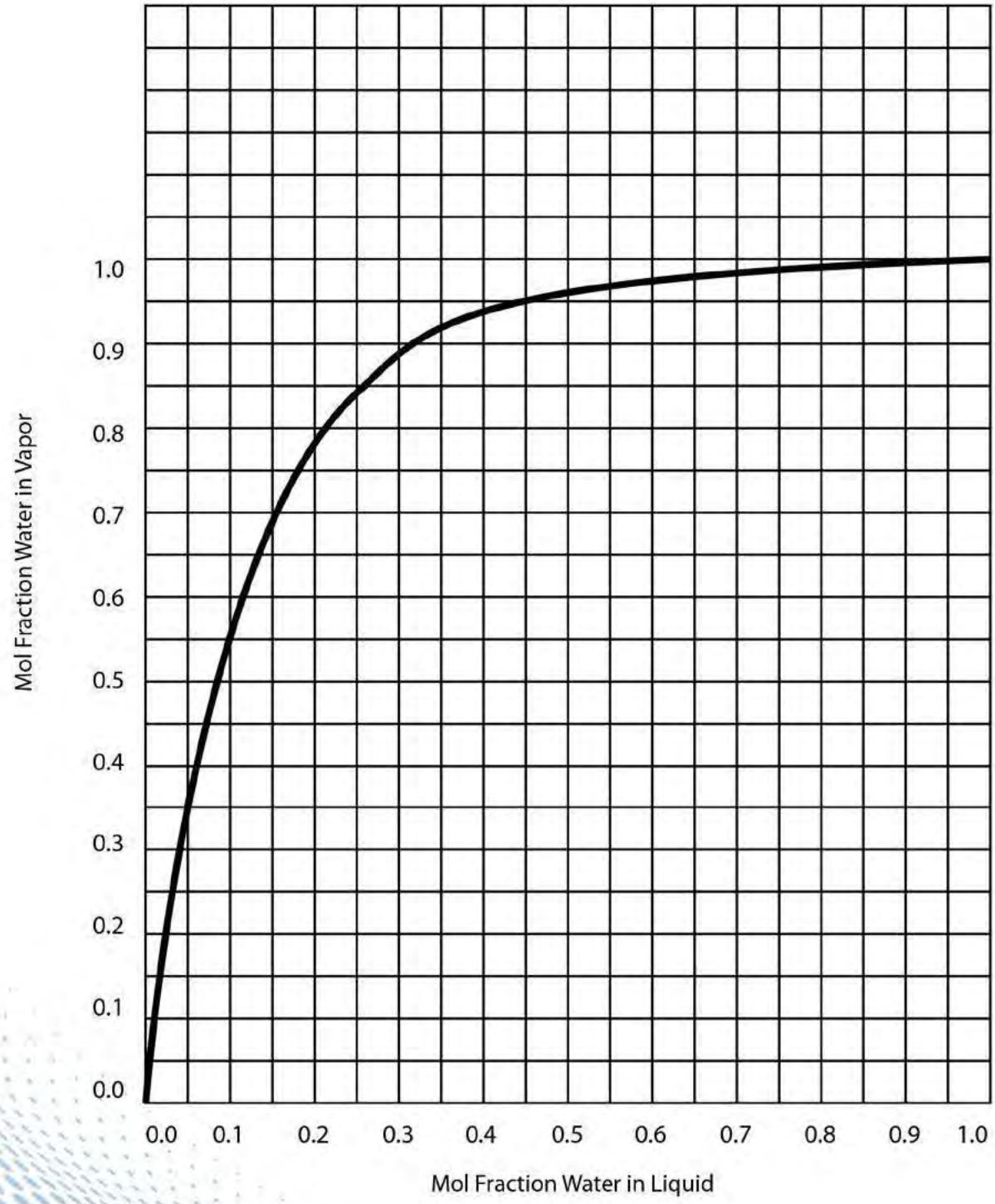


Figure 12

Heat Capacity and Density of DMSO

Temperature, °C	Cp (liquid), cal/(g)(°C)	Density, grams/cc
30	0.47	1.096
60	0.47	1.062
100	0.48	1.023
150	0.52	0.974

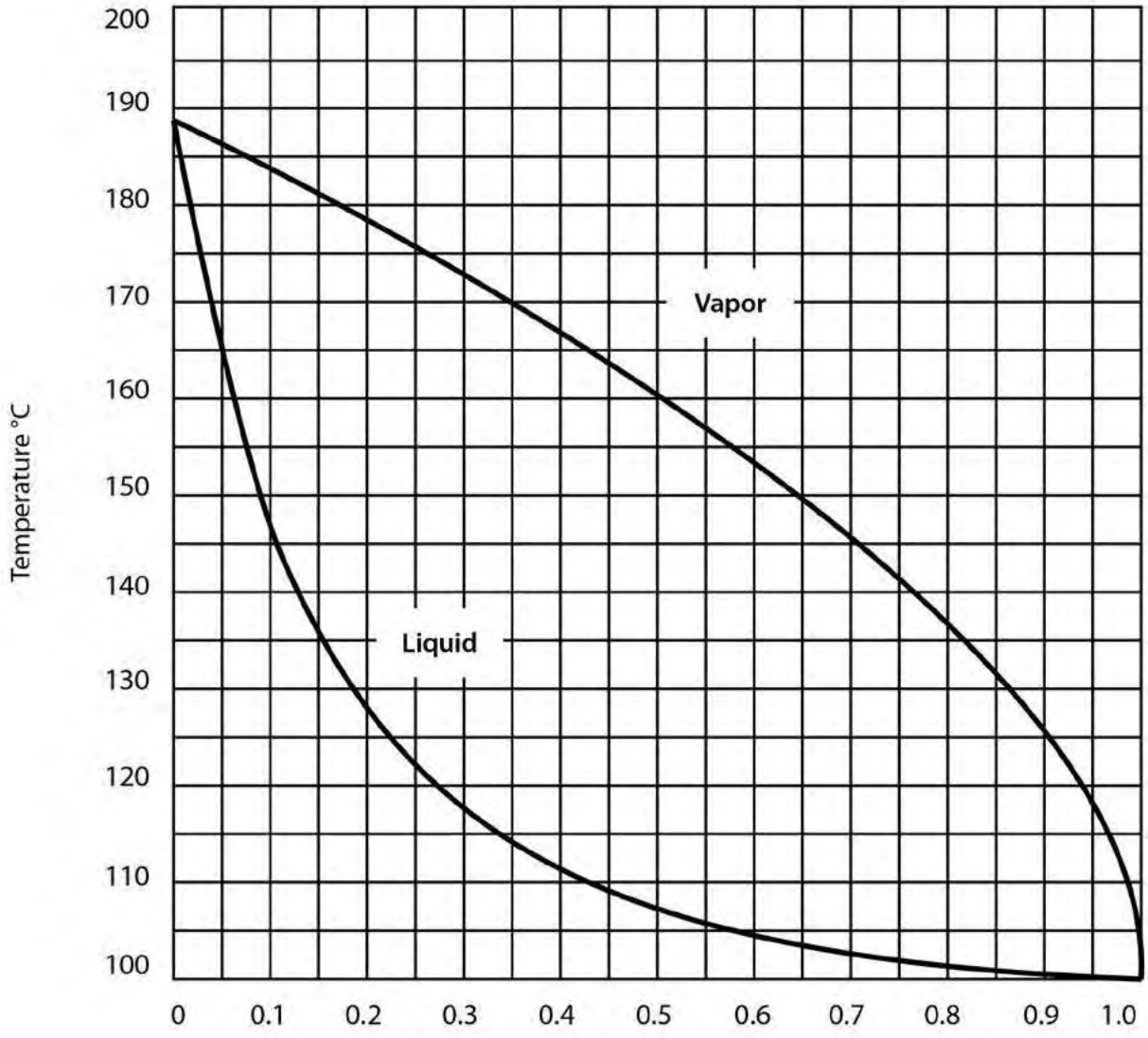
Figure 13

Vapor-Liquid Equilibrium for DMSO-Water Solutions (One atmosphere pressure)

Temperature, °C	Mol Fraction Water in Liquid	Mol Fraction Water in Vapor
100.0	1.000	1.000
100.6	0.988	0.9998
101.0	0.975	0.9997
102.0	0.945	0.9994
103.3	0.909	0.9989
105.0	0.865	0.9983
108.0	0.810	0.997
113.0	0.740	0.994
118.0	0.675	0.990
120.0	0.645	0.986
130.0	0.513	0.964
143.0	0.378	0.921
149.0	0.313	0.890
165.0	0.176	0.773
174.5	0.100	0.628
177.0	0.081	0.573
183.0	0.046	0.353
184.6	0.034	0.282
187.7	0.011	0.100
189.0	0.000	0.000

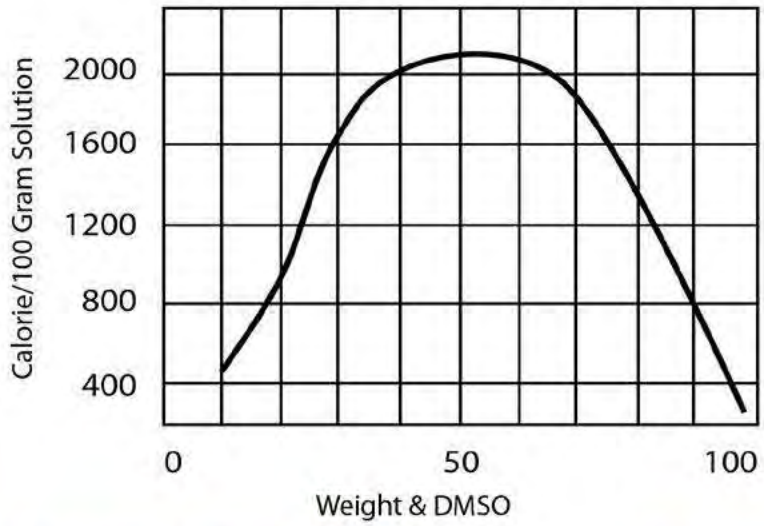
Boiling Point/ Temperature Curves: DMSO Water Solutions (One Atmosphere Pressure)

Figure 14



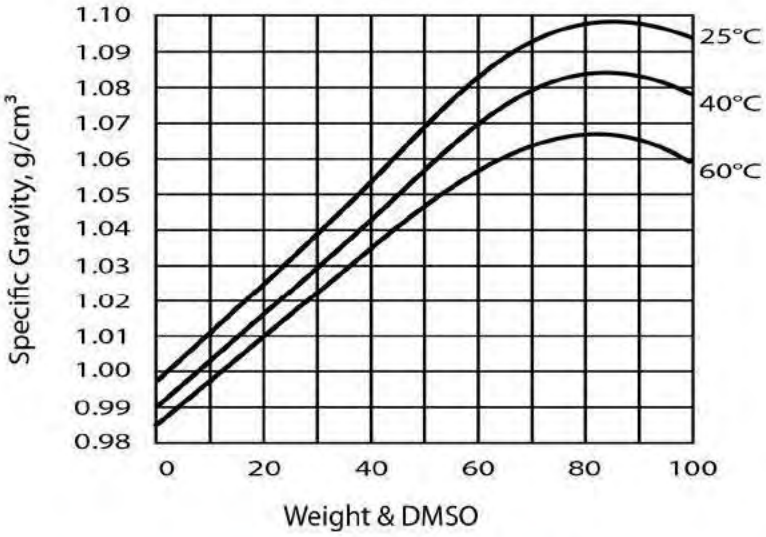
Heat of Mixing of DMSO - H_2O System at 32°C

Figure 15



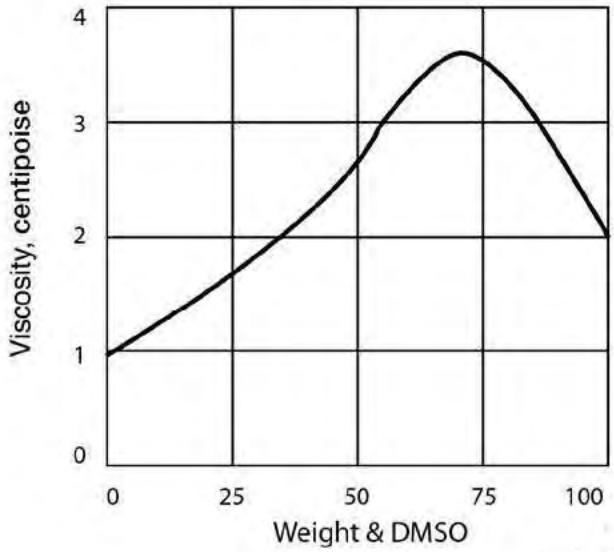
Specific Gravity of DMSO Water Solutions

Figure 16



Viscosity of DMSO Water Solutions

Figure 17



Chemical and Thermal Stability of DMSO

DMSO is highly stable at temperatures below 150°C. For example, holding DMSO at 150°C for 24 hours, one could expect a loss of between 0.1 and 1.0%. Retention times even in batch stills are usually considerably less than this, and therefore, losses would be correspondingly less. It has been reported that only 3.7% of volatile materials are produced during 72 hours at the boiling point (189°C) of DMSO.

Slightly more decomposition, however, can be expected with the industrial grade material. Thus, about 5% DMSO decomposes at reflux after 24 hours. Al- most half of the weight of the volatile materials is paraformaldehyde. Dimethyl sulfide, dimethyl disulfide, bis(methylthio)methane and water are other volatile products. A small amount of dimethyl sulfone can also be found. The following sequence of reactions explains the formation of these decomposition products:

$$H_3CSOCH_3 \rightarrow H_3CSH + HCHO \rightarrow (HCHO)x$$
$$2H_3CSH + HCHO \rightarrow (H_3CS)_2CH_2 + H_2O$$
$$2H_3CSH + CH_3SOCH_3 \rightarrow H_3CSSCH_3 + H_3CSCH_3 + H_2O$$
$$2H_3CSOCH_3 \rightarrow H_3CSO_2CH_3 + H_2CSCH_3$$

DMSO is remarkably stable in the presence of most neutral or basic salts and bases. When samples of DMSO (300g) are refluxed for 24 hours with 100g each of sodium hydroxide, sodium carbonate, sodium chloride, sodium cyanide, sodium acetate and sodium sulfate, little or no decomposition takes place in most cases. The results are shown in *Figure 18*.

Figure 18

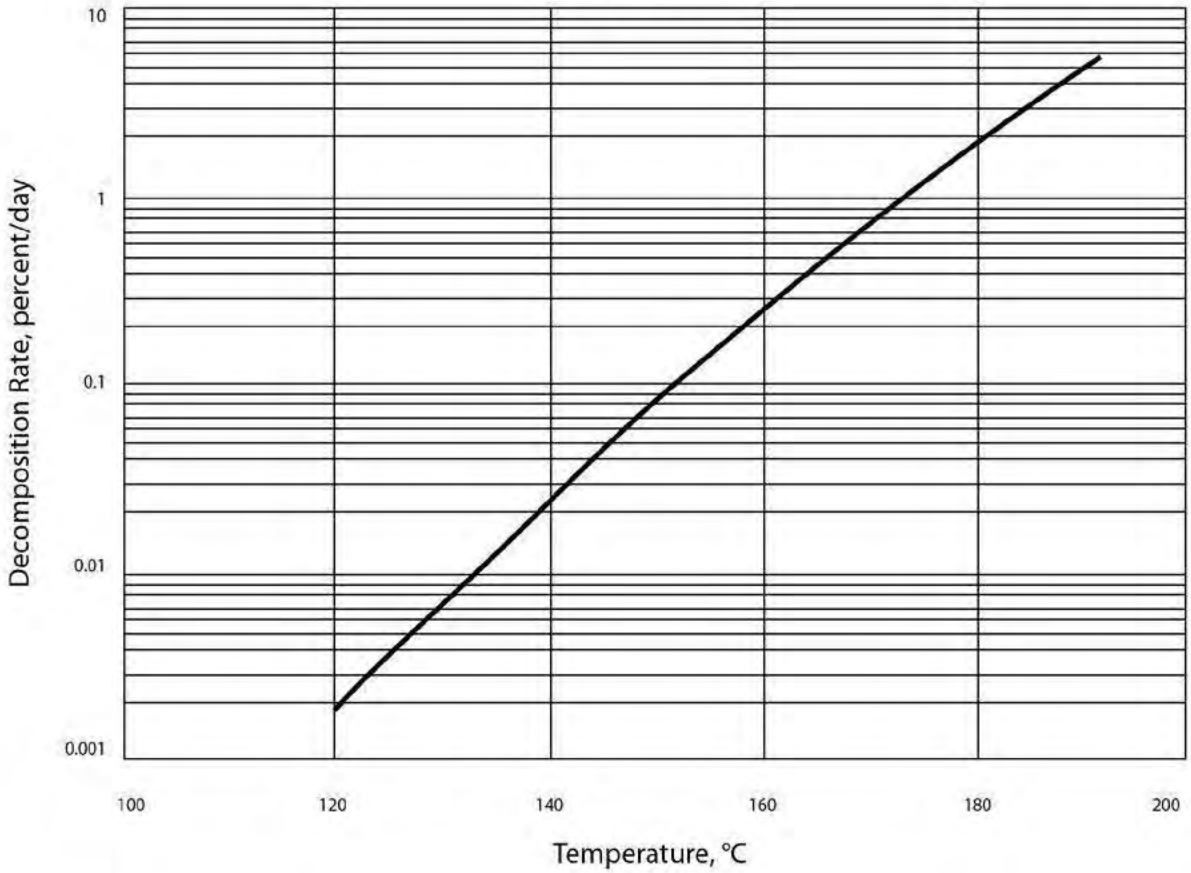
Results of Reflux with DMSO, and various materials (24 hours)

Compound (100g) in 300g DMSO	Reflux Temp., °C	DMSO Recovered % of Original	% Decomposition Products				
			DMS[a]	DMDS[b]	BMTM[c]	HCHO[d]	MM[e]
NaOH	185-140[f]	93.7	63	31	-	-	-
Na_2CO_3	190	96.3	-	14	-	-	-
NaCl	190	98.7	-	15	-	-	-
NaCN	148-164[g]	100.0	-	-	-	-	-
NaOAc	182-187	97.0	22	33	8	20	-
Na_2SO_4	181-148[h]	85.4		-			
DMSO Only	189	98.0	15	30	30	-	-

(a) Dimethyl sulfide
(b) Dimethyl Disulfide
(c) Bis-(methylthio)methane
(d) Methyl mercaptan
(e) Formaldehyde
(f) Reflux temperature decreased from 185°C to 140°C over the first 16 hours.
(g) Reflux temperature was 148°C for 20 hours; increased to 164°C during the last 4 hours.
(h) Reflux temperature decreased gradually from 181°C to 148°C.

Thermal Stability of DMSO

Figure 19



DMSO does not seem to be hydrolyzed by water and very little decomposition of DMSO takes place when it is heated under reflux for periods of 5 to 16 hours. The following tests, shown in Figure 16, have been performed: 1) 10 parts DMSO + 1 part water, 2) 60 parts DMSO + 5 parts water + 1 part sodium hydroxide, 3) 60 parts DMSO + 12 parts water + 1 part sodium bicarbonate, 4) DMSO alone.

Figure 20

Refluxing of DMSO and Mixtures, for shorter periods

Composition of Sample Parts	Reflux Temp., °C	Time, hr	Organic Products Composition, %			
			DMSO	DMS	DMDS	BMTM
10 DMSO: 1 H_2O	152	5 15	100 99.7	0 0.15	0 0	0 0.15
60 DMSO: 5H_2O:1 NaOH	155	5 8	99.8 99.3	0.1 0.6	0.1 0.1	0 0
60 DMSO: 12 H_2O: 1 $NaHCO_3$	131	6 12	99.9 99.8	0.1 0.2	0 0	0 0
DMSO Only	191	5 9 16	99.8 99.1 99.0	0.1 0.2 0.2	0.1 0.2 0.2	0 0.5 0.6

DMSO is also stable in the presence of concentrated sulfuric or hydrochloric acid at 100°C for up to 120 minutes of heating at atmospheric pressure. Phosphoric acid causes more rapid decomposition of DMSO than does sulfuric or hydrochloric acid. Detected decomposition products are dimethyl sulfide, dimethyl disulfide, and, in smaller quantity, formaldehyde. The results are shown in *Figure 21*:

Figure 21

Effect of heating DMSO with Concentrated Acids

Acid	Conc.	Temp., °C	Time, min.	DMSO % left	% of decomposition product		
					DMS[a]	DMDS[b]	HCHO[c]
H_2SO_4	36N	100	15 30 120	99 99 98	100 100 100		
H_2SO_4	36N	125	15 150 210	86 86 80	7 7 10	93 93 90	
H_3PO_4	85%	100	15 30 45 60 120 150	92 89 89 87 87 86	25 45 45 46 46 50	75 55 55 54 54 50	 some
H_3PO_4	85%	125	15 60 150	84 82 82	25 33 33	75 67 67	

Figure 21

Effect of heating DMSO with Concentrated Acids

Acid	Conc.	Temp., °C	Time, min.	DMSO % left	% of decomposition product		
					DMS[a]	DMDS[b]	HCHO[c]
HCI	12N	95	15	99	100		
			30	99	100		
			60	99	100		
			120	98	100		
HCI	12N	115	15	93	100		
			30	92	100		
			45	87	100		
			60	87	100		
			120	87	100		some

(a) Dimethyl Sulfide (b) Dimethyl Disulfide (c) Formaldehyde

Thermal Decomposition of DMSO

Figure 22

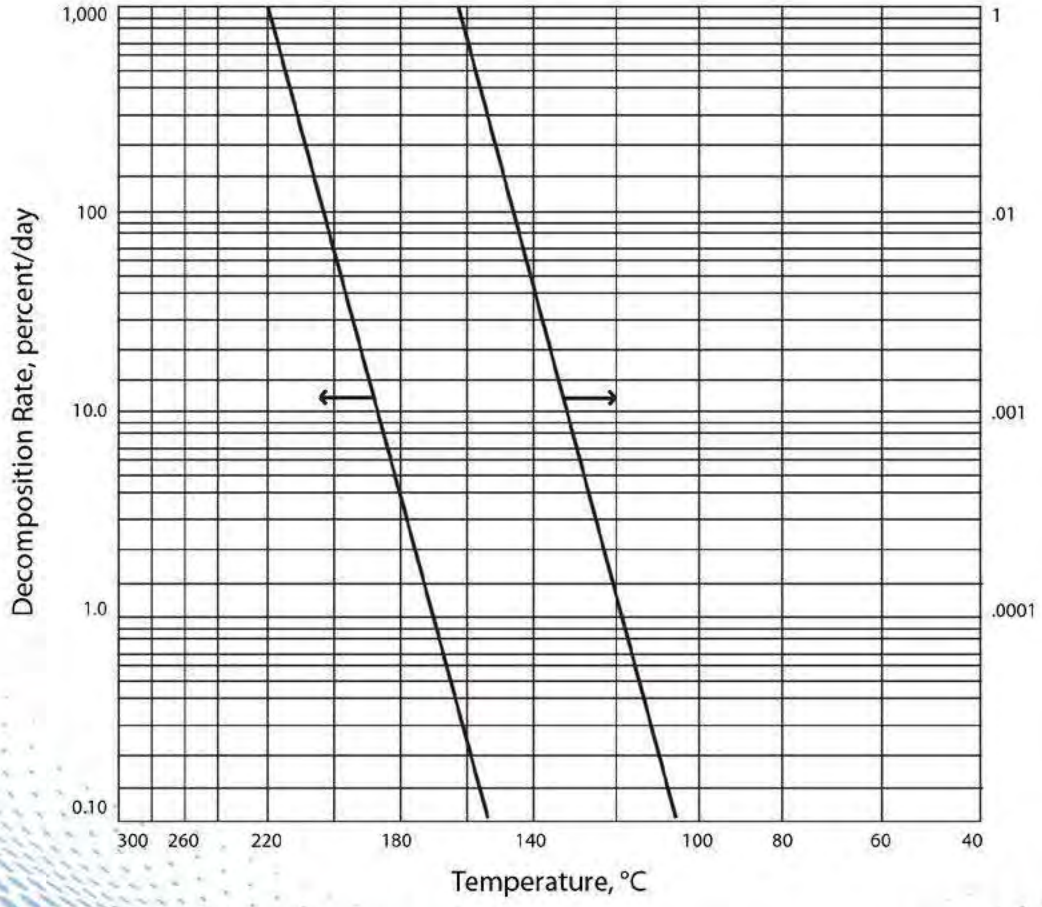


Figure 23

Comparative Viscosities of Common Solvents

Solvent	Viscosity, cps at 25°	
Dimethyl Sulfoxide (DMSO)	**2.0**	
Dimethylformamide (DMF)	0.8	
N-Methyl-2-pyrrolidone (NMP)	1.6	
Butyrolactone	1.7	
Cyclohexanone	2.1	
Isophorone	2.5	
Diacetone alcohol	3.0	
Propylene Carbonate	4.0	
Sulfolane	10.3	at 30°

Figure 24

Comparative Evaporation Times for Common Organic Solvents

Solvent	90% Evaporation Times, seconds
Dimethyl Sulfoxide (DMSO)	**17,600**
Dimethylformamide (DMF)	1,570
N-Methyl-2-pyrrolidone (NMP)	2,280
Butyrolactone	3,840
Cyclohexanone	15,400
Isophorone	20,000
Diacetone alcohol	23,700
Propylene Carbonate	119,660
Sulfolane	>1,000,000

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