The fact that all points in Figure 1 fall on the single line confirms the absence of complexes higher than HF_2^- and of polynuclear species.

The stability constants were evaluated using a least squares technique based on the following mass-balance relationships:

$$C_H = [H^+]\{1 + \beta_1[F^-] + \beta_2[F^-]^2\} \quad (7)$$

$$C_F = [F^-] + [H^+]\{\beta_1[F^-] + 2\beta_2[F^-]^2\} \quad (8)$$

The equilibrium constant K_2 is obtained from

$$K_2 = \beta_2/\beta_1 \quad (9)$$

For each experimental point, $[F^-]$ is obtained from the observed E; β_1 and β_2 are chosen intuitively; and $[H^+]$ values are calculated from Equation 7. A new set of β's is obtained from Equation 8 by minimizing the function

$$\sum_1^k \{1 - FX_k/X_k\}^2 \quad (10)$$

where

$$FX_k = \beta_1[F^-]_k + 2\beta_2[F^-]_k^2 \quad (11)$$

and

$$X_k = \{(C_F)_k - [F^-]_k\}/[H^+]_k \quad (12)$$

The process is repeated using the new β's to generate new $[H^+]$ values, and the β's are further refined until convergence is achieved. The resulting β's along with their standard deviations are given in Table III. The standard deviations of log β_1 and log β_2 were obtained by the pit-mapping method of Sillén (*14*). The variance in log K_2 is taken as the sum of the variances of log β_1 and log β_2.

Figure 2 is a plot of the deviation of FX/X from the theoretical value. Although there is some scatter at low $\bar{n}$ (high C_H/C_F) values, there is no systematic deviation that would indicate the presence of species other than HF and HF_2^-.

The enthalpies and entropies for Equations 1 and 3 were obtained by conventional methods, and the results are given in Table IV.

Conclusions

The above results once again confirm the existence of HF and HF_2^- and the absence of other complexes. The temperature coefficients of the equilibrium constants appear to be more accurate than previous estimates (*6*). The entropy change for Equation 1 of 23.8 equiv. units (molal units) is in good agreement with the value of 22.0 equiv. units (molar units) quoted in ref. 7 for 0.5*M* $NaClO_4$ solutions. The major disagreement between all the works listed in Table I appears to be associated with β_2 and hence K_2.

Literature Cited

(1) Ostwal, W. J., *Prakt. Chem.*, **32,** 300 (1885).
(2) Pick, H., *Nernst-Festschr.*, **1912,** p 300.
(3) Davies, C. W., Hudleston, L. J., *J. Chem. Soc.*, **125,** 260 (1924).
(4) Roth, W. A., *Lieb. Ann. Chem.*, **542,** 35 (1939).
(5) Brosset, C., *Svk. Kem. Tidskr.*, **54,** 155 (1942).
(6) Broene, H. H., DeVries, T., *J. Amer. Chem. Soc.*, **69,** 1644 (1947).
(7) Connick, R. E., Hepler, L. G., Hugus, Z. Z., Kury, J. W., Latimer, W. M., and Tsao, M.-S., *ibid.*, **78,** 1827 (1956).
(8) Mesmer, R. E., *Anal. Chem.*, **40,** 443 (1968).
(9) Neumann, G., Sillén, L. G., quoted by Butler, ref. *11*.
(10) Srinivasan, K., Rechnitz, G. A., *Anal. Chem.*, **40,** 509 (1968).
(11) Butler, J. N., "Ion Selective Electrodes," R. A. Durst, Ed., Chap. 5, NBS Spec. Pub. 314, 1969.
(12) International Critical Tables, Vol III, McGraw-Hill, New York, N.Y., 1928.
(13) Bjerrum, J., "Metal Ammine Formation in Aqueous Solution," P. Haase and Son, Copenhagen, 1957.
(14) Sillén, L. G., *Acta Chem. Scand.*, **16,** 159 (1962).

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Isothermal Vapor-Liquid Equilibrium Data of DMSO Solutions by Total Pressure Method. DMSO-Acetone, DMSO-Tetrahydrofuran, and DMSO-Ethyl Acetate Systems

Yoshimasa Sassa, Ryoichi Konishi,[1] and Takashi Katayama[2]
Department of Chemical Engineering, Faculty of Engineering Science, Osaka University, Toyonaka, Osaka, Japan

Isothermal vapor-liquid equilibrium data were obtained by the total pressure method for the binary mixtures of dimethyl sulfoxide (DMSO) with acetone, tetrahydrofuran, or ethyl acetate at 25°, 35°, and 45°C. These data were reduced to obtain excess Gibbs free energies.

The extensive applications of dimethyl sulfoxide (DMSO) as solvent and reaction medium have been markedly increased in recent years (*8*). In spite of the increased use of DMSO, few phase equilibrium data for the systems containing DMSO have been studied.

As DMSO has a strong polarity, it is highly self-associated and has the ability to make molecular complexes with other compounds. For the fundamental understanding of the effects of the strong molecular interactions on the thermodynamic excess properties, systematic studies of vapor-liquid equilibria for DMSO mixtures have been projected. This paper reports vapor-liquid equilibrium data for the DMSO-acetone, DMSO-tetrahydrofuran, and DMSO-ethyl acetate systems at 25°, 35°, and 45°C.

Experimental

Total vapor pressures for the three systems studied were measured as a function of composition at constant temperature. A schematic diagram of the apparatus described here (Figure 1) was taken from the studies of

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[1] Present address, Mitui Senboku Petroleum Chemical Co., Osaka, Japan.

[2] To whom correspondence should be addressed.

Quitzsch and coworkers (*12*) and Arm and coworkers (*1*). The apparatus consists of two cells, A and A′, approximately 60 ml each for the liquid container; a small null manometer, F; a mercury reservoir, E; a magnetic stirrer, C; and the manometer, D, which is a mercury manometer and can be exchangeable to a dibutyl phthalate manometer for the measurements of low vapor pressures.

After mercury was placed in the reservoir (E) by a hypodermic syringe from the stopcock, dissolved gas in the mercury was removed by evacuating and warming carefully. The liquid sample of known composition was placed in the cell (A) and frozen with liquid nitrogen. A vacuum of about 10^{-3} mm Hg was effected rather quickly to avoid vaporization, the stopcock was closed, and the liquid was melted to remove dissolved gas. These procedures were repeated several times. Finally, the sample was distilled between the two cells for perfect degassing.

After the sample had been degassed, the mercury in the mercury reservoir was introduced to the small null manometer by rotating the equilibrium cell at the taper joint (G). The cell was gradually warmed and thermostated. The liquid in the equilibrium cell was magnetically stirred to assure perfect mixing. Equilibrium was attained in about 30 min. Arms of the small null manometer were adjusted to about the same levels by bleeding dry nitrogen gas into the reference side of the manometer through a capillary. The difference between the mercury (or dibutyl phthalate) level in both arms of the manometer tube (D, 12-mm diameter) was read by a PCTM-1000 cathetometer from Nakamura Optical Co. The small null manometer was read by using a traveling microscope from Shimazu Seisakasho Co., and the difference was added to the pressure difference in the manometer (D). All manometer readings were corrected for gravity and temperature. The liquid composition was corrected by considering the vapor volume.

A calibrated glass thermometer was used for temperature measurements which were accurate within 0.03°C. Temperature deviation of 0.03°C would cause a maximum pressure deviation of 0.6 mm Hg for the DMSO–acetone system at 45°C. The temperature of the bath was thermostated to ±0.01°C. This uncertainty in temperature causes a maximum error of ±0.10% in the vapor pressure. Vapor pressures were measured to within ±0.10 mm Hg.

Pure vapor pressures of DMSO were measured by introducing degassed DMSO into the small null manometer and by using the dibutyl phthalate manometer as the manometer (D). Densities of dibutyl phthalate were preliminarily measured as a function of temperature. Vapor pressures of pure DMSO were measured to within ±0.01 mm Hg.

Spectrograde DMSO, acetone, tetrahydrofuran, and ethyl acetate from Merck Co. were used. DMSO and acetone were dried over molecular sieves prior to the experiments. In the titration with Carl Fisher reagent, water was present in DMSO to about 0.07 mol %. Physical properties of these materials in this work are summarized in Table I.

Results and Data Reduction

The experimentally determined vapor pressures of DMSO–acetone, DMSO–tetrahydrofuran, and DMSO–ethyl acetate systems are listed in column 2 of Table II. Two separate runs of *P-x* data were taken for the DMSO–acetone system at 35°C to ascertain the reproducibility of the data. Average deviation between the two runs was about 0.3% in pressure as shown in Table II. These vapor-pressure data over the whole range of composition were reduced to calculate the excess Gibbs free energy by Barker's method (2) of successive approximation. That is, the total vapor pressures in a binary mixture are calculated from the following equation (*11*).

$$P_{\text{calcd}} = \frac{x_1\gamma_1 f_1^\circ}{\phi_1} + \frac{x_2\gamma_2 f_2^\circ}{\phi_2} \qquad (1)$$

Based on Equation 1, the coefficients of the three-parameter Redlich-Kister equation (*13*), the Renon NRTL equation (*14*), and the Wilson equation (*18*) were calculated so that the criteria $\Sigma[(P_{\text{exptl}} - P_{\text{calcd}})/P_{\text{exptl}}]^2$ = minimum were satisfied. Fugacity coefficients (ϕ_i) were calculated by using second-virial coefficients as given elsewhere (*11*). The pure-component second-virial coefficients and the cross-virial coefficients were estimated by the method of Prausnitz et al. (*11*). The critical properties

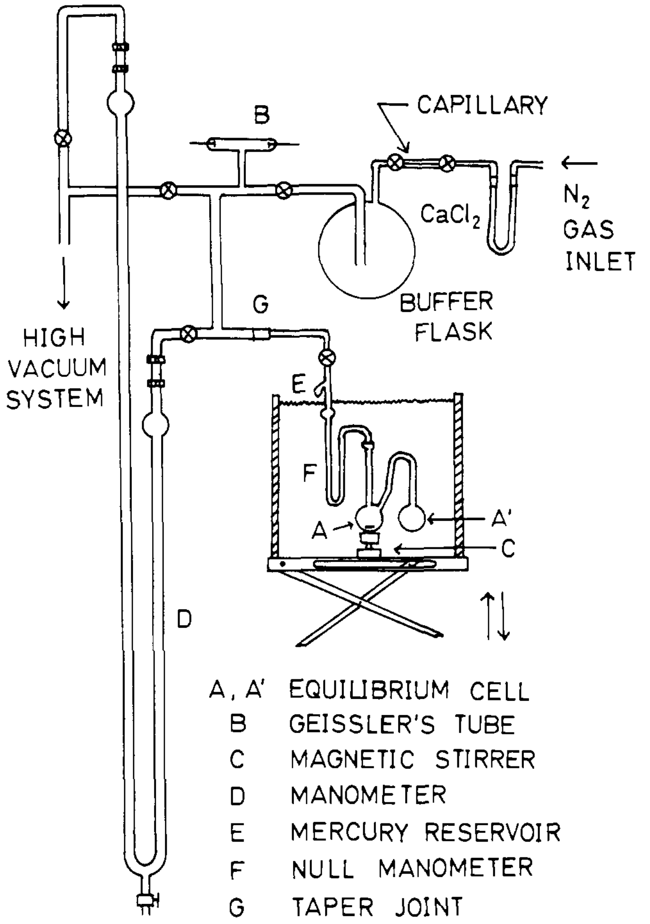

Figure 1. Schematic diagram of apparatus

Table I. Physical Constants of Materials Used

	Refractive index		Vapor press, mm Hg	
Component	Measured	Lit	Measured	Lit
		25°C		
DMSO	1.4772	1.4773 (*10*)	0.59	0.582 (*9*)
Acetone	1.3564	1.35662 (*17*)	231.2	229.4 (*17*)
Tetrahydrofuran	1.4049	1.4048 (*15*)	161.7	162.02 (*15*)
Ethyl acetate	1.3701	1.37012[a] (*17*)	95.4	94.5 (*6*)

[a] At 25.2°C.

Table II. Isothermal Vapor-Liquid Equilibria

x_1	P_{exptl}, mm Hg	P_{calcd}, mm Hg	y_1	ln γ_1	ln γ_2	G^E, cal/mol
DMSO(1)-acetone(2) system at 25°C						
0.0000	231.2	...	0.0000	0.7954	0.0000	0
0.0989	210.6	210.4	0.0005	0.6018	0.0098	41
0.1977	193.5	192.1	0.0010	0.4500	0.0360	70
0.2998	174.2	174.4	0.0015	0.3265	0.0767	90
0.4000	156.6	157.1	0.0020	0.2311	0.1280	100
0.5019	137.9	138.7	0.0026	0.1550	0.1903	102
0.6017	119.2	118.9	0.0034	0.0974	0.2611	96
0.6974	97.8	97.5	0.0046	0.0557	0.3382	84
0.7973	71.5	71.5	0.0069	0.0250	0.4291	63
0.9006	39.1	39.2	0.0139	0.0061	0.5356	35
1.0000	0.59	...	1.0000	0.0000	0.6518	0
35°C, Run 1						
0.0000	349.3	...	0.0000	0.7158	0.0000	0
0.0990	317.1	318.1	0.0007	0.5578	0.0081	38
0.1978	290.6	289.2	0.0013	0.4265	0.0309	67
0.2999	261.4	261.5	0.0020	0.3144	0.0679	87
0.4001	234.8	234.8	0.0027	0.2246	0.1162	98
0.5021	205.8	206.7	0.0035	0.1511	0.1765	100
0.6019	177.3	176.8	0.0047	0.0948	0.2458	95
0.6976	144.9	144.7	0.0063	0.0539	0.3216	83
0.7975	105.8	105.9	0.0094	0.0239	0.4103	63
0.9008	57.8	57.8	0.0190	0.0057	0.5127	34
1.0000	1.19	...	1.0000	0.0000	0.6215	0
Run 2						
0.0000	349.3	...	0.0000	0.7180	0.0000	0
0.1040	315.5	316.7	0.0007	0.5458	0.0092	40
0.2015	287.4	288.3	0.0014	0.4169	0.0323	67
0.2972	261.3	262.1	0.0020	0.3142	0.0664	86
0.4432	223.6	222.4	0.0030	0.1928	0.1374	99
0.4916	208.9	208.8	0.0035	0.1603	0.1659	100
0.5979	177.1	177.1	0.0047	0.1005	0.2374	95
0.7085	140.1	140.1	0.0066	0.0536	0.3258	81
0.8014	103.8	104.1	0.0097	0.0254	0.4127	63
0.9015	58.0	57.9	0.0190	0.0064	0.5217	35
1.0000	1.19	...	1.0000	0.0000	0.6474	0
45°C						
0.0000	514.0	...	0.0000	0.6697	0.0000	0
0.0991	465.7	469.1	0.0009	0.5264	0.0074	37
0.1980	427.5	425.4	0.0017	0.4055	0.0284	65
0.3001	383.1	383.4	0.0025	0.3010	0.0630	85
0.4004	343.1	343.0	0.0034	0.2161	0.1087	96
0.5024	300.1	300.9	0.0045	0.1461	0.1662	97
0.6021	257.2	256.7	0.0060	0.0920	0.2328	94
0.6978	209.8	209.5	0.0081	0.0525	0.3062	82
0.7978	152.5	152.8	0.0122	0.0233	0.3927	62
0.9009	83.4	83.3	0.0244	0.0056	0.4926	34
1.0000	2.20	...	1.0000	0.0000	0.5991	0
DMSO(1)-Tetrahydrofuran(2) system at 25°C						
0.0000	161.7	...	0.0000	1.6300	0.0000	0
0.0998	149.8	149.2	0.0013	1.1393	0.0244	80
0.2005	141.2	140.5	0.0020	0.8027	0.0829	137
0.3015	133.0	132.9	0.0024	0.5644	0.1621	168
0.3986	124.9	125.1	0.0029	0.3966	0.2520	183
0.5026	115.0	115.4	0.0034	0.2626	0.3615	185
0.6006	103.8	104.2	0.0041	0.1675	0.4782	173
0.7009	89.6	89.3	0.0052	0.0946	0.6139	148
0.7989	70.3	70.0	0.0072	0.0438	0.7665	112
0.8990	42.2	42.3	0.0129	0.0115	0.9487	63
1.0000	0.59	...	1.0000	0.0000	1.1674	0
35°C						
0.0000	245.9	...	0.0000	1.5977	0.0000	0
0.0999	227.2	225.9	0.0017	1.1133	0.0241	81
0.2006	213.7	212.5	0.0026	0.7824	0.0817	136
0.3017	200.6	200.6	0.0032	0.5486	0.1594	170
0.3988	187.8	188.5	0.0038	0.3847	0.2473	185
0.5029	173.0	173.4	0.0046	0.2540	0.3542	186
0.6008	155.5	155.9	0.0056	0.1617	0.4676	174
0.7011	133.5	133.2	0.0071	0.0911	0.5991	149
0.7992	104.2	103.8	0.0098	0.0420	0.7467	112
0.8992	62.2	62.4	0.0176	0.0110	0.9220	63
1.0000	1.19	...	1.0000	0.0000	1.1313	0
45°C						
0.0000	364.8	...	0.0000	1.5249	0.0000	0
0.1000	335.9	334.7	0.0020	1.0717	0.0227	81
0.2008	315.6	313.9	0.0032	0.7569	0.0775	135
0.3019	295.5	295.4	0.0040	0.5321	0.1524	169
0.3991	276.4	276.9	0.0048	0.3730	0.2378	184
0.5032	253.0	253.9	0.0058	0.2458	0.3420	186
0.6012	227.2	227.6	0.0071	0.1560	0.4526	173
0.7014	194.0	194.0	0.0090	0.0875	0.5803	148
0.7994	150.8	150.8	0.0126	0.0401	0.7228	112
0.8993	89.5	89.7	0.0226	0.0104	0.8906	63
1.0000	2.20	...	1.0000	0.0000	1.0893	0
DMSO(1)-ethyl acetate(2) system at 25°C						
0.0000	95.4	...	0.0000	1.4323	0.0000	0
0.0988	88.0	87.8	0.0020	1.0598	0.0186	72
0.1954	81.9	82.0	0.0032	0.7908	0.0645	122
0.2913	77.1	77.1	0.0041	0.5876	0.1295	156
0.4045	71.4	71.4	0.0051	0.4047	0.2266	177
0.4830	67.0	67.1	0.0059	0.3044	0.3065	181
0.6038	59.5	59.5	0.0073	0.1823	0.4517	171
0.6963	52.4	52.2	0.0090	0.1107	0.5849	151
0.7969	41.4	41.5	0.0121	0.0521	0.7579	116
0.8991	25.8	25.8	0.0211	0.0138	0.9730	66
1.0000	0.59	...	1.0000	0.0000	1.2380	0
35°C						
0.0000	151.6	...	0.0000	1.3710	0.0000	0
0.0989	140.4	139.3	0.0024	1.0210	0.0176	72
0.1955	130.3	130.0	0.0040	0.7653	0.0613	122
0.2914	121.7	121.9	0.0052	0.5700	0.1238	155
0.4047	112.2	112.5	0.0065	0.3927	0.2180	178
0.4831	105.8	105.6	0.0075	0.2954	0.2956	181
0.6039	93.0	93.3	0.0094	0.1765	0.4371	171
0.6965	81.8	81.5	0.0115	0.1067	0.5668	151
0.7970	64.5	64.6	0.0157	0.0500	0.7343	116
0.8992	39.8	39.8	0.0275	0.0131	0.9415	65
1.0000	1.19	...	1.0000	0.0000	1.1942	0
45°C						
0.0000	233.0	...	0.0000	1.3404	0.0000	0
0.0990	215.3	214.4	0.0029	0.9955	0.0173	72
0.1956	199.5	199.8	0.0047	0.7451	0.0601	123
0.2916	186.9	187.1	0.0062	0.5546	0.1211	156
0.4049	173.0	172.3	0.0078	0.3823	0.2128	178
0.4834	160.9	161.3	0.0091	0.2877	0.2883	182
0.6042	141.4	141.9	0.0114	0.1722	0.4258	172
0.6967	124.0	123.5	0.0141	0.1044	0.5521	152
0.7972	97.4	97.5	0.0192	0.0491	0.7158	117
0.8993	60.0	60.0	0.0338	0.0129	0.9191	66
1.0000	2.20	...	1.0000	0.0000	1.1686	0

Table III. Critical Properties and Parameters Characterizing Vapor-Phase Nonideality

	T_c, K	P_c, atm	v_c, cc/mol	ω	ω_H	μ, Debye	η
DMSO	707 (*9*)	57.7 (*9*)	276.0 (*9*)	0.425[a]	0.187[b]	4.30 (*9*)	0.0[b]
Acetone	508.7 (*11*)	46.6 (*11*)	213.5 (*11*)	0.309 (*11*)	0.187 (*11*)	2.88 (*11*)	0.0 (*11*)
Tetrahydrofuran	538.7[c]	52.2[c]	222.5[c]	0.255[a]	0.252[b]	1.70 (*16*)	0.28[b]
Ethyl acetate	523.3 (*11*)	37.8 (*11*)	286.0 (*11*)	0.373 (*11*)	0.278 (*11*)	1.78 (*11*)	0.50 (*11*)

[a] Calculated by the equation of Edmister (*4*). [b] Determined from similar substance or homomorph. [c] Calculated by Fishtine's method (*5*).

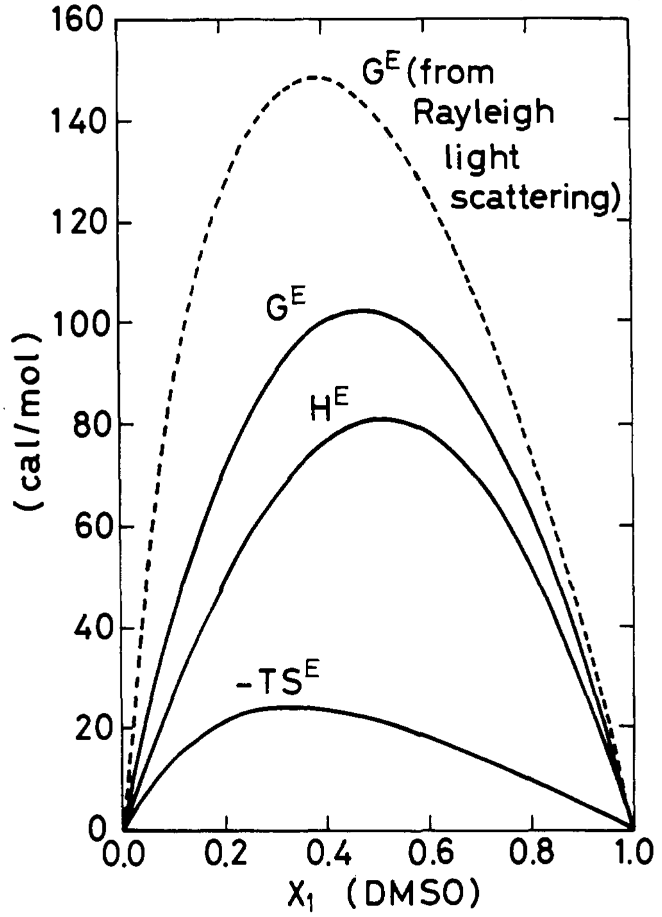

Figure 2. Excess thermodynamic functions for DMSO-acetone system at 25°C. Data of H^E; Clever and Pigott (*3*). Broken-curve; G^E determined from Rayleigh light scattering (*3, 7*)

and other parameters for estimating the second-virial coefficient are shown in Table III. The pure component fugacity (f_i°) was calculated as suggested by Prausnitz et al. (*11*).

Columns 3-7 of Table II show the calculated vapor-liquid equilibria of DMSO-acetone, DMSO-tetrahydrofuran, and DMSO-ethyl acetate systems by the Renon NRTL equation. Table IV shows the coefficients of the Redlich-Kister equation, the NRTL equation, and the Wilson equation and the comparisons of the results by these equations. Although all three equations correlate the data satisfactorily, the NRTL equation gives slightly better fitting in average. The excess Gibbs free energies calculated by these equations give almost the same values.

Discussion

Columns 5 and 6 of Table II show the activity coefficients of DMSO-acetone, DMSO-tetrahydrofuran, and DMSO-ethyl acetate systems, respectively. These systems are moderately nonideal. The DMSO-acetone system is more ideal than the DMSO-tetrahydrofuran system. The smaller nonideality of the DMSO-acetone system is considered to result from the stronger dipole-dipole interaction between DMSO and acetone (*8*). The temperature dependency of the activity coefficient is considerable for the DMSO-acetone system but negligibly small for the DMSO-tetrahydrofuran and DMSO-ethyl acetate systems.

The excess enthalpy of the DMSO-acetone system at 25°C has been reported by Clever and Pigott (*3*). Values of excess entropy have been calculated by combining the excess enthalpy with the excess Gibbs free energy obtained in this work. Figure 2 shows the values of G^E, H^E, and TS^E of the DMSO-acetone system at 25°C and shows a comparison between the excess Gibbs free energy obtained in this work and those determined from the Rayleigh light scattering (*3, 7*). As shown in Figure 2, the excess Gibbs free energy obtained in this work is about 40% less than the value determined from the Rayleigh light scattering at equimolar mixture.

Nomenclature

f_i = liquid-phase fugacity of component *i*, mm Hg
G^E = excess Gibbs free energy, cal/mol
H^E = excess enthalpy, cal/mol
P = vapor pressure, mm Hg
R = gas constant, cal/mol K
S^E = excess entropy, cal/mol K
T = temperature, K
v = liquid molar volume, cc/mol
x_i = mole fraction of component *i* in the liquid phase
y_i = mole fraction of component *i* in the vapor phase

Greek Letters

γ_i = liquid-phase activity coefficient of component *i*
η = vapor-phase association constant
μ = dipole moment, Debye
ϕ_i = vapor-phase fugacity coefficient of component *i*
ω = acentric factor
ω_H = acentric factor of homomorph of polar component

Subscripts

1 = DMSO component
2 = second component, acetone, tetrahydrofuran, or ethyl acetate
c = critical property

Superscript

° = pure component

Table IV. Parameters of Various Equations for Excess Gibbs Free Energy

		Redlich-Kister, 3-parameter[a]				Wilson, 2-parameter[b]			NRTL, 3-parameter[c]			
System	Temp, °C	B	C	D	σ^d	A_{12}	A_{21}	σ^d	τ_{12}	τ_{21}	α	σ^d
DMSO(1)–acetone(2)	25	0.6910	−0.0651	0.0233	0.37	0.5498	0.8271	0.37	0.3153	0.5585	0.9068	0.36
	35 (Run 1)	0.6553	−0.0455	0.0125	0.24	0.5948	0.8078	0.24	0.2689	0.4916	0.6763	0.26
	(Run 2)	0.6524	−0.0333	0.0303	0.27	0.6321	0.7684	0.45	0.3556	0.4702	1.0147	0.29
	45	0.6247	−0.0345	0.0095	0.33	0.6273	0.7987	0.33	0.2641	0.4470	0.6456	0.33
DMSO(1)–tetrahydrofuran(2)	25	1.2506	−0.1919	0.1228	0.56	0.2941	0.6543	0.61	0.6240	1.2174	0.6627	0.35
	35	1.2188	−0.1934	0.1198	0.58	0.2981	0.6756	0.63	0.5991	1.1984	0.6772	0.38
	45	1.1779	−0.1836	0.1077	0.51	0.3128	0.6906	0.53	0.5656	1.1405	0.6825	0.28
DMSO(1)–ethyl acetate(2)	25	1.2212	−0.0831	0.1031	0.27	0.4008	0.5499	0.62	0.7352	0.9875	0.6836	0.27
	35	1.1813	−0.0763	0.0917	0.40	0.4177	0.5642	0.62	0.7029	0.9381	0.6894	0.36
	45	1.1514	−0.0741	0.0944	0.32	0.4300	0.5725	0.64	0.6932	0.9188	0.7174	0.29

[a] Redlich-Kister equation (*13*): $\dfrac{G^E}{RT} = x_1x_2[B + C(x_1 - x_2) + D(x_1 - x_2)^2]$

[b] Wilson equation (*18*): $\dfrac{G^E}{RT} = x_1 \ln (x_1 + A_{12}x_2) + x_2 \ln (x_2 + A_{21}x_1)$

[c] NRTL equation (*14*): $\dfrac{G^E}{RT} = x_1x_2\left[\dfrac{\tau_{21} \exp(-\alpha\tau_{21})}{x_1 + x_2 \exp(-\alpha\tau_{21})} + \dfrac{\tau_{12} \exp(-\alpha\tau_{12})}{x_2 + x_1 \exp(-\alpha\tau_{12})}\right]$

[d] Standard deviation in relative pressure, %; N, number of experimental points: $100 \times \sqrt{\Sigma \left(\dfrac{P_{\text{exptl}} - P_{\text{calcd}}}{P_{\text{exptl}}}\right)^2 / N}$

Literature Cited

(1) Arm, H., Daeniker, H., Schaller, R., *Helv. Chim. Acta*, **48**, 1772 (1965).
(2) Barker, J. A., *Aust. J. Chem.*, **6**, 207 (1953).
(3) Clever, H. L., Pigott, S. P., *J. Chem. Thermodyn.*, **3**, 221 (1971).
(4) Edmister, W. C., *Petrol. Refiner*, **37**, 173 (1958).
(5) Fishtine, S. H., *Ind. Eng. Chem. Fundam.*, **2**, 149 (1963).
(6) Geiseler, G., Mehnert, E., *Z. Phys. Chem.* (*Frankfurt*), **64**, 26 (1969).
(7) Haynes, L. L., Schmidt, R. L., Clever, H. L., *J. Chem. Eng. Data*, **15**, 534 (1970).
(8) Jacob, S. W., Rosenbaum, E. E., Wood, D. C., "Dimethyl Sulfoxide," Vol I, Marcel Dekker, New York, N.Y., 1971.
(9) Jose, J., Philippe, R., Clecht, P., *Bull. Soc. Chim. Fr.*, 2860 (1971).
(10) Lindberg, J. J., Kenttämaa, J., Nissema, A., *Suomen Kem.*, **B34**, 156 (1961).
(11) Prausnitz, J. M., Eckert, C. A., Orye, R. V., O'Connell, J. P., "Computer Calculations for Multicomponent Vapor-Liquid Equilibria," Prentice-Hall, Englewood Cliffs, N.J., 1967.
(12) Quitzsch, K., Hüttig, R., Vogel, H.-G., Geseman, H.-J., Geiseler, G., *Z. Phys. Chem.* (*Leipzig*), **223**, 225 (1963).
(13) Redlich, O., Kister, A. T., *Ind. Eng. Chem.*, **40**, 345 (1948).
(14) Renon, H., Prausnitz, J. M., *AIChE J.*, **14**, 135 (1968).
(15) Signer, R., Arm, H., Daeniker, H., *Helv. Chim. Acta*, **52**, 2347 (1969).
(16) Stecher, P. G., "The Merck Index," 8th ed., Merck & Co., Rahway, N.J., 1968.
(17) Timmermans, J., "Physico-Chemical Constants of Pure Organic Compounds," Vol I, Elsevier, New York, N.Y., 1950.
(18) Wilson, G. M., *J. Amer. Chem. Soc.*, **86**, 127 (1964).

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Permeability of Teflon Polytetrafluoroethylene Resin and Buna-*N* Butadiene-Nitrile Rubber to Deuterium[1]

Roy G. Derrick and McIntyre R. Louthan, Jr.
Savannah River Laboratory, E. I. du Pont de Nemours & Co., Aiken, S.C. 29801

The permeability, ϕ, of Teflon and buna-*N* to deuterium at 0.16–5 atm between 196 and 441K is given by: $\phi_{\text{Teflon}} = 2.8 \times 10^{-4} \exp(-4950/RT)$ and $\phi_{\text{Buna-}N} = 1.02 \times 10^{-2} \exp(-6700/RT)$ cm^3 (NTP gas) cm^{-1} atm^{-1} sec^{-1}. Temperature dependence of deuterium diffusivity, D, in these materials was calculated from measurements of the rate of rise to, and decline from, steady-state permeation. Deuterium solubilities, S, were also calculated.

Teflon polytetrafluoroethylene resin and buna-*N*, a nitrile rubber, are often used as gasket materials to seal valves, transducers, and/or secondary containers in hydrogen handling systems (*1, 3, 5*). Systems handling deuterium, an hydrogen isotope, are similarly constructed. Permeation data for Teflon and buna-*N* are necessary to predict system responses to various deuterium exposures where low-level permeation through the gaskets must be controlled. The permeability and the diffusivity of deuterium in these gasket materials were measured over a range of temperatures.

Experimental

The permeability was calculated from measurements of the steady-state deuterium flux through membranes exposed to 0.16–5 atm deuterium gas in the test apparatus sketched in Figure 1. Test specimens were ~0.050 cm thick by about 4.83 cm in diameter. High-purity

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[1] Address correspondence to A. E. Symonds, Technical Information Service, Savannah River Laboratory, E. I. du Pont de Nemours & Co., Aiken, S.C. 29801.