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Solid–Liquid Phase Diagram and Excess Properties at 303.16 and 313.16 K of Dimethyl Sulfoxide (1) + Sulfolane (2) Binary System

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Volumes on mixing and dielectric constants of the binary system dimethyl sulfoxide (1) + sulfolane (2) were measured, at 303.16 and 313.16 K, over the entire composition range $0 \leq x \leq 1$. Solid–liquid equilibrium temperatures were also taken. As already reported, in the case of some other binary mixtures involving sulfolane, more than one phase diagram may occur owing to the occasional formation of different solid phases. Cryoscopic data, which refer to sulfolane solutions in equilibrium with rotational crystal I, supply evidence for the deposition of mixed crystals. A partition coefficient, not depending on composition, $K = 0.25$ was calculated. In the case of solutions in equilibrium with ordinary crystal II an improved method, proposed by one of us, allows to calculate, down to the eutectic temperature, solvent activities, a_s, and rational activity coefficients, γ_s; these do not differ from unity noticeably. As it concerns the behavior of the dimethyl sulfoxide as solvent, cryoscopic data are indicative of the existence of at least two different crystalline phases with comparable stability. The extents of excess properties, on the whole, agree in picturing this binary system as regular not quite athermal mixtures.

Introduction

The increasing use of mixed solvents in electrochemical studies prompted this apprasial of selected mixtures of solvents with moderately high dielectric constant.

The thermodynamic and physical properties of dimethyl sulfoxide (Me_2SO) and sulfolane solutions ($\epsilon = 40$–46) were studied over the entire composition range. In these mixtures only negligible interactions are expected between components because of the predominant aliphatic character of dimethyl sulfoxide (*1*) and the steric hindrance of the globular molecule of sulfolane (*2*, *3*).

Furthermore, the two substances possess comparable polarity and hence mixtures are expected to be an almost isodielectric medium whose properties depend on composition monotonically.

In this report we present the solid–liquid phase diagram and excess volumes and dielectric constants of this binary system over the entire composition range, at 303.16 and 313.16 K.

Experimental Section

Materials, Apparatus, and Procedure. Sulfolane, kindly supplied by Shell Italia, was purified and carefully dried as already reported (*2*). Properties of the purified sample (Table I) strictly agree with the literature data (*3*, *4*). Rudi Pont dimethyl sulfoxide (Me_2SO) was distilled repeatedly under reduced pressure. Then the collected product was stored over molecular sieves, 5-Å type, at least 48 h and distilled under vacuum shortly before use. The purity of the substance was better than 99.8%. Its melting point was 291.58 K which agrees with the Garnsey and Prue value (*5*) ($T = 291.70$ K).

Solutions were prepared by weight (reduced to mass), stored in dark containers, and protected from moisture as far as possible.

Densities were measured at 303.16 and 313.16 K with an Anton Paar (Austria) vibrating tube densimeter (*6*).

Dielectric constants were measured, at 2 MHz, with a W.T.W. dielectric constant measuring apparatus by using the heterodyne beat method. The measuring cell, Type DFL 2/S, was thermostated by water circulation within 0.01 K. The apparatus as well as the calibration procedure were described elsewhere (*6*, *7*).

The maximum error on density did not exceed 1×10^{-5} g·cm^{-3} and the maximum error on dielectric constant was estimated to be 0.01.

Apparatus and procedure for carrying out cryoscopic measurements were described elsewhere (*8*). Temperatures were measured with a platinum resistance thermometer, using a G2 Model Müller Bridge. The accuracy in measuring temperatures was better than 0.005 K. Both cooling and heating curves were taken for each solution; initial freezing temperatures and final melting temperatures agreed within 0.01 K.

For the sake of uniformity with previous works sulfolane is indicated as component 2 but, in the case of cryoscopic data, in order to avoid misunderstanding between solvent and substance 1 and solute and substance 2, we indicate as x_s, a_s, and γ_s, and x_D, a_D, and γ_D, molar fraction, activity, and rational activity coefficient of sulfolane and dimethyl sulfoxide, respectively.

Results and Discussion

Excess Volumes. Excess volumes of mixing dimethyl sulfoxide (1) + sulfolane (2) are shown graphically in Figure 1. The system exhibits negative deviations from ideality, never exceedng 0.1 cm^3 mol^{-1} and only slightly increasing with temperature. The minimum is skewed toward the region richer in the smaller component (dimethyl sulfoxide), as expected. The experimental data, at each temperature, were fitted by a least-squares computer program to smoothing equations of the type

$$V^E = x_1x_2\{A + B(x_2 - x_1) + C(x_2 - x_1)^2 + ...\} \qquad (1)$$

The parameters of eq 1 and the standard deviations σ of smoothing equations, at each temperature, are included in Table II; V^E values, as a function of mole fraction, x_2, of sulfolane, are summarized in Table III, as well as deviations δV^E of the smoothing equations.

The data supply evidence for the supposition that in dimethyl sulfoxide (1) + sulfolane (2) mixtures interactions between like and unlike molecules are of very limited importance and result in only scarcely detectable volume contractions, whereas the asymmetry in the V^E–x_2 curves has to be ascribed mainly to the difference in volumes of pure substances.

Dielectric Constants. Deviations from ideality of dielectric constants, $\epsilon_{1,2}{}^E$, over the entire composition range, at two temperatures, are shown graphically in Figure 2. They are calculated on the basis of a linear dependence of $\epsilon_{1,2}$ values on ideal volume fractions, φ, in the case of ideal mixtures. The equation

$$\epsilon_{1,2} = \bar{\epsilon}_1\varphi_1 + \bar{\epsilon}_2\varphi_2 = \epsilon_1{}^0\varphi_1 + \epsilon_2{}^0\varphi_2 + \epsilon_{1,2}{}^E \qquad (2)$$

has been illustrated elsewhere (*9*); in it $\epsilon_{1,2}$ is the measured dielectric constant of a solution with ideal composition φ_i; $\epsilon_i{}^0$

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Table I. Description and Physical Properties of Component Liquids

			V^0/cm^3 mol^{-1}		ϵ		mp/K	
	source	T/K	obsd	lit.^{a}	obsd	lit.^{a}	obsd	lit.^{a}
Me$_2$SO	Rudi Pont reagent grade	303.16	71.667	71.656 (*1*)	45.64	45.82 (*1*)	291.58	291.70 (*5*) 291.71 (*1*)
		313.16	72.338	72.326 (*1*)	44.47	44.55 (*1*)		
sulfolane	Shell Italia	303.16	95.215	95.160 (*6*) 95.200 (*4*)	43.16	43.30 (*6*)	301.61	301.61 (*2*, *4*)
		313.16	95.892	95.856 (*6*) 95.891 (*4*)	42.10	42.05 (*6*) 42.12 (*4*)		

^{a}Figures in parentheses are reference numbers.

Table II. Parameters A, B, C, D and A', B', C' and Standard Deviations σ of the Smoothing Equations

T/K	A	B	C	D	σ
303.16	-0.299	0.088	-0.090	-0.083	0.002
313.16	-0.321	0.087	-0.099	-0.111	0.001

T/K	A'	B'	C'	σ
303.16	1.320	-0.079	0.350	0.01
313.16	0.805	-0.388	-0.043	0.01

Table III. Molar Excess Volumes, V^E, at 303.16 and 313.16 K and Deviations δV^E from Smoothing Equations

T = 303.16 K			T = 313.16 K		
x_2	V^E/ cm^3 mol^{-1}	$10^3\delta V^E$/ cm^3 mol^{-1}	x_2	V^E/ cm^3 mol^{-1}	$10^3\delta V^E$/ cm^3 mol^{-1}
0.0227	-0.009	0	0.1009	-0.036	0
0.1009	-0.036	-1	0.1233	-0.043	0
0.1233	-0.040	1	0.3580	-0.080	1
0.3580	-0.076	-1	0.3956	-0.083	-1
0.3956	-0.076	-1	0.5570	-0.077	0
0.6475	-0.066	2	0.6475	-0.069	-1
0.7372	-0.054	-2	0.7372	-0.061	0
0.8711	-0.036	1	0.8711	-0.040	0
0.9045	-0.028	0			

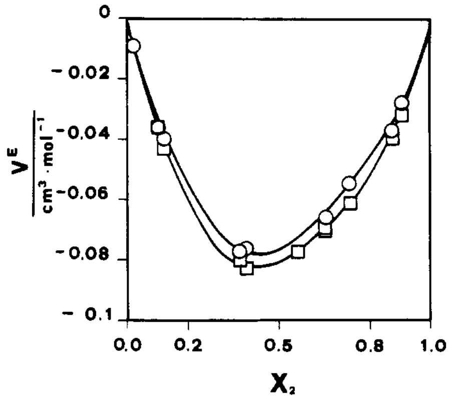

Figure 1. Excess volumes, V^E, as a function of sulfolane mole fraction, x_2: ○, T = 303.16 K; □, T = 313.16 K.

and $\bar{\epsilon}_i$ are the dielectric constants of the component i in the pure state and at the volume fraction φ_i, respectively.

Experimental data were fitted by a least-squares computer program to smoothed equations of the type

$$\epsilon_{1,2}^E = \varphi_1\varphi_2\{A' + B'(\varphi_2 - \varphi_1) + C'(\varphi_2 - \varphi_1)^2 + ...\} \quad (3)$$

The parameters of eq 3 as well as deviations σ of smoothed equations are also included in Table II. Measured dielectric constants, $\epsilon_{1,2}$, as well as $\epsilon_{1,2}^E$ values recalculated by eq 3 at 303.16 and 313.16 K, are reported in Table IV together with deviations $\delta\epsilon_{1,2}^E$ of smoothed equations.

The extent of positive deviations, which steadily increase with decreasing temperature and never exceed $0.4\epsilon_{1,2}$ strongly support the conclusions drawn from volume measurements of only scarcely noticeable interactions between the two components, probably dipole-dipole interactions.

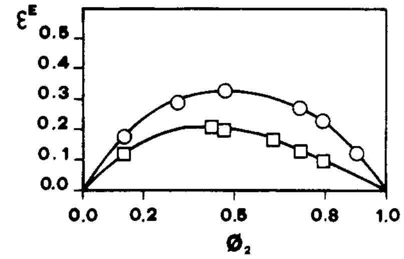

Figure 2. Deviations from ideality, $\epsilon_{1,2}^E$, of dielectric constants as a function of sulfolane volume fraction, φ_2; ○, T = 303.16 K; □, T = 313.16 K.

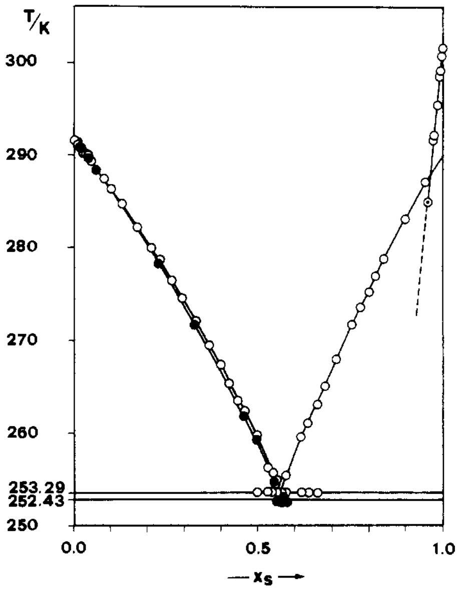

Figure 3. Solid-liquid phase diagram of dimethyl sulfoxide (1)-sulfolane system: ○, stable system; ●, metastable system.

Table IV. Measured Dielectric Constants $\epsilon_{1,2}$ at 303.16 and 313.16 K, Excess Dielectric Constants $\epsilon_{1,2}^E$, and Deviations $\delta\epsilon_{1,2}^E$ from Smoothing Equations

T = 303.16 K				T = 313.16 K			
φ_2	$\epsilon_{1,2}$	$\epsilon_{1,2}^E$	$\delta\epsilon_{1,2}^E$	φ_2	$\epsilon_{1,2}$	$\epsilon_{1,2}^E$	$\delta\epsilon_{1,2}^E$
0.130	45.50	0.18	0.00	0.130	44.28	0.12	0.00
0.309	45.16	0.29	-0.01	0.425	43.68	0.22	0.01
0.465	44.82	0.33	0.00	0.465	43.57	0.20	-0.01
0.709	44.16	0.28	0.00	0.625	43.16	0.17	0.00
0.788	43.92	0.24	0.00	0.709	42.91	0.12	-0.01
0.900	43.54	0.13	0.00	0.788	42.70	0.10	0.01

Phase Diagram. Figure 3 shows the solid-liquid phase diagram as obtained by thermal analysis (heating and freezing curves). Related data are summarized in Table V, VI, and VII; as already reported (*2*) pure sulfolane exhibits a mesomorphic rotational phase I in the region 301.6-288.5 K, the latter temperature being the transition temperature crystal I ↔ crystal II (crystal II is an ordinary crystalline form of sulfolane). The

Table V. Sulfolane Solutions of Dimethyl Sulfoxide in Equilibrium with Crystal I Cryoscopic Data[a]

x_s	m	T/K	ϑ/m	$(\vartheta/m)_i$	K
1.0000	0.0000	301.610		65.00	
0.9976	0.0198	300.649	48.54	64.65	0.25
0.9941	0.0495	299.243	47.82	64.13	0.25
0.9921	0.0663	298.461	47.50	63.83	0.25
0.9869	0.1101	295.443	46.93	63.09	0.26
0.9842	0.1335	295.335	47.00	62.70	0.25
0.9758	0.2062	292.064	46.30	61.51	0.25
0.9699	0.2582	289.753	45.92	60.69	0.25
0.9575	0.3694	284.801	45.50	59.00	0.23

[a] Sulfolane molar fraction, x_s; dimethyl sulfoxide molality, m; initial freezing points, T/K; molar depressions, ϑ/m, ideal molar depressions, $(\vartheta/m)_i$, by eq 4; partition coefficient, K.

Table VI. Sulfolane Solutions of Dimethyl Sulfoxide in Equilibrium with Crystal II Cryoscopic Data[a]

			ϑ				
x_s	m	T/K	obsd	eq 5	ϑ/m	a_s (eq 6)	δ_s
1.0000	0.0000	290.234	0.000	0.000	7.690	1.000	1.000
0.8974	0.9518	283.034	7.200	7.145	7.565	0.893_4	0.996
0.8372	1.6178	278.419	11.815	11.795	7.303	0.829_2	0.990
0.8170	1.8484	276.894	13.340	13.320	7.217	0.808_7	0.990
0.7998	2.0658	275.480	14.754	14.715	7.142	0.790_8	0.989
0.7759	2.4034	273.504	16.730	16.796	6.961	0.764_4	0.985
0.7528	2.7324	271.678	18.556	18.726	6.791	0.740_5	0.984
0.7307	3.0667	269.733	20.501	20.589	6.685	0.718_1	0.983
0.7100	3.3995	267.933	22.301	22.350	6.560	0.697_4	0.982
0.6794	3.9271	265.097	25.137	24.970	6.401	0.667_5	0.982
0.6588	4.3092	263.474	26.760	26.759	6.210	0.647_8	0.983
0.6358	4.7667	261.181	29.053	28.815	6.095	0.625_6	0.984
0.6148	5.2127	259.557	30.677	30.773	5.885	0.605_1	0.984
0.5751	6.1474	255.329	34.905	34.976	5.678	0.563_0	0.980
0.5603	6.5305	[253.01][b]					

[a] Sulfolane mole fractions, x_s; dimethyl sulfoxide molalities, m; initial freezing points, T; freezing point depressions, ϑ; molar depressions, ϑ/m; sulfolane activities, a_s; rational activity coefficients, γ_a. [b] Value in brackets refers to peritectic points.

Table VII. Cryoscopic Data of Sulfolane Solutions in Dimethyl Sulfoxide[a]

x_s	m	T/K	ϑ	ϑ/m
0.0000	0.0000	291.583		
0.0075	0.0963	291.188	0.395	4.102
0.0156	0.2030	290.768	0.815	4.015
0.0230	0.3015	290.358	1.225	4.063
		290.279[b]	1.304	4.325
0.0269	0.3532	290.171	1.412	3.998
0.0308	0.4069	289.963	1.620	3.981
0.0378	0.5024	289.657	1.926	3.834
		289.559[b]	2.024	4.029
0.0451	0.6048	289.248	2.335	3.861
		289.154[b]	2.429	4.016
0.0610	0.8312	288.364	3.219	3.873
		288.315[b]	3.268	3.932
0.0777	1.0783	287.437	4.146	3.845
0.0992	1.4096	286.282	5.301	3.761
0.1295	1.9042	284.730	6.853	3.599
0.1710	2.6409	282.232	9.351	3.541
0.2087	3.3751	279.988	11.595	3.435
0.2321	3.8677	278.595	12.988	3.358
		278.373[b]	13.210	3.415
0.2648	4.6102	276.421	15.162	3.289
0.2942	5.3346	274.509	17.074	3.201
0.3300	6.3026	272.102	19.481	3.091
		271.906[b]	19.677	3.122
0.3662	7.3936	269.560	22.023	2.979
0.3940	8.3213	267.397	24.216	2.910
0.4213	9.3188	265.426	26.157	2.807
0.4453	10.2757	263.463	28.120	2.737
0.4676	11.2396	262.325	29.258	2.603
		261.865[b]	29.718	2.644
0.4957	12.5792	259.810	31.773	2.526
		259.340[b]	32.243	2.563
0.5249	14.1396	256.387	35.196	2.489
0.5384	14.9296	255.844	35.739	2.394
0.5524	15.7959	255.175	36.408	2.305
		254.549[b]	37.034	2.345
0.5599	16.2825	[253.184][c]		

[a] Sulfolane mole fractions, x_s; sulfolane molalities, m; initial freezing points of dimethyl sulfoxide, T; freezing point depressions, ϑ; molar depressions, ϑ/m. [b] Values refer to the lower melting dimethyl sulfoxide crystalline phase. [c] Value in brackets refers to peritectic points.

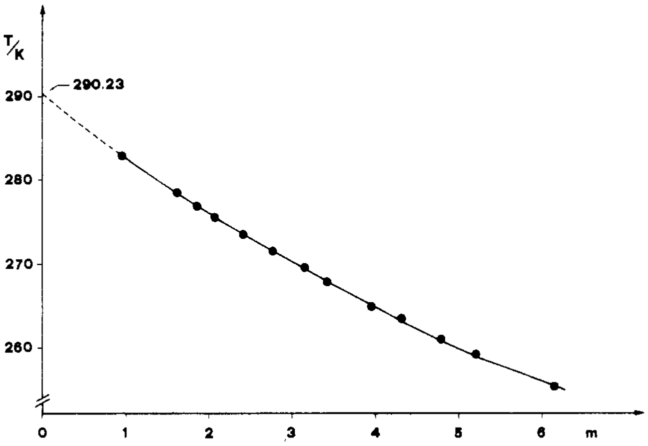

Figure 4. Sulfolane solutions of dimethyl sulfoxide in equilibrium with crystal II. Initial freezing points, T, vs. dimethyl sulfoxide molality, m.

presence of dimethyl sulfoxide, as solute, results in lowering the transition temperature. This effect as well as the molar depressions of freezing point ϑ/m, which, on extrapolation to $m = 0$, do not gain the cryoscopic constant $\lambda_I = 65$ K kg mol^{-1} of sulfolane support the hypothesis of a deposition of mixed crystals.

A partition coefficient $K = 0.25$ (Table V), not influenced by composition, may be calculated at each molality on the basis of the actual freezing point depressions and the ideal depressions ϑ_i calculated by the equation

$$\vartheta_i = 65m - 17.914m^2 + 5.015m^3 - 1.409m^4 \qquad (4)$$

derived from thermal data of sulfolane (*10*). Husar and Kreevoy (*11*) report a cryoscopic constant of 47.3 and hence $K = 0.26$ for some dilute solutions of dimethyl sulfoxide in sulfolane.

In Table VI data are summarized concerning cryoscopic behavior of sulfolane solutions of dimethyl sulfoxide in equilibrium with ordinary crystal II.

Initial freezing points of solutions, T, exhibit an almost linear dependence on molality, m, of dimethyl sulfoxide (Figure 4) down to the eutectic point (T_e = 253.29 K) and check, on extrapolation to $m = 0$, the virtual melting point of crystal II (290.23 K) (*2, 10*). Starting from this temperature, freezing point depressions, ϑ, and molar depressions, ϑ/m, are calculated at each composition and are included in Table VI together with $(\vartheta/m)_0 = \lambda_{II} = 7.690$ as derived from previous data (*2, 10*).

When all data in column 6 (Table VI) are ascribed unit weight, parameters of the equation

$$\frac{\vartheta}{m} = 7.720 - 0.149m - 0.0872m^2 + 0.094m^3 \qquad (5)$$

were calculated by a least-squares computer program. Equation 5 reproduces the values of depressions, ϑ, in the limits of experimental error. The so calculated values of ϑ, were introduced into eq 6 which was derived by one of us (*10*) from

$$\log a_s = -0.0156\{\vartheta + 3.446 \times 10^{-3}\vartheta^2 + 1.187 \times 10^{-5}\vartheta^3 + 4.091 \times 10^{-8}\vartheta^4\} + 5.4715\{5.936 \times 10^{-6}\vartheta^2 + 2.272 \times 10^{-8}\vartheta^3 + 1.057 \times 10^{-10}\vartheta^4\} \qquad (6)$$

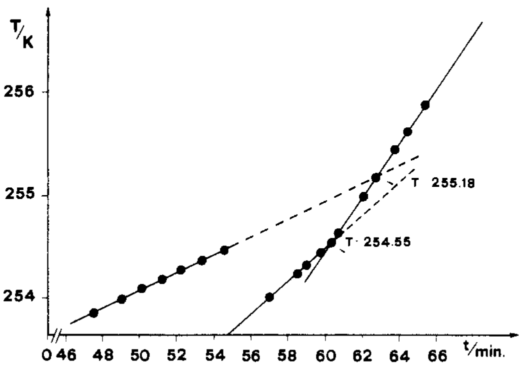

Figure 5. Heating curve of a sulfolane solution in dimethyl sulfoxide with m = 15.796.

cryoscopic data of sulfolane solutions of nitrobenzene in equilibrium with crystal II, which were tested and found to behave ideally.

Thus finally the activities, a_s, of sulfolane as solvent in equilibrium with crystal II and the rational activity coefficients, γ_s, were calculated at each composition and included in Table VI.

These values of γ_s do not differ noticeably from unity; the deviations moreover might be ascribed to some incertitude in extrapolating cryoscopic data of sulfolane solutions in equilibrium with crystal II beyond the molality domain of solutions in equilibrium with crystal I rather than to real deviations from ideality.

Now we turn our attention to the left-hand side of phase diagram (Figure 3). Solutions of sulfolane in dimethyl sulfoxide generally exhibit final melting temperatures which strictly agree with initial freezing points; however, for some solutions we may take occasionally freezing curves with two undercooling regions; hence on extrapolation across the undercooling regions, two different initial freezing temperatures may be taken. The same behavior is observed in some heating curves which clearly exhibit two different final melting temperatures (Figure 5). The difference between the two temperatures noticeably exceeds experimental error on T but in no case exceeds 1 K.

Hence the conclusions may be drawn that dimethyl sulfoxide may solidify to two crystalline phases with comparable stability. (Their freezing points should not differ from each other remarkably.) At this point we call attention to the fact that Garnsey and Prue (*5*) in a review of cryoscopic studies in selected solvents report two sets of values concerning the cryoscopic constant of dimethyl sulfoxide, the former of them ranging within 3.9 and 4.1, the latter ranging within 4.36 and 4.4. Both these values are supported by data in Table VII which summarizes the cryoscopic behavior of sulfolane solutions in dimethyl sulfoxide. The presence of more than one crystalline phase of each component justifies the occurrence of a multiple phase diagram. This is a frequent feature of binary mixtures involving sulfolane (*10*, *12*, *13*), as far as the plastic crystal I seems to possess a peculiar ability in evidencing latent forms of the other component.

The solid lines in Figure 3 represent indeed the two sets of initial freezing points of sulfolane solutions in dimethyl sulfoxide. Correspondingly two eutectic points $x_s = 0.56$ at $T = 253.29$ and $x_s = 0.58$ at $T = 252.43$ are observed. The occurrence of some peritectic points indicates that, if the transition crystal I → crystal II is avoided by sudden cooling, the metastable crystal I may form two different solid–liquid phase diagrams with each of the two dimethyl sulfoxide crystalline forms. Because of the extreme metastability of the system in this region, no information on the type of phase diagram may be drawn from experimental data.

On the whole volumetric, dielectric, and cryoscopic data agree in picturing dimethyl sulfoxide (1)–sulfolane (2) solutions as an almost ideal system, as otherwise expected.

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Registry No. Me_2SO, 67-68-5; sulfolane, 126-33-0.

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