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Vapor Pressures of Pure Diethyl Sulfoxide from (298.15 to 318.15) K and Vapor−Liquid Equilibria of Binary Mixtures of Diethyl Sulfoxide with Water

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Total vapor pressure measurements and vapor−liquid equilibrium data are reported for the pure diethyl sulfoxide and diethyl sulfoxides + water binary system in the temperature range of (298.15 to 318.15) K. All mixtures show negative deviations from ideality due to strong interactions between diethyl sulfoxide and water molecules that are even stronger than those between dimethyl sulfoxide and water.

Introduction

Diethyl sulfoxide (DESO) and dimethyl sulfoxides (DMSO) show unusual physicochemical properties.[1−4] DESO exhibits strong self-associative effects in the structure that are stronger than those exhibited by DMSO. The existence of a strong intermolecular DESO−DESO interaction also involving SO···HC hydrogen bonds has been suggested.[2,3]

Raman and Fourier transform infrared (FTIR) studies have shown that very strong interactions take place between DESO and water. These are stronger than those between DESO molecules in the pure liquid and those between DMSO and water.[4] This behavior could explain the strong deviations from ideality observed in these systems and could be also related to their biological properties. Recently, the biomedical significance of DESO has been reported.[5,6] In this respect, it should be noted that our recent investigations have shown that the DESO + water system could provide amorphous, glassy systems, thus avoiding ice crystallization, over a wide range of concentration and even at very low cooling rates. The results also confirm that DESO, more than DMSO, is able to penetrate living tissues without causing significant damage.[6]

The present work describes data on vapor pressure obtained for the binary system DESO + water. The results obtained confirm that a deviation from ideality like that in DMSO + water solutions but to a greater extent arises from strong intermolecular interactions occurring in this system.

Experimental Section

Materials. DESO was prepared and purified according to procedures in ref 7. Its purity, tested by gas chromatography (GC), was found to be greater than 99.5 mass %; the water content, after drying on molecular sieves, was <0.01 mass %. Twice-distilled water was used. DESO and water were degassed separately and then mixed under vacuum.

Vapor Pressure. The apparatus used to measure vapor pressure consists of a molybdenum glass vessel, a thermometer with an accuracy of ±0.02 K, a constant-temperature bath, a vacuum pump, and a stirrer. Figure 1 shows the schematic diagram of the experimental apparatus.

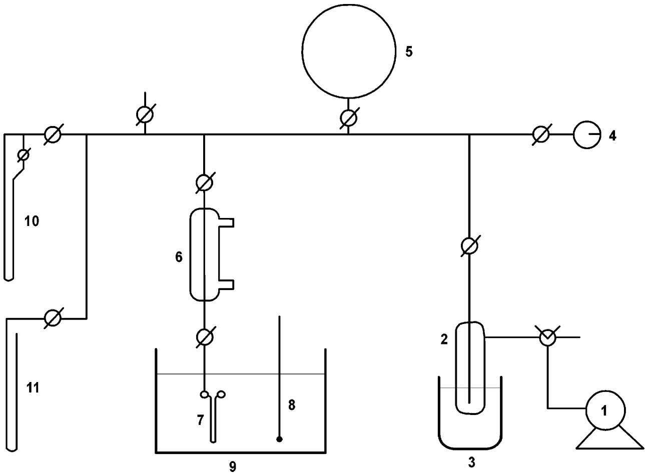

Figure 1. Experimental apparatus: (1) vacuum pump; (2) trap; (3) Dewar with liquid nitrogen; (4) gauge; (5) ballast vessel; (6) condenser; (7) isoteniscope; (8) thermometer; (9) glass thermostat; (10) oil manometer; (11) mercury manometer.

A sample solution was initially prepared to the desired concentration and placed in the vessel (isoteniscope) with an approximate volume of 40 cm^3, which was connected to the apparatus through a reflux condenser. The entire apparatus was then evacuated. The details of this experimental procedure were as follows. Two flasks with known quantities of DESO and water by virtue of a special delivery tube were connected to the vacuum setup. Three freeze−thaw cycles have been performed. Then the flasks were turned upside down, and both liquids were flowing down into the isoteniscope. The latter was frozen by liquid nitrogen allowing the total transfer of two components. After that, the cavity together with the stopcock was disconnected from the vacuum setup and was connected to the apparatus for the measurements of vapor pressure. The average estimated uncertainties of concentrations calculated from the residual in the flasks did not exceed 3%.

The vapor pressure of the solution was determined using a U-tube oil manometer by which the pressure can be determined from the difference between the two oil levels. For this goal, a BM-1-type diffusion oil (Russian State Standard, GOST, number 5671-70) with a density of $d^{20} = 0.870\ \mathrm{g{\cdot}cm^{-3}}$ and a molar mass of about 450 was used. This

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Table 1. Vapor Pressure of Pure DESO

T/K	P/Pa
298.15	20.2
303.15	33.9
308.15	43.8
313.15	68.1
318.15	92.4

Table 2. Total Vapor Pressures of the DESO + Water Binary System as a Function of the Liquid-Phase Mole Fraction of DESO at Three Different Temperatures

	P_{tot}/kPa		
x_{DESO}	T = 293.15 K	T = 298.15 K	T = 303.15 K
0.000	2.3341	3.1608	4.2403
0.0443	2.2174	3.0101	4.0409
0.0583	2.0229	2.7912	3.7589
0.1101	1.7019	2.3681	3.1802
0.1565	1.4491	2.0423	2.7717
0.2178	1.1962	1.6630	2.2855
0.2564	1.0406	1.4394	1.9645
0.3022	0.8850	1.2351	1.6922
0.3577	0.7148	1.0017	1.4101
0.4261	0.5543	0.7780	1.0892
0.5126	0.3987	0.5641	0.7877
0.6256	0.2237	0.3064	0.4279
0.7791	0.1069	0.1459	0.2042
0.8758	0.0486	0.0681	0.1069
1.000		0.0202	0.0339

oil is characterized by lower vapor pressure at room temperature (no more than 4 × 10^{-8} Pa) and in fact is insoluble in both DMSO and DESO. The calibration of the oil manometer was checked by measuring the vapor pressure of pure water[8] and DMSO. It should be noted that the vapor pressures listed in the Tables are the average values obtained after at least five measurements.

Results

The vapor pressures for pure DESO were measured in the range of temperature from (298.15 to 318.15) K. The experimental values are listed in Table 1. It is estimated that the data in the Table are accurate to ±2 Pa under the experimental conditions. Using the known Clausius–Clapeyron equation through the linear dependence of ln P versus T^{-1}, we estimated a value for the enthalpy of vaporization for pure DESO: $\Delta H° = 58.7 \pm 3.3$ kJ·mol^{-1}. The correlation coefficient of the linear least-squares method is 0.99531. The value reported by Mackle and O'Hare [9] in their early work is $\Delta H° = 62 \pm 1$ kJ·mol^{-1}.

The enthalpy of vaporization for DMSO calculated with the same procedure is (54.3 ± 1.5) kJ·mol^{-1}. The correlation coefficient of the linear least-squares method is 0.9985.

According to a previous report,[9] the enthalpy of vaporization for DMSO is (52.9 ± 0.4 kJ·mol^{-1}).

It should be noted that in the literature there is controversy concerning the value of the DESO melting point. We believe that the value +24.5 °C (297.65 K) is more exact because it corresponds to the sample with a purity of >99.5 mass %.[7]

The measured vapor pressures of DESO (1) + water (2) mixtures are given in Table 2. The vapor pressures were measured at various concentrations (x_1, molar ratio) at three different temperatures: (293.15, 298.15, and 303.15) K. A negative deviation from ideality was observed. Figure 2 represents the dependence of vapor pressure on the molar ratio of DESO at 298.15 K. For comparison, the corresponding literature data[10] for DMSO + water are depicted in Figure 2.

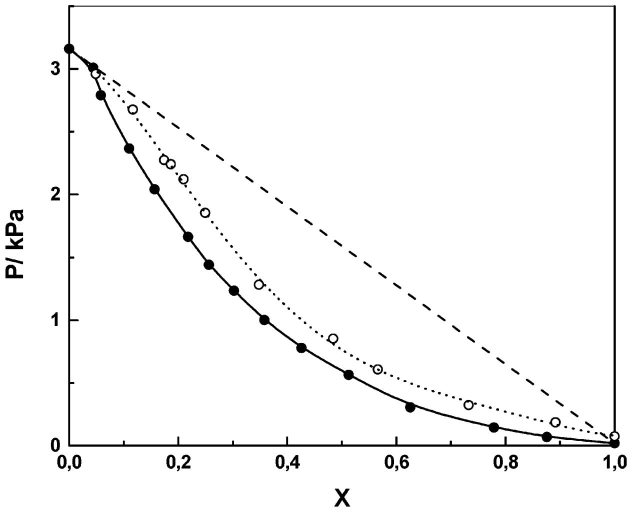

Figure 2. Total vapor pressure at 298.15 K: ●, DESO (1) + water (2), this work; ○, DMSO (1) + water (2), literature values.[10]

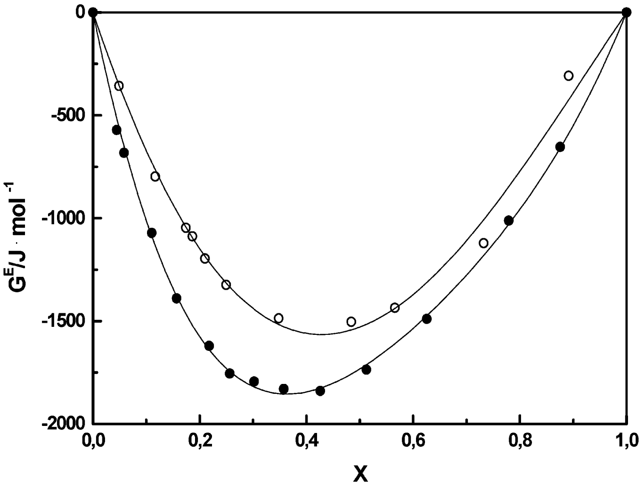

Figure 3. Excess Gibbs energies of mixing at 298.15 K: ●, DESO (1) + water (2), this work; ○, DMSO (1) + water (2), literature values.[10]

To calculate the partial pressures of each component from the total pressures, a graphical integration of the Gibbs–Duhem equation described in ref 10 has been used. Then the activity coefficients and excess Gibbs energies were obtained (Table 3).

These results unambiguously show that in the DESO + water system the deviation from ideality is more pronounced compared to the DMSO + water system. Indeed, excess Gibbs energies of mixing for the DESO + water system are also more negative than those obtained for the DMSO + water system in Figure 3. These observations are well explainable and consistent with other physicochemical measurements confirming the existence of strong DESO + water interactions.[4,6] The results in Tables 2 and 3 show obviously that strong interactions exist between DESO and water, as suggested by a spectroscopic study of DESO + water mixtures.[4] Also, the calorimetric data[6] suggest the existence of a network of strong interactions between the DESO and water molecules. The glass-forming tendency of these solutions was discussed in terms of existing competitive interactions between molecules of DESO, on one hand, and DESO and water molecules, on the other hand. The results are well explainable on the basis of the model structure of DESO + water solutions.

Table 3. Partial Pressures, Activity Coefficients, and Excess Gibbs Energies of DESO + Water Mixtures

$T = 298.15$/K							$T = 303.15$/K						
x_{DESO}	P_{tot}/Pa	P_{DESO}/Pa	P_{water}/Pa	γ_{DESO}	γ_{water}	G^{E}/J·mol^{-1}	x_{DESO}	P_{tot}/Pa	P_{DESO}/Pa	P_{water}/Pa	γ_{DESO}	γ_{water}	G^{E}/J·mol^{-1}
0.0000	3160.8	0.000	3160.800		1.000	0	0.0000	4240.3	0.000	4240.300		1.000	0
0.0443	3010.1	0.005	3010.095	0.006	0.996	−571	0.0443	4040.9	0.011	4040.889	0.007	0.997	−561
0.0583	2791.2	0.030	2791.170	0.025	0.938	−682	0.0583	3758.9	0.065	3758.835	0.033	0.941	−645
0.1101	2368.1	0.175	2367.925	0.079	0.842	−1072	0.1101	3180.2	0.377	3179.823	0.101	0.843	−1019
0.1565	2042.3	0.370	2041.930	0.117	0.766	−1389	0.1565	2771.7	0.794	2770.906	0.150	0.775	−1290
0.2178	1663.0	0.910	1662.090	0.207	0.672	−1620	0.2178	2285.5	1.688	2283.812	0.229	0.689	−1543
0.2564	1439.4	1.358	1438.042	0.262	0.612	−1755	0.2564	1964.5	2.647	1961.853	0.305	0.622	−1656
0.3022	1235.1	2.129	1232.971	0.349	0.559	−1794	0.3022	1692.2	3.851	1688.349	0.376	0.571	−1730
0.3577	1001.7	3.272	998.428	0.453	0.492	−1830	0.3577	1410.1	5.746	1404.354	0.474	0.516	−1743
0.4261	778.0	4.762	773.238	0.553	0.426	−1839	0.4261	1089.2	8.444	1080.756	0.585	0.444	−1749
0.5126	564.1	6.929	557.171	0.669	0.362	−1736	0.5126	787.7	12.103	775.597	0.696	0.375	−1672
0.6256	306.4	11.086	295.314	0.877	0.250	−1489	0.6256	427.9	19.076	408.824	0.899	0.258	−1446
0.7791	145.9	14.964	130.936	0.951	0.188	−1012	0.7791	204.2	25.620	178.580	0.970	0.191	−981
0.8758	68.1	17.511	50.589	0.989	0.129	−654	0.8758	106.9	29.472	77.428	0.993	0.147	−615
1.0000	20.2	20.200	0.000	1.000		0	1.0000	33.9	33.900	0.000	1.000		0

Table 4. Parameters of the Redlich−Kister Equation (Eq 1)

T/K	B	C	D	σ
298.15	−2.79618	1.30090	−1.10320	25.01
303.15	−2.64432	1.18108	−0.97223	28.51

Table 5. Values of Parameters Appearing in Equation 2 and the Resulting Average Deviation ΔP_{av}

T/K	A_{21}	A_{12}	α_{21}	α_{12}	ΔP_{av}/kPa
298.15	−2.241955	−6.009926	−3.06793	−14.9511	0.16578
303.15	−1.96932	−6.80886	−3.4763	−59.3863	1.35463

The excess Gibbs energies of mixing were fit to the Redlich−Kister equation with parameters B, C, and D.[10]

$$G^{\mathrm{E}} = RTx_1x_2[B + C(2x_1 - 1) + D(2x_1 - 1)^2] \qquad (1)$$

The parameters B, C, and D chosen are given in Table 4. Besides that, to calculate virial coefficients a data reduction procedure proposed by Abbott and Van Ness was included using the four-parameter modified Margules equation.[11] The optimum four-suffix parameters A_{12}, A_{21}, α_{21}, and α_{12} by minimizing the sum of the squares of the differences between the experimental and calculated data have been determined by means of mathematical program

$$\frac{G^{\mathrm{E}}}{RTx_1x_2} = A_{21}x_1 + A_{12}x_2 - \frac{\alpha_{12}\alpha_{21}x_1x_2}{\alpha_{12}x_1 + \alpha_{21}x_2} \qquad (2)$$

where x_1 and x_2 represent the mole fractions of components 1 and 2 and A_{12}, A_{21}, α_{21}, and α_{12} represent the Margules equation constants. Parameter values of Margules equation constants and resulting average deviations between calculated and experimental pressures ΔP_{av} are given in Table 5. The average deviation ΔP_{av} was calculated from the four-suffix Margules model. Figure 3 illustrates the good agreement between the experimental and calculated data for the use of the modified Margules equation.

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