

Table II. Smoothed Data for Binary Systems

Pressure P.S.I.A.	100° F.		160° F.		Pressure P.S.I.A.	100° F.		160° F.	
	Mole Fraction Nitrogen		Mole Fraction Nitrogen			Mole Fraction Nitrogen		Mole Fraction Nitrogen	
	Liquid Phase	Vapor Phase	Liquid Phase	Vapor Phase		Liquid Phase	Vapor Phase	Liquid Phase	Vapor Phase
80	0.0090	0.9977	0.0090	0.9910	80	0.0085	0.9801	0.0085	0.8500
100	0.0106	0.9982	0.0106	0.9935	100	0.0105	0.9850	0.0104	0.8840
150	0.0158	0.9989	0.0157	0.9960	150	0.0156	0.9915	0.0156	0.9500
250	0.0261	0.9995	0.0261	0.9989	250	0.0260	0.9955	0.0260	0.9651
500	0.0502	0.9998	0.0510	0.9993	500	0.0510	0.9965	0.0522	0.9894
750	0.0730	0.9998	0.0750	0.9992	750	0.0770	0.9969	0.0790	0.9912
1000	0.0950	0.9998	0.0980	0.9992	1000	0.1030	0.9969	0.1050	0.9939
1250	0.1180	0.9997	0.1210	0.9991	1250	0.1260	0.9968	0.1300	0.9938
1500	0.1400	0.9997	0.1430	0.9991	1500	0.1490	0.9967	0.1530	0.9937
1750	0.1600	0.9997	0.1650	0.9990	1750	0.1720	0.9966	0.1760	0.9936
2000	0.1810	0.9997	0.1850	0.9989	2000	0.1920	0.9964	0.1970	0.9935
2250	0.2000	0.9997	0.2050	0.9988	2250	0.2110	0.9962	0.2170	0.9933
2500	0.2180	0.9996	0.2230	0.9987	2500	0.2280	0.9961	0.2360	0.9931
2750	0.2340	0.9995	0.2400	0.9986	2750	0.2450	0.9959	0.2540	0.9929
3000	0.2500	0.9994	0.2560	0.9984	3000	0.2610	0.9956	0.2700	0.9926
3250	0.2640	0.9993	0.2710	0.9982	3250	0.2770	0.9954	0.2860	0.9924
3500	0.2780	0.9991	0.2860	0.9980	3500	0.2920	0.9950	0.301	0.9920
3750	0.2910	0.9990	0.3000	0.9978	3750	0.3080	0.9948	0.317	0.9915
4000	0.3040	0.9987	0.3160	0.9975	4000	0.3230	0.9944	0.3320	0.9910
4250	0.3170	0.9984	0.3310	0.9971	4250	0.3380	0.9940	0.3490	0.9902
4500	0.3300	0.9980	0.3460	0.9966	4500	0.3540	0.9935	0.3640	0.9894
4750	0.3410	0.9975	0.3620	0.9960	4750	0.3700	0.9929	0.3820	0.9882
5000	0.3520	0.9968	0.3800	0.9950	5000	0.3860	0.9921	0.4000	0.9860

nitrogen used was OP grade with a minimum purity of 99.9 mole %.

RESULTS

The results of analysis are tabulated in Table I, A P-X diagram for each isotherm was prepared similar to that shown in Figure 1. In Figure 2 the four isotherms are shown. It can be seen that the solubility of nitrogen in normal decane increases with temperature. This fact is in agreement with findings of other investigators (1, 4).

Smoothed data for each isotherm were obtained by plotting the best curve passing through experimental data points on a P-X diagram. These are tabulated in Table II.

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Densities, Refractive Indices, Molar Refractions, and Viscosities of Ethylene Glycol Dimethyl Ether-Water Solutions at 25°

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DENSITIES, refractive indices, and viscosities of mixtures of water and ethylene glycol dimethyl ether have been determined at 25° C. as part of a study of polyether and polyether-water solvent systems. These data as well as the molar refractions of these solutions are presented.

EXPERIMENTAL

Technical ethylene glycol dimethyl ether (Ansul Chemical Co., Ansul E-121) was treated with lithium aluminum

hydride and then fractionated immediately before use. The ether had a boiling point of 85.2° (uncorr.), gave a negative peroxide test (2), and analysis by gas chromatography indicated a purity of 99.9+ per cent. Water used for the solutions was distilled from dilute potassium permanganate solution in a seasoned all Pyrex assembly.

The mixtures were prepared in 100 ml. batches by weighing out the liquids to the nearest tenth of a milligram. Refractive indices were measured at 25.00 ± 0.01° with a Bausch and Lomb Precision Refractometer (Abbe) using the sodium D line. Readings were reproducible to within ± 0.00003.

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Densities, refractive indices and viscosities of mixtures of water and ethylene glycol dimethyl ether have been determined at 25° C. Molar refractions are also presented. The refractive index values of the solutions pass through a maximum at about 50 mole per cent ether after marked increase from pure water to 20 mole per cent ether. The partial molal volume of the ether passes through a minimum which is 10 per cent less than the ideal molar volume at 4 mole per cent ether. The viscosity exhibits a maximum at 17 mole per cent ether. The interaction of this ether with water is greater than that of dioxane but less than that of the monomethyl ether of ethylene glycol.

Densities were determined at 25.00 ± 0.05° with five Ostwald pycnometers of 4 ml. capacity and a Mettler balance capable of a precision of ±0.00002 gm. The densities for five determinations were identical within ±0.0001 gram per ml. or better.

Viscosities were determined at 25.00 ± 0.05° with an Ostwald viscometer having a flow time of 63.5 sec. for water. The maximum deviations based on flow time were ±0.002 centipoise except as noted in the table.

All data are shown in Table I, and solution composition is indicated as mole fraction of ethylene glycol dimethyl ether (X_2).

RESULTS

The refractive index values of the ethylene glycol dimethyl ether-water solutions pass through a maximum at about 50 mole per cent after a very marked increase from pure water to 20 mole per cent ether (Figure 1). However, the molar refraction increases almost linearly with mole per cent of ether, with all mixtures having a small negative deviation from linearity as shown in Figure 2. This deviation is greater than the deviations observed by Schott for water-dioxane mixtures (5).

The density data were used to calculate the partial molal volumes using the graphical method of intercepts (4). These are shown in Figure 3 along with the results of

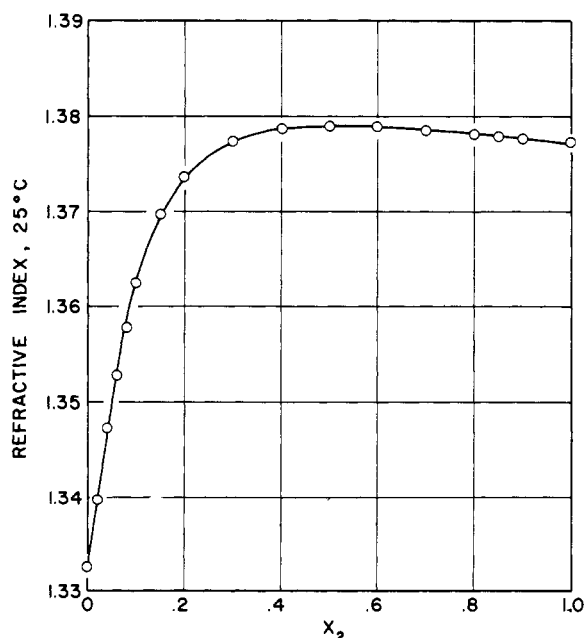


Figure 1. Refractive indices of water-ethylene glycol dimethyl ether as a function of mole fraction of ether.

Table I. Densities, Refractive Indices, Molar Refractions, and Viscosities of Water-Ethylene Glycol Dimethyl Ether

X_2	d_4^{25} obsd.	N_D^{25} obsd.	$[R]_{1,2}$ exptl. ^a	Viscosity (centipoises)
0.0000	0.99707	1.33251	3.712	0.894
0.0190	0.9926	1.33977	4.091	1.166
0.0408	0.9895	1.34730	4.526	...
0.0608	0.9871	1.35293	4.920	1.748
0.0802	0.9840	1.35778	5.308	...
0.1011	0.9809	1.36261	5.731	2.092
0.1521	0.9704	1.36983	6.753	2.104
0.1999	0.9590	1.37358	7.715	1.935 ^b
0.2992	0.9361	1.37739	8.972	1.432
0.4048	0.9166	1.37868	11.896	1.074 ^c
0.4985	0.9030	1.37905	13.811	...
0.5970	0.8916	1.37895	15.825	0.684
0.7015	0.8813	1.37861	17.972	...
0.8010	0.8733	1.37820	19.991	0.506
0.8516	0.8698	1.37793	21.048	...
0.8985	0.8664	1.37771	22.019	...
0.9446	0.8638	1.37759	22.966	...
1.0000	0.8605	1.37730	24.107	0.432

$$^a [R]_{1,2} \text{ exptl.} = \frac{N_{12}^2 - 1}{N_{12}^2 + 2} \cdot \frac{x_1 M_1 + x_2 M_2}{d_{12}}$$

^b +0.010

^c ±0.012

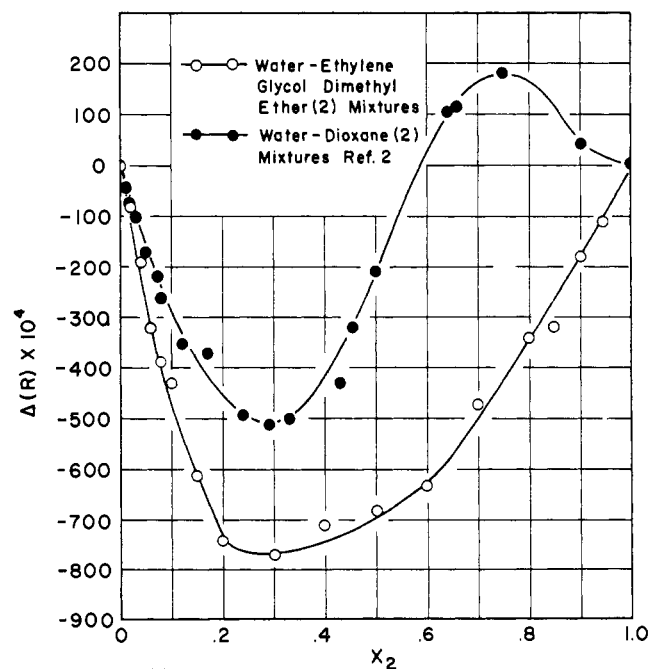


Figure 2. Differences between experimental and additive molar refractions of water-ethylene glycol dimethyl ether and water-dioxane as a function of mole fraction of ether.

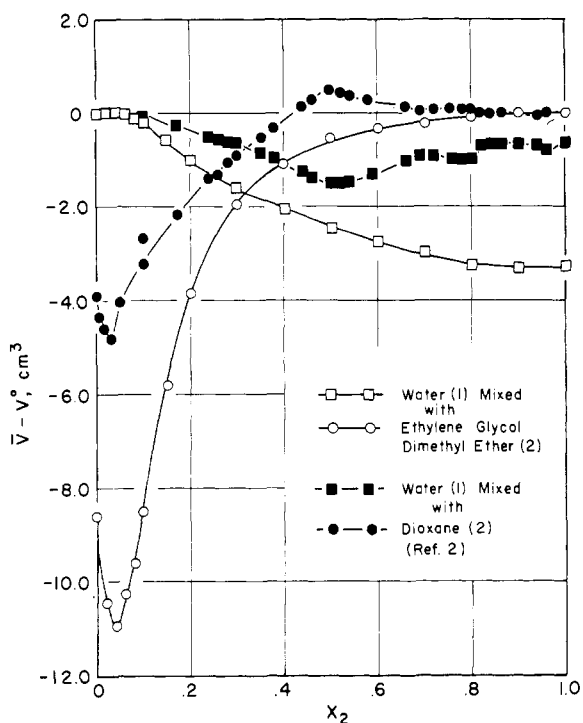


Figure 3. Partial molal volumes (molal volume of pure component subtracted from its partial molal volume) of water-ethylene glycol dimethyl ether and water-dioxane as a function of mole fraction of ether.

Schott for the water-dioxane system (5). The minimum in the ethylene glycol dimethyl ether ($X_2 = 0.040$) curve is slightly more than twice as great as the similar minimum for dioxane. The water curve in the present study does not exhibit the eccentricity shown in the dioxane system, but it is noteworthy that there is a large negative deviation in the partial molal volume of the water in the ether-rich solutions.

The viscosity of the water-ethylene glycol dimethyl ether system exhibits a maximum at about 17 mole per cent which is much sharper than the maximum observed in the dioxane-water (3) system. These data are shown in Figure 4 along with similar results for dioxane and water (3).

DISCUSSION

These data are a direct indication that the interaction of the ethylene glycol dimethyl ether with water is significantly greater than that of dioxane with water. A possible explanation for the greater interaction rests upon the high degree of order to be expected in the case of a hydrogen-bonded dioxane-water complex. A larger number of molecular conformations which permit hydrogen-bonding to water are probably available to the glycol ether molecule. Further, one would expect the glycol molecule to penetrate the hydrogen-bonded lattice of water with greater ease than the bulkier dioxane molecule. This is significantly reflected

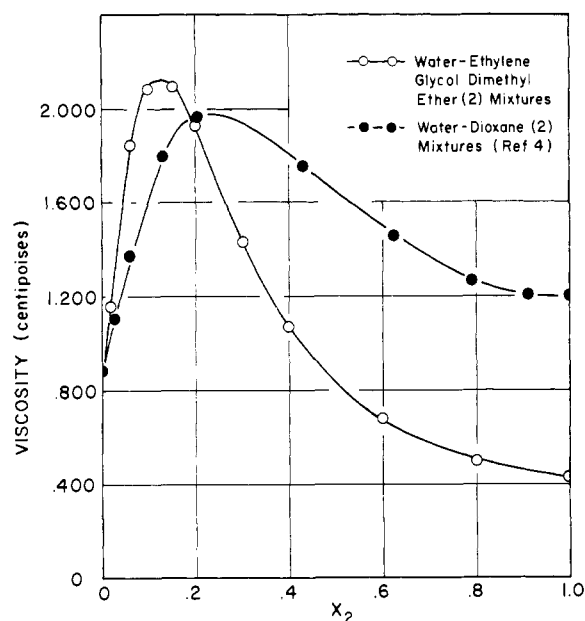


Figure 4. Viscosities of water-ethylene glycol dimethyl ether and water-dioxane as a function of mole fraction of ether.

in the 10 per cent difference between the minimum partial molal volume of the glycol ether and its ideal value. It is also noteworthy that there is a 9 per cent difference between the partial molal volume of water and the ideal molal volume at high ether concentrations. These interactions are not as great as are observed in a system where proton donor groups are present on both components. Calculation of the data of Chu and Thompson for ethylene glycol monomethyl ether shows a difference of 15 per cent between the minimum partial molal volume of the ether and its ideal value (1).

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