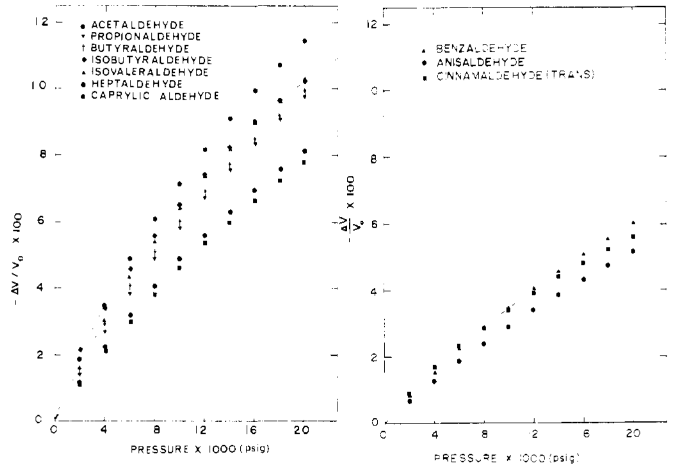

Figure 3. Compressibility diagrams

In case of highly volatile and poisonous liquids, the secondary pump was replaced by a stainless steel and aluminum bomb. The sample was forced into the system by the use of high pressure nitrogen.

RESULTS

Viscosity data are given in Table I with the compressibility data for all the aldehydes studied. The viscosity data are estimated to be correct within ±1%. The errors associated with the compressibility data are below ±0.4%.

The equation which correlated the viscosity data with pressure is:

$$\eta = \eta_o \exp mP \qquad (1)$$

where η_o represents viscosity under atmospheric conditions and m is a constant specific to each substance. m is plotted against a number of carbon atoms in Figure 1. Equation 1 correlates aldehyde data to a confidence level of 95%.

Graphical representation of viscosity data is given in Figure 2. The slopes of the straight lines indicate the magnitude of m. Compressibility diagrams for aliphatic and aromatic aldehydes are presented in Figure 3.

NOMENCLATURE

η = viscosity, cp.
η_o = viscosity under atmospheric conditions, cp.
m = constant, Equation 1
P = pressure, p.s.i.

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Densities, Refractive Indices, Molar Refractions, Viscosities, and Dielectric Constants of Triethylene Glycol Dimethyl Ether–Water Solutions at 25° C.

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Densities, refractive indices, viscosities, and dielectric constants of mixtures of water and triethylene glycol dimethyl ether have been determined at 25° C. Molar refractions are also presented. The refractive indices of the solutions increase sharply from pure water to 0.2 mole fraction ether and then increase slowly to the value for the pure ether. The partial molal volume of the ether passes through a minimum which is about 8% less than the ideal molal volume at 0.03 mole fraction ether. The viscosity exhibits a pronounced maximum at 0.14 mole fraction ether. The dielectric constant increases smoothly with water content.

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

EXPERIMENTAL

Technical triethylene glycol dimethyl ether (Ansul Chemical Co., Ansul E-161) was distilled over sodium under a pressure of 1.5 mm. of Hg at 79° C. A controlled amount of nitrogen was allowed to bubble through the boiling ether. Ether distilled under these conditions contains less than 0.01% water as measured by the Karl Fischer reagent. At 25° C., the ether has a refractive index of 1.4209 and density of 0.9795 compared with the respective values of 1.4233 at 20° C. and 0.974 at 24° C. reported by Zellhoefer (*8*). Water used for the solutions was distilled from dilute potassium permanganate solution in a seasoned all borosilicate glass assembly. Solutions were prepared as described earlier (*6*).

Table I. Densities, Viscosities, and Partial Molal Volumes of Water–Triethylene Glycol Dimethyl Ether at 25° C.

			Partial Molal Volumes	
X_2	d_4^{25}, Obsd.	Viscosity, Cp.	Ether, V_2	Water, V_1
0.0000	0.99704	0.8937	169.0	18.07
0.0077	1.0010	1.15	168.5	18.07
0.0143	1.0044	1.38	167.2	18.08
0.0255	1.0100	1.83	166.7	18.08
0.0484	1.0185	2.79	169.2	17.98
0.0796	1.0237	3.89	171.2	17.84
0.0814	1.0241	3.95	171.7	17.79
0.0934	1.0248	4.25	173.5	17.62
0.1022	1.0248	4.40	174.1	17.56
0.1092	1.0245	4.49	175.0	17.46
0.1166	1.0243	4.60	175.5	17.39
0.1407	1.0228	4.68	177.0	17.17
0.1731	1.0191	4.63	179.0	16.80
0.2117	1.0155	4.39	179.8	16.63
0.2745	1.0099	3.87	180.2	16.53
0.3483	1.0031	3.29	181.0	16.15
0.4311	0.9981	2.90	181.4	15.87
0.5899	0.9896	2.41	181.7	15.29
0.7450	0.9858	2.16	181.8	15.16
0.7839	0.9842	2.10	181.8	15.16
0.8687	0.9825	2.04	181.8	15.16
1.0000	0.9795	1.96	181.8	15.16

Table II. Refractive Indices, Molar Refractions, and Dielectric Constants of Water–Triethylene Glycol Dimethyl Ether at 25° C.

X_2	n_D^{25}, Obsd.	$[R]_{1,2}$, Exptl.	Dielectric Constant
0.0000	1.3323	3.712	78.54
0.00714	1.3397	4.011	74.55
0.0152	1.3470	4.345	70.58
0.0214	1.3522	4.604	66.92
0.0277	1.3572	4.868	64.76
0.0372	1.3638	5.264	61.33
0.0497	1.3711	5.782	57.33
0.0625	1.3775	6.315	51.81
0.0775	1.3838	6.944	49.29
0.0921	1.3888	7.559	46.01
0.1149	1.3946	8.514	41.42
0.1401	1.3993	9.578	37.03
0.1772	1.4044	11.150	31.73
0.2296	1.4088	13.363	26.19
0.2646	1.4108	14.849	23.58
0.3000	1.4126	16.351	21.46
0.4845	1.4172	24.175	14.39
0.6771	1.4193	32.353	10.49
1.0000	1.4209	46.134	7.62

Densities were determined at 25.00 ± 0.05° C. with an Ostwald pycnometer of 4 ml. capacity and a Mettler balance capable of a precision of ±0.0002 gram. Triplicate measurements were identical within ±0.0005 gram per ml.

Viscosities were determined at 25.00 ± 0.05° C. with an Ostwald viscometer. Flow times were reproducible within 0.01 minute for measurements ranging from 1 to 5 minutes.

Table I shows densities, viscosities, and partial molal volumes with solution composition given as mole fraction of triethylene glycol dimethyl ether (X_2).

Dielectric constants and refractive indices were determined with a second series of solutions. Dielectric constants were measured with a General Radio 716-CS1 bridge at 1.0 megacycle using a thermostated stainless steel cell of the type described by Lind and Fouss (*2*). Solutions were prepared by weight and placed immediately in the cell. Capacitance readings on the bridge became constant in about 1 minute and were observed after 5 minutes. Uncertainty in the reported dielectric constants is less than 0.1%.

Refractive indices were measured at 25.00 ± 0.05° C. with a Bausch and Lomb Refractometer (Abbé) using the sodium D line. Readings were reproducible to within ±0.0001.

Table II shows refractive indices, molar refractions, and dielectric constants with solution composition given as mole fraction of triethylene glycol dimethyl ether (X_2). Molar refractions were calculated using density values interpolated from the data in Table I.

RESULTS

As was observed in the case of ethylene glycol dimethyl ether and diethylene glycol dimethyl ether (*6, 7*), the refractive index values of the aqueous solutions increase sharply to about 0.2 mole fraction ether and then increase slowly to the value for the pure ether. The molar refraction of the solutions is linear with composition.

The density data were used to calculate the partial molal volumes by the graphical method of intercepts (*3*). The results of this calculation are shown in Table I. Figure 1 shows the differences between the calculated partial molal

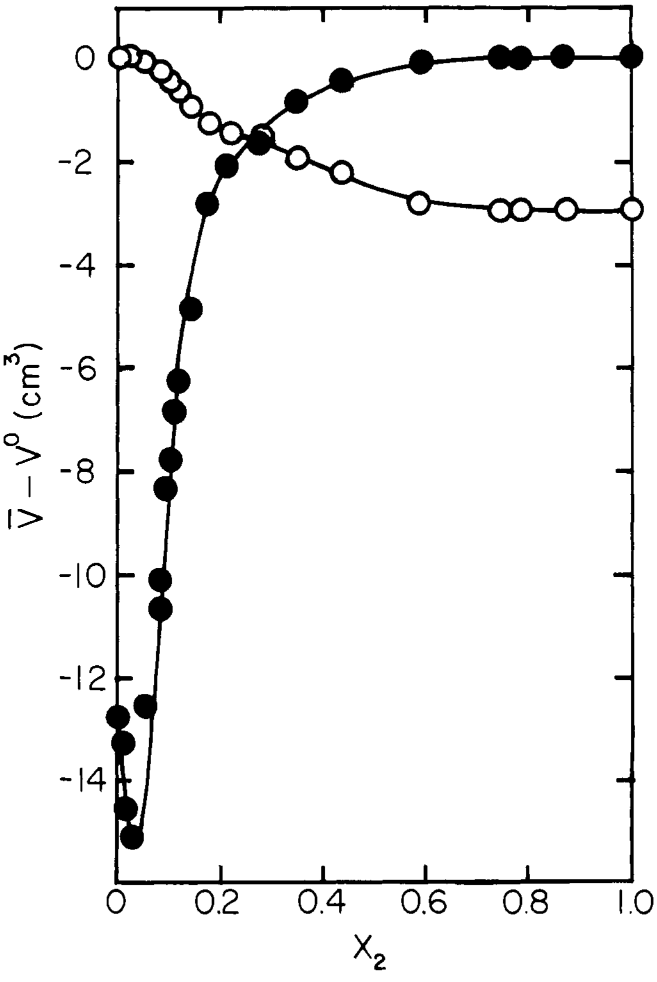

Figure 1. Partial molal volumes (molal volume of pure component subtracted from its partial molal volume) of water–triethylene glycol dimethyl ether as a function of mole fraction of ether (X_2)

○ Water

● Ether

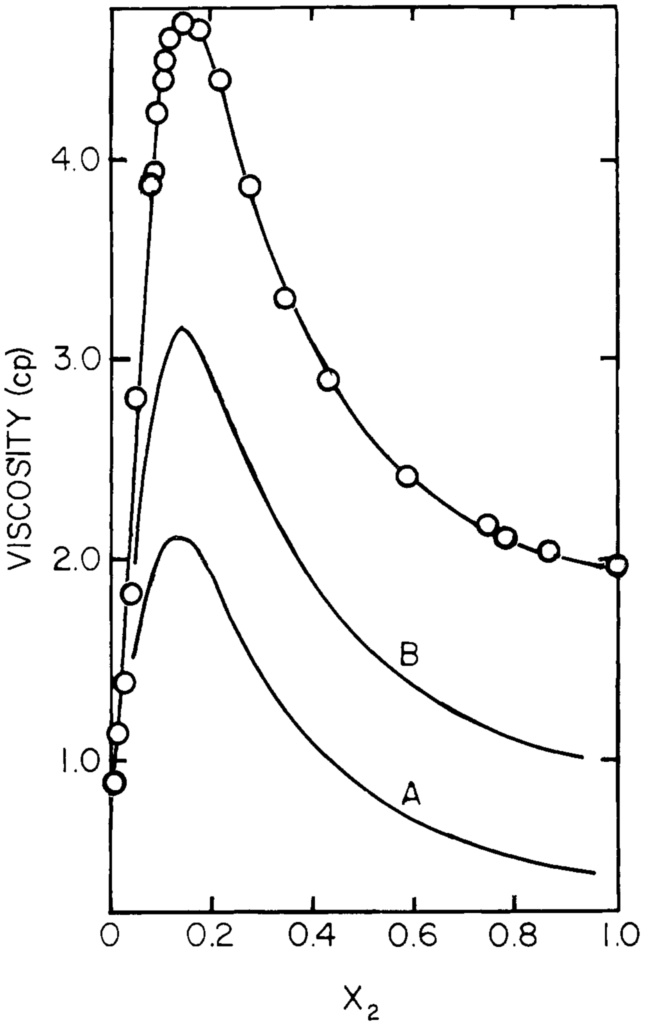

Figure 2. Viscosity of water–triethylene glycol dimethyl ether as a function of mole fraction of ether

A. Water–ethylene glycol dimethyl ether (*6*)

B. Water–diethylene glycol dimethyl ether (*7*)

volume and the ideal volume. These results follow the pattern observed for the ethers studied earlier (*6, 7*) and for dioxane-water (*4*). This is the largest volume difference observed in the series at the minimum in the curve, but the percentage decrease in molal volume is only 8% compared with 10% in the case of both ethylene glycol dimethyl ether–water and diethylene glycol dimethyl ether–water.

Figure 2 shows the viscosity data of the triethylene glycol dimethyl ether system as well as the viscosity of the ethylene glycol dimethyl ether–water and the diethylene glycol dimethyl ether–water system (*6, 7*). The variation in the maximum viscosity in the series of ethers is consistent with the increase in viscosity in the series of ethers owing to increased molecular weight and size. The maximum in viscosity is probably a result of strong hydrogen bonding between the water and the ether molecules. Schott (*5*) has related the maximum deviation of fluidity from the Kendall equation (*1*) fluidity to the hydration number of ether oxygens in dioxane, ethylene glycol dimethyl ether, and diethylene glycol dimethyl ether. The results here are consistent with his results. The maximum deviation is at a mole fraction of ether of 0.102, corresponding to a water–ether oxygen ratio of 2.20, with a deviation of 354% of predicted fluidity from observed fluidity.

The dielectric constant increases smoothly with increasing weight per cent of water, with a small positive deviation from linearity which parallels the deviation of specific volume from linearity—e.g., the dielectric constant increases with volume per cent water.

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