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Densities, Viscosities, Refractive Indices, and Molar Refractions of the Binary System Tetraethylene Glycol Dimethyl Ether–Water at 25 °C

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Densities, viscosities, and refractive indices of tetraethylene glycol dimethyl ether and water solutions have been determined at 25.00 °C as part of a study of binary solvent systems. These data as well as the molar refractions and partial molal volumes are presented. The refractive indices of the solutions increase sharply, with increasing ether mole fraction, from the value of pure water to 0.20 mole fraction of ether and then they increase at a slower rate 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 0.0075 mole fraction of ether. The viscosity exhibits a maximum at about 0.14 mole fraction of ether.

Introduction

As part of research designed to investigate physiochemical properties of binary solvent systems, the properties of density, viscosity, and refractive index have been determined for mixtures of tetraethylene glycol dimethyl ether and water at 25.00 °C. Also reported are the calculated molar refractions, partial molal volumes, and water–ether oxygen ratio.

Experimental Section

Technical-grade tetraethylene glycol dimethyl ether (Ansul Chemical Co., Ansul E-181) was distilled from sodium under a pressure of 6 mmHg at 115 °C. A controlled amount of nitrogen was bubbled through the boiling ether. Ether distilled under these conditions contains less than 0.01% water as measured by the Karl Fisher reagent and gave a negative peroxide test. At 25.00 °C the ether had a refractive index ($n^{25}{}_D$) of 1.4332 and a density ($d^{25}{}_4$) of 1.0047 compared with the respective values of 1.4320 and 1.0090 (*1*). Water used for the solutions was distilled from deionized water in a closed-system distilling apparatus. Solutions were prepared in 50-g samples by weighing the liquids to the nearest tenth of a milligram.

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

X_2[a]	W_2,[b] %	$d^{25}{}_4$-(obsd)[c]	viscosity, cP	partial molal vol, mL V_2[d]	V_1[e]
0.0000	0.0000	0.9971	0.8937	203.94	18.09
0.0075	8.54	1.0033	1.323	203.41	18.09
0.0142	15.12	1.0090	1.533	203.61	18.08
0.0297	27.39	1.0190	2.433	205.33	18.04
0.0419	35.06	1.0253	3.198	206.98	17.98
0.0593	43.74	1.0323	4.289	209.27	17.86
0.0784	51.23	1.0359	5.240	211.42	17.70
0.1139	61.34	1.0368	6.253	214.38	17.39
0.1398	66.73	1.0360	6.469	215.88	17.18
0.1543	69.25	1.0351	6.411	216.58	17.05
0.1672	71.24	1.0350	6.408	217.08	16.96
0.1972	75.19	1.0309	6.200	218.05	16.74
0.2273	78.40	1.0301	5.915	218.77	16.55
0.3237	85.52	1.0243	5.112	220.09	16.06
0.4635	91.42	1.0169	4.334	220.86	15.58
0.5569	93.94	1.0151	4.179	221.08	15.36
0.6402	95.65	1.0119	3.780	221.19	15.20
0.7613	97.52	1.0078	3.495	221.27	15.02
0.8245	98.30	1.0073	3.443	221.29	14.93
1.0000	100.00	1.0047	3.295	221.31	14.76

[a] X_2 is the mole fraction of the ether. [b] W_2 is the weight percent of the ether. [c] $d^{25}{}_4$(obsd) is the observed density of the solution in g/mL. [d] For the ether. [e] For water.

Densities were determined at 25.00 °C with an Ostwald pycnometer of 2.9404-mL capacity. Triplicate measurements were identical within ±0.0009 g/mL.

Viscosities were determined at 25.00 °C with an Ubbelohde viscometer. Flow times were reproducible within ±0.0035 min for flow times ranging from 1.5 to 11 min.

Table I shows the densities, the viscosities, and the partial molal volumes with solution composition given both as mole fraction of ether (X_2) and as weight percent of the ether (W_2).

Refractive indices were measured with a separate set of solutions at 25.00 ± 0.01 °C with a Bausch and Lomb refractometer, Abbe type, using the sodium D line. Readings were reproducible within ±0.0002.

Table II shows refractive indices and molar refractions with solution composition given as mole fraction of tetraethylene glycol dimethyl ether (X_2). Also presented are the density data

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Table II. Densities, Refractive Indices, and Molar Refractions of Tetraethylene Glycol Dimethyl Ether at 25 °C

X_2 [a]	$d^{25}{}_4$(obsd) [b]	$n^{25}{}_D$(obsd) [c]	$(R)_{12}$-(exptl) [d]
0.0000	0.99708	1.3323	3.709
0.0076	1.0035	1.3461	4.153
0.0144	1.0098	1.3533	4.503
0.0295	1.0186	1.3680	5.313
0.0419	1.0254	1.3775	5.968
0.0594	1.0322	1.3880	6.892
0.0781	1.0352	1.3962	7.888
0.1144	1.0370	1.4070	9.824
0.1409	1.0357	1.4120	11.243
0.1543	1.0351	1.4148	12.382
0.1672	1.0350	1.4158	12.646
0.1972	1.0309	1.4188	14.274
0.2273	1.0301	1.4212	15.872
0.3237	1.0243	1.4262	21.055
0.4635	1.0169	1.4292	28.581
0.5569	1.0151	1.4308	33.588
0.6402	1.0119	1.4312	38.076
0.7613	1.0078	1.4320	44.659
0.8245	1.0073	1.4323	48.034
1.0000	1.0047	1.4332	57.523

[a] X_2 is the mole fraction of the ether. [b] $d^{25}{}_4$(obsd) is the observed density in g/mL. [c] $n^{25}{}_D$(obsd) is the observed index of refraction. [d] $(R)_{12}(\text{exptl}) = \{(n_{12}^2 - 1)/(n_{12}^2 + 2)\}(X_1M_1 + X_2M_2)/d_{12}$ is the experimental molar refraction. n_{12} is equal to $n^{25}{}_D$ where 1 indicates solvent and 2 indicates solute. M_1 is the molecular weight of solvent (H_2O). M_2 is the molecular weight of solute (tetraglyme). d_{12} is the density of the solution. A reference for the equation is: Schott, H. *J. Chem. Eng. Data* 1961, *6*, 19-20.

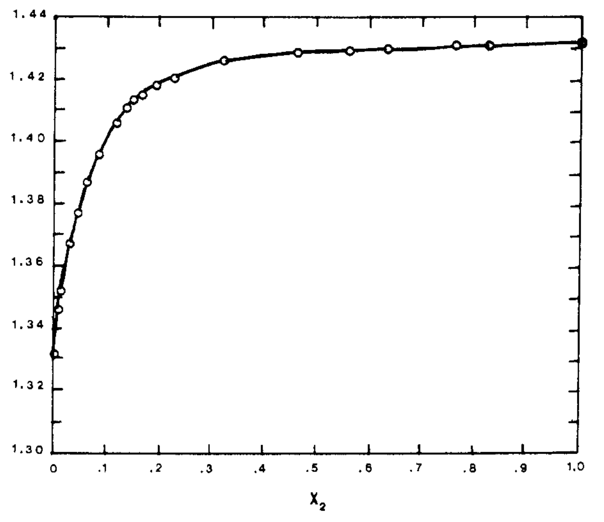

Figure 1. Refractive indices of tetraethylene glycol dimethyl ether-water solutions as a function of mole fraction of ether (X_2).

used for the determination of the molar refraction.

Results and Discussion

As was observed with ethylene glycol dimethyl ether, diethylene glycol dimethyl ether, and triethylene glycol dimethyl ether (*2-4*), the refractive index values increase quickly to about 0.20 mole fraction of the ether (Figure 1) and then they increase more slowly to the value for the pure ether. The molar refraction values of the solutions are shown to be linear with composition, which is in close agreement with the previous ethers (*2-4*). A Pearson *r* correlation coefficient for this line was found to be 0.999 98.

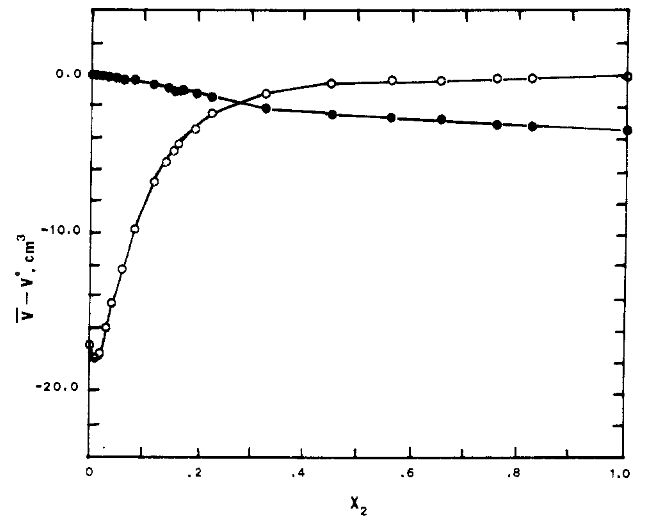

Figure 2. Partial molal volumes (molal volume of pure subtracted from its partial molal volume) of tetraethylene glycol dimethyl ether-water as a function of mole fraction of ether (X_2): (●) water, (○) ether.

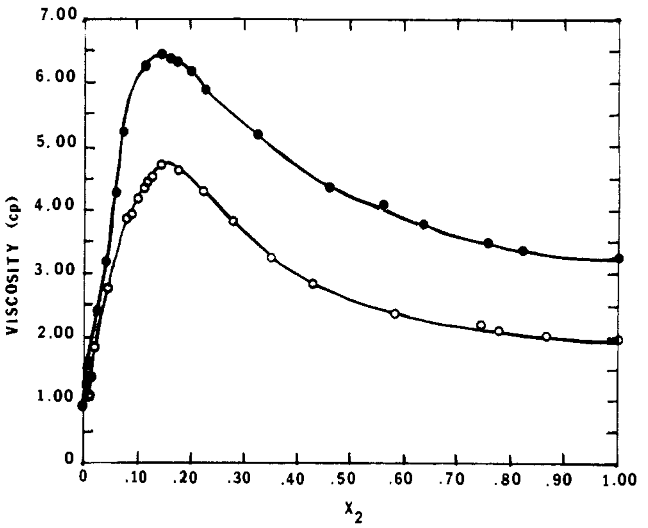

Figure 3. Viscosity of tetraethylene glycol dimethyl ether-water solutions as a function of mole fraction of ether (X_2): (●) tetraethylene glycol dimethyl ether-water, (○) triethylene glycol dimethyl ether-water (*4*).

The density data were used to determine the partial molal volumes by the graphical method of intercepts (*5*). The partial molal volumes are shown in Table I. Figure 2 shows the differences between the partial molal volumes of ether and the molal volume of pure ether, and the differences between the partial molal volume of water and the molal volume of pure water (*2-4*). This is the largest volume difference observed in the series of ethers. The percentage decrease in molal volume for tetraethylene glycol dimethyl ether is about 8%. This is compared to an 8% decrease for triethylene glycol dimethyl ether, a 10% decrease for diethylene glycol dimethyl ether, and a 10% decrease for ethylene glycol dimethyl ether (*2-4*).

Figure 3 shows the viscosity data for tetraethylene glycol dimethyl ether and also the data for triethylene glycol dimethyl ether (*4*). The viscosity data for the diethylene glycol dimethyl ether and ethylene glycol dimethyl ether (*2*, *3*) are also in agreement with Figure 3. The variation of the maximum viscosity in this ether series is consistent with the increase in molecular weight and size. The maximum in viscosity increases as the ethers become more complex. This maximum in viscosity is probably due to the strong hydrogen bonding between the ether oxygens and the water molecules.

Schott (*6*) developed a relationship between the maximum deviation of fluidity and the hydration number of ether oxygens. He reported that the maximum number for the water-ether oxygen ratio in the smaller ethers in this series would be 2.03 ± 0.05. He postulated that, since two is the maximum number of water molecules that can be bound to each of the ether linkages by secondary valence forces, the excess water must be held in a different manner.

A regression analysis provided the functional relationship between viscosity and mole fraction:

$$1.0038 - 0.086435X - 0.028081X^2 + 0.10627X^3$$

where X is the mole fraction of ether. From this relationship the maximum deviation in the fluidity for tetraethylene glycol dimethyl ether occurred at a mole fraction of ether of 0.0815. This corresponded to a water-ether oxygen ratio of 2.254, with a deviation of 439% of predicted fluidity from observed fluidity. Wallace (*4*) reported that for triethylene glycol dimethyl ether the maximum deviation of fluidity occurs at a mole fraction of ether of 0.102, which corresponds to a water-ether oxygen ratio of 2.20, and a deviation of 354% of predicted fluidity from observed fluidity. It can be seen from these increasing water-ether oxygen ratios that there must be more than two water molecules for each ether linkage. Perhaps these excess water molecules are being trapped in the spaces within a particular arrangement of the ethers. This could be explained if the ethers were able to coil, or orient themselves in a spiral, much like a helix.

Registry No. Tetraethylene glycol dimethyl ether, 143-24-8.

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Vapor-Liquid Equilibria in Binary Systems Formed by Thiophene and Light Alcohols

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Isothermal vapor pressure data over the whole range of composition were obtained for five binary systems: thiophene-methanol, thiophene-ethanol, thiophene-1-propanol, thiophene-2-propanol, and thiophene-1-butanol. Data for the first four systems were obtained at temperatures of 308.15, 313.15, and 318.15 K. For the last system, temperatures of 318.15, 328.15, and 338.15 K were used. Excess Gibbs energy equations suggested by Wilson and Renon-Prausnitz (NRTL) were used in the reduction of data. The Wilson equation gives a better fit than the NRTL equation for all these systems.

Introduction

Vapor-liquid phase equilibria measurements continue to be of major importance in thermodynamics, not only for their direct use in process design but also for their importance in the testing and extension of fluid mixture theories. As part of a program to investigate and to predict the phase equilibria in multicomponent systems, it became necessary to obtain vapor-liquid equilibrium data for a number of binary systems.

The aim of this work was to provide vapor-liquid isothermal equilibrium data for binary systems formed by thiophene and light alcohols.

This paper reports the results of these measurements and their correlation by the Wilson and NRTL equations.

Experimental Section

Materials**.** Analytical-grade reagents from Merck were used. Ethanol, 1-propanol, and 2-propanol were used without further purification, after gas chromatography failed to show any significant impurity. The certified minimum purities of these materials were 99.8%, 99.7%, and 99.7%, respectively. Thiophene, methanol, and 1-butanol were redistilled in a high-efficiency packed column. A heart cut was collected by discarding the first 20% distillate and the last 20% residue. The physical properties of these materials given in Tables I and II compare well with those reported in the literature (*1-3*).

Table I. Physical Properties of the Pure Compounds at 293.15 K

	density/(g cm^{-3})		refractive index	
	obsd	lit.	obsd	lit.
thiophene	1.0639	1.064 4^b	1.5290	1.528 7^b
methanol	0.7911	0.791 31^a	1.3290	1.328 40^a
ethanol	0.7910	0.789 37^a	1.3616	1.361 43^a
1-propanol	0.8043	0.803 75^a	1.3855	1.385 56^a
2-propanol	0.7853	0.785 45^a	1.3776	1.377 2^a
1-butanol	0.8096	0.809 7^a	1.3993	1.399 3^a

[a] Reference *2*. [b] Reference *1*.

Vapor Pressure Measurements**.** The vapor pressures of the systems were measured at constant temperature as a function of composition by using a static equilibrium cell. The apparatus, which is described in detail by Vera (*4*), is shown schematically in Figure 1. It was in some respects similar to those used by several other authors: Renon (*5*), Hermsen (*6*), Orye (*7*), Harris (*8*), and Sassa (*9*). Briefly the major items were a large-diameter mercury manometer, measuring the difference in pressure between the reference high vacuum and measuring manifold systems, and a thermostatic bath containing the vapor pressure cell assembly. The latter consisted of a mercury null manometer connected to the static cell. Stirring of the contents

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