Liquid Densities and Refractive Indices of Binary Mixtures for the Dimethyl Ether of a Glycol + Ethanol from T = 288.15 K to 318.15 K

Su-Chen Ku and Chein-Hsiun Tu*

Department of Applied Chemistry, Providence University, Shalu, Taiwan 433, Republic of China

Experimental results are reported for densities, ρ, and refractive indices, n_D, of $\{(x)CH_3(OCH_2CH_2)_\nu$-$OCH_3 + (1 - x)C_2H_5OH\}$ for $\nu = 1-4$ at T = (288.15, 298.15, 308.15, and 318.15) K and atmospheric pressure over the entire mole fraction range. Densities were measured with a vibrating-tube densimeter, and excess volumes molar volumes, V^E, for the mixtures were derived. Refractive indices were measured using a digital refractometer, and deviations as a function of mole fraction, Δn_D, were calculated from the experimental data. The excess molar volumes are negative in every case and become more negative as the ν of the glycol increases. The deviations in refractive indices are generally positive and increase as the ν of the glycol increases. Excess molar volumes increase as the temperature increases, while deviations in refractive indices decrease as the temperature increases. The temperature has no significant effect on V^E of the glycols with $\nu = 3$ and 4 in ethanol. Values of excess volumes and deviations in refractive indices as a function of composition were fitted to the Redlich−Kister equation.

Introduction

Polyalkylene glycol ethers are interesting compounds with multiple etheric oxygen (−O−) groups in their molecules. Many of them have been used as sonar transducer fill fluids in underwater Navy research.[1] On the other hand, ethanol is a widely used solvent with protic and self-associated properties. Upon mixing together, these mixtures might generate interesting properties due to specific interactions, hydrogen bond effects, and so forth. For these reason, we measure densities and refractive indices for the four binary systems formed by ethylene glycol dimethyl ether ($CH_3OCH_2CH_2OCH_3$), diethylene glycol dimethyl ether $\{CH_3(OCH_2CH_2)_2OCH_3\}$, triethylene glycol dimethyl ether $\{CH_3(OCH_2CH_2)_3OCH_3\}$, and tetraethylene glycol dimethyl ether $\{CH_3(OCH_2CH_2)_4OCH_3\}$ with ethanol at the temperatures 288.15 K, 298.15 K, 308.15 K, and 318.15 K and atmospheric pressure over the entire composition range.

This study might be useful for the understanding of the thermodynamic behavior of liquid mixtures under the influence of the changes of the $-OCH_2CH_2-$ unit for species with a common alkyl chain and their sensitivities to variations in composition and temperature under atmospheric pressure. The experimental results of this study have been used to calculate mixing properties such as excess molar volume, V^E, and deviations in refractive index, Δn_D. The literature dealing with the thermodynamic studies on the mixtures containing polyethylene glycol ethers and alcohols is relatively limited.[2,3] Several previous results were shown for the mixtures with water at T = 298.15 K.[4−7] As far as we know, no literature data are available for the mixtures with ethanol.

Experimental Section

Materials. The chemicals used were of analytical grade and obtained from Aldrich, Tedia, and SHOWA. The gas chromatographic analysis of pure components showed that the major peak area exceeded 99.9% for ethanol and ethylene glycol dimethyl ether, 99.6% for di- and tetraethylene glycol dimethyl ether, and 99.3% for triethylene glycol dimethyl ether. All chemicals were used without further purification. The purity of the final sample was also checked by measuring the densities and refractive indices at the temperature 298.15 K, which agreed reasonably well with the corresponding literature values, as shown in Table 1.

Table 1. Comparison of Measured Densities and Refractive Indices of Pure Components with Literature Values at 298.15 K

	ρ/g·cm^{-3}		n_D	
compound	this study	lit.	this study	lit.
ethanol	0.785 18	0.784 93[a] 0.785 2[b] 0.785 04[c]	1.359 10	1.359 41[a] 1.359 2[c]
ethylene glycol dimethyl ether	0.861 48	0.862 1[a] 0.860 5[d] 0.861 32[e]	1.377 23	1.377 30[d]
diethylene glycol dimethyl ether	0.938 65	0.938 41[a] 0.938 73[f] 0.939 24[g]	1.405 77	1.405 8[a]
triethylene glycol dimethyl ether	0.980 13	0.981 17[g] 0.979 5[h] 0.980 01[i]	1.420 87	1.420 9[i]
tetraethylene glycol dimethyl ether	1.006 57	1.006 27[g] 1.006 62[h] 1.004 7[j]	1.430 32	1.433 2[j]

[a] Reference 8. [b] Reference 9. [c] Reference 10. [d] Reference 4. [e] Reference 11. [f] Reference 12. [g] Reference 7. [h] Reference 5. [i] Reference 13. [j] Reference 6.

Procedure. Liquids were dried over activated molecular sieves type 0.4 nm from Aldrich. All dried liquids were boiled to remove dissolved air. Samples were prepared by mass in a 50-cm^3 Erlenmeyer flask provided with a joint stopper, using a Precisa 262SMA balance with an accuracy of $\pm 3 \times 10^{-5}$ g. The uncertainty of the mole fraction in composition was believed to be less than $\pm 1 \times 10^{-4}$. Densities were measured with an Anton Paar DMA-58

* Corresponding author. E-mail: chtu@pu.edu.tw.

10.1021/je0302304 CCC: $27.50
Published on Web 02/06/2004

Table 2. Experimental Densities, ρ/g·cm^{-3}, and Refractive Indices, n_D, for Binary Mixtures at 288.15 K

x	ρ/g·cm^{-3}	n_D	x	ρ/g·cm^{-3}	n_D	x	ρ/g·cm^{-3}	n_D
(x)Ethylene Glycol Dimethyl Ether + (1 − x)Ethanol								
0.0000	0.7936	1.3632	0.1500	0.8142	1.3681	0.6000	0.8530	1.3776
0.0045	0.7945	1.3633	0.2000	0.8199	1.3695	0.6499	0.8560	1.3783
0.0086	0.7952	1.3634	0.2500	0.8252	1.3709	0.7000	0.8587	1.3790
0.0125	0.7958	1.3635	0.3000	0.8301	1.3721	0.7499	0.8613	1.3796
0.0165	0.7964	1.3636	0.3500	0.8346	1.3732	0.7999	0.8637	1.3802
0.0205	0.7970	1.3638	0.4000	0.8388	1.3742	0.8500	0.8661	1.3808
0.0305	0.7985	1.3642	0.4500	0.8427	1.3751	0.9000	0.8683	1.3813
0.0500	0.8013	1.3649	0.5000	0.8464	1.3760	0.9499	0.8704	1.3818
0.1000	0.8079	1.3666	0.5500	0.8498	1.3768	1.0000	0.8724	1.3824
(x)Diethylene Glycol Dimethyl Ether + (1 − x)Ethanol								
0.0000	0.7936	1.3632	0.1500	0.8426	1.3780	0.5999	0.9174	1.4007
0.0045	0.7956	1.3636	0.2000	0.8550	1.3817	0.6500	0.9225	1.4022
0.0085	0.7971	1.3641	0.2500	0.8659	1.3851	0.6999	0.9271	1.4036
0.0125	0.7987	1.3645	0.3000	0.8757	1.3881	0.7499	0.9313	1.4049
0.0165	0.8003	1.3650	0.3500	0.8845	1.3907	0.7999	0.9353	1.4060
0.0205	0.8018	1.3655	0.4000	0.8924	1.3931	0.8499	0.9390	1.4072
0.0305	0.8055	1.3666	0.4500	0.8996	1.3953	0.8998	0.9424	1.4082
0.0500	0.8126	1.3687	0.4999	0.9060	1.3973	0.9498	0.9457	1.4092
0.1000	0.8287	1.3737	0.5500	0.9120	1.3990	1.0000	0.9486	1.4101
(x)Triethylene Glycol Dimethyl Ether + (1 − x)Ethanol								
0.0000	0.7936	1.3632	0.1500	0.8664	1.3862	0.6000	0.9573	1.4149
0.0045	0.7967	1.3641	0.2000	0.8829	1.3915	0.6500	0.9627	1.4166
0.0085	0.7993	1.3648	0.2500	0.8969	1.3960	0.7000	0.9675	1.4181
0.0125	0.8017	1.3656	0.3000	0.9092	1.3998	0.7500	0.9720	1.4195
0.0165	0.8042	1.3664	0.3500	0.9198	1.4032	0.7999	0.9761	1.4208
0.0205	0.8066	1.3672	0.4000	0.9292	1.4061	0.8499	0.9799	1.4220
0.0305	0.8124	1.3691	0.4499	0.9374	1.4087	0.8998	0.9834	1.4231
0.0500	0.8230	1.3724	0.5000	0.9448	1.4110	0.9498	0.9867	1.4241
0.1000	0.8467	1.3799	0.5500	0.9514	1.4131	1.0000	0.9897	1.4250
(x)Tetraethylene Glycol Dimethyl Ether + (1 − x)Ethanol								
0.0000	0.7936	1.3632	0.1500	0.8880	1.3936	0.6000	0.9857	1.4248
0.0045	0.7979	1.3644	0.2000	0.9073	1.3999	0.6499	0.9909	1.4264
0.0085	0.8014	1.3656	0.2500	0.9233	1.4050	0.7000	0.9956	1.4279
0.0125	0.8048	1.3667	0.3000	0.9366	1.4093	0.7498	0.9998	1.4292
0.0165	0.8082	1.3678	0.3500	0.9479	1.4129	0.7999	1.0036	1.4304
0.0205	0.8115	1.3689	0.4000	0.9576	1.4159	0.8499	1.0070	1.4315
0.0305	0.8195	1.3714	0.4500	0.9660	1.4186	0.8997	1.0102	1.4326
0.0500	0.8336	1.3760	0.5000	0.9734	1.4209	0.9496	1.0132	1.4335
0.1000	0.8641	1.3858	0.5500	0.9799	1.4230	1.0000	1.0160	1.4344

Table 3. Experimental Densities, ρ, and Refractive Indices, n_D, for Binary Mixtures at 298.15 K

x	ρ/g·cm^{-3}	n_D	x	ρ/g·cm^{-3}	n_D	x	ρ/g·cm^{-3}	n_D
(x)Ethylene Glycol Dimethyl Ether + (1 − x)Ethanol								
0.0000	0.7852	1.3591	0.1500	0.8050	1.3639	0.6000	0.8427	1.3729
0.0045	0.7860	1.3592	0.2000	0.8106	1.3652	0.6499	0.8455	1.3736
0.0086	0.7866	1.3593	0.2500	0.8157	1.3664	0.7000	0.8482	1.3742
0.0125	0.7871	1.3594	0.3000	0.8205	1.3676	0.7499	0.8507	1.3748
0.0165	0.7877	1.3596	0.3500	0.8249	1.3686	0.7999	0.8531	1.3754
0.0205	0.7883	1.3597	0.4000	0.8290	1.3696	0.8500	0.8554	1.3759
0.0305	0.7898	1.3601	0.4500	0.8328	1.3705	0.9000	0.8575	1.3764
0.0500	0.7925	1.3608	0.5000	0.8363	1.3714	0.9499	0.8595	1.3768
0.1000	0.7990	1.3624	0.5500	0.8396	1.3722	1.0000	0.8615	1.3772
(x)Diethylene Glycol Dimethyl Ether + (1 − x)Ethanol								
0.0000	0.7852	1.3591	0.1500	0.8336	1.3739	0.5999	0.9077	1.3965
0.0045	0.7870	1.3596	0.2000	0.8458	1.3776	0.6500	0.9126	1.3980
0.0085	0.7886	1.3601	0.2500	0.8566	1.3810	0.6999	0.9172	1.3993
0.0125	0.7901	1.3605	0.3000	0.8663	1.3839	0.7499	0.9214	1.4006
0.0165	0.7917	1.3610	0.3500	0.8750	1.3866	0.7999	0.9254	1.4018
0.0205	0.7932	1.3615	0.4000	0.8829	1.3889	0.8499	0.9290	1.4029
0.0305	0.7969	1.3626	0.4500	0.8899	1.3911	0.8998	0.9324	1.4039
0.0500	0.8038	1.3647	0.4999	0.8964	1.3931	0.9498	0.9357	1.4049
0.1000	0.8197	1.3696	0.5500	0.9023	1.3948	1.0000	0.9387	1.4058
(x)Triethylene Glycol Dimethyl Ether + (1 − x)Ethanol								
0.0000	0.7852	1.3591	0.1500	0.8573	1.3823	0.6000	0.9477	1.4108
0.0045	0.7882	1.3600	0.2000	0.8736	1.3875	0.6500	0.9531	1.4125
0.0085	0.7907	1.3608	0.2500	0.8877	1.3919	0.7000	0.9580	1.4140
0.0125	0.7932	1.3616	0.3000	0.9000	1.3958	0.7500	0.9624	1.4154
0.0165	0.7956	1.3624	0.3500	0.9105	1.3991	0.7999	0.9665	1.4167
0.0205	0.7980	1.3632	0.4000	0.9198	1.4020	0.8499	0.9703	1.4179
0.0305	0.8037	1.3650	0.4499	0.9280	1.4046	0.8998	0.9738	1.4189
0.0500	0.8142	1.3684	0.5000	0.9353	1.4069	0.9498	0.9771	1.4199
0.1000	0.8377	1.3760	0.5500	0.9419	1.4090	1.0000	0.9801	1.4209

Table 3 (Continued)

x	ρ/g·cm^{-3}	n_D	x	ρ/g·cm^{-3}	n_D	x	ρ/g·cm^{-3}	n_D
(x)Tetraethylene Glycol Dimethyl Ether + (1 − x)Ethanol								
0.0000	0.7852	1.3591	0.1500	0.8789	1.3897	0.6000	0.9763	1.4208
0.0045	0.7894	1.3604	0.2000	0.8981	1.3960	0.6499	0.9815	1.4225
0.0085	0.7929	1.3615	0.2500	0.9141	1.4011	0.7000	0.9862	1.4239
0.0125	0.7963	1.3627	0.3000	0.9274	1.4053	0.7498	0.9904	1.4252
0.0165	0.7996	1.3638	0.3500	0.9386	1.4089	0.7999	0.9942	1.4264
0.0205	0.8029	1.3649	0.4000	0.9483	1.4120	0.8499	0.9977	1.4275
0.0305	0.8108	1.3674	0.4500	0.9567	1.4146	0.8997	1.0009	1.4285
0.0500	0.8249	1.3720	0.5000	0.9641	1.4170	0.9496	1.0038	1.4294
0.1000	0.8551	1.3819	0.5500	0.9706	1.4190	1.0000	1.0066	1.4303

Table 4. Experimental Densities, ρ, and Refractive Indices, n_D, for Binary Mixtures at 308.15 K

x	ρ/g·cm^{-3}	n_D	x	ρ/g·cm^{-3}	n_D	x	ρ/g·cm^{-3}	n_D
(x)Ethylene Glycol Dimethyl Ether + (1 − x)Ethanol								
0.0000	0.7766	1.3551	0.1500	0.7958	1.3596	0.6000	0.8321	1.3682
0.0045	0.7773	1.3552	0.2000	0.8012	1.3609	0.6499	0.8349	1.3688
0.0086	0.7779	1.3553	0.2500	0.8061	1.3621	0.7000	0.8375	1.3694
0.0125	0.7784	1.3554	0.3000	0.8107	1.3631	0.7499	0.8399	1.3700
0.0165	0.7790	1.3555	0.3500	0.8150	1.3641	0.7999	0.8422	1.3705
0.0205	0.7796	1.3557	0.4000	0.8189	1.3651	0.8500	0.8445	1.3710
0.0305	0.7810	1.3560	0.4500	0.8226	1.3659	0.9000	0.8466	1.3715
0.0500	0.7836	1.3566	0.5000	0.8260	1.3667	0.9499	0.8485	1.3719
0.1000	0.7900	1.3582	0.5500	0.8292	1.3675	1.0000	0.8504	1.3722
(x)Diethylene Glycol Dimethyl Ether + (1 − x)Ethanol								
0.0000	0.7766	1.3551	0.1500	0.8245	1.3697	0.5999	0.8978	1.3920
0.0045	0.7784	1.3555	0.2000	0.8365	1.3734	0.6500	0.9028	1.3935
0.0085	0.7799	1.3560	0.2500	0.8473	1.3767	0.6999	0.9073	1.3949
0.0125	0.7815	1.3565	0.3000	0.8569	1.3797	0.7499	0.9115	1.3961
0.0165	0.7830	1.3569	0.3500	0.8655	1.3823	0.7999	0.9154	1.3973
0.0205	0.7844	1.3574	0.4000	0.8732	1.3846	0.8499	0.9191	1.3984
0.0305	0.7881	1.3585	0.4500	0.8802	1.3867	0.8998	0.9225	1.3994
0.0500	0.7950	1.3606	0.4999	0.8867	1.3887	0.9498	0.9257	1.4003
0.1000	0.8107	1.3654	0.5500	0.8925	1.3904	1.0000	0.9287	1.4012
(x)Triethylene Glycol Dimethyl Ether + (1 − x)Ethanol								
0.0000	0.7766	1.3551	0.1500	0.8483	1.3782	0.6000	0.9383	1.4067
0.0045	0.7795	1.3559	0.2000	0.8645	1.3834	0.6500	0.9437	1.4084
0.0085	0.7820	1.3567	0.2500	0.8786	1.3879	0.7000	0.9486	1.4099
0.0125	0.7844	1.3575	0.3000	0.8907	1.3917	0.7500	0.9530	1.4113
0.0165	0.7868	1.3583	0.3500	0.9013	1.3950	0.7999	0.9571	1.4126
0.0205	0.7892	1.3590	0.4000	0.9105	1.3979	0.8499	0.9608	1.4137
0.0305	0.7949	1.3609	0.4499	0.9186	1.4005	0.8998	0.9643	1.4148
0.0500	0.8054	1.3644	0.5000	0.9259	1.4028	0.9498	0.9676	1.4158
0.1000	0.8288	1.3720	0.5500	0.9324	1.4049	1.0000	0.9707	1.4167
(x)Tetraethylene Glycol Dimethyl Ether + (1 − x)Ethanol								
0.0000	0.7766	1.3551	0.1500	0.8699	1.3857	0.6000	0.9671	1.4168
0.0045	0.7807	1.3564	0.2000	0.8891	1.3920	0.6499	0.9723	1.4184
0.0085	0.7842	1.3575	0.2500	0.9050	1.3971	0.7000	0.9770	1.4199
0.0125	0.7876	1.3586	0.3000	0.9182	1.4013	0.7498	0.9812	1.4212
0.0165	0.7909	1.3598	0.3500	0.9295	1.4049	0.7999	0.9850	1.4224
0.0205	0.7942	1.3608	0.4000	0.9392	1.4080	0.8499	0.9884	1.4234
0.0305	0.8020	1.3634	0.4500	0.9475	1.4106	0.8997	0.9916	1.4244
0.0500	0.8161	1.3680	0.5000	0.9549	1.4130	0.9496	0.9946	1.4253
0.1000	0.8462	1.3779	0.5500	0.9613	1.4150	1.0000	0.9974	1.4262

vibrating-tube densimeter thermostatically controlled to within ±0.01 K, with a stated accuracy of $\pm 2 \times 10^{-5}$ g·cm^{-3}. Calibration was performed at atmospheric pressure periodically, in accordance with specifications, using deionized water and dry air. Precautions were taken in order to avoid evaporation losses and air dissolved during the experimental work. Refractive indices, n_D, were measured with a digital Abbe refractometer RX-5000 (ATAGO, Tokyo, Japan) thermostatically controlled to ±0.05 K, with a stated uncertainty of ±0.000 02 units.

A set with the compositions varying from 0.0045 to 0.95 mole fraction of glycol was prepared for each system. An average of at least three measurements was taken for each composition. The uncertainty of the density measurements for the systems investigated was estimated to be less than $\pm 1 \times 10^{-4}$ g·cm^{-3}. The excess molar volumes were calculated from density data, and the uncertainties were estimated to be within $\pm 1 \times 10^{-2}$ cm^3·mol^{-1}. The uncertainty of the refractive index measurements for the systems investigated was within $\pm 4 \times 10^{-4}$.

Results and Discussion

The molar excess volumes, V^E, have been calculated from density data according to the equation

$$V^E = (x_1M_1 + x_2M_2)/\rho - (x_1M_1/\rho_1 + x_2M_2/\rho_2) \quad (1)$$

where V and ρ are the molar volume and density of the mixture. x_1, V_1, M_1, x_2, V_2, and M_2 are the mole fraction, molar volume, and molecular weight of pure components 1 and 2, respectively. The deviations in refractive index from the mole fraction average, Δn_D, are given by

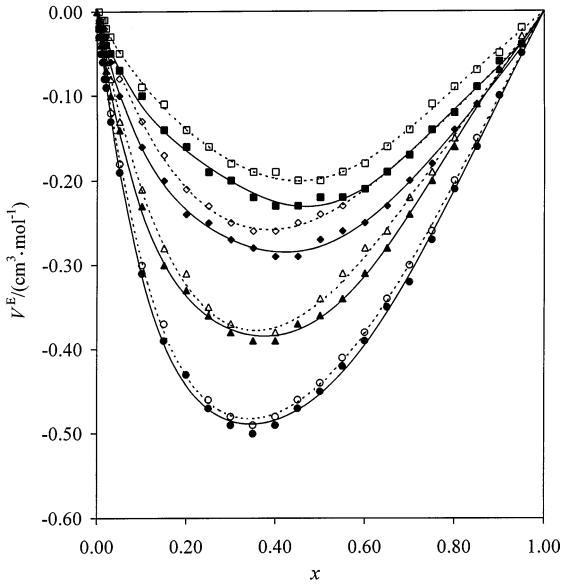

Figure 1. Experimentally derived excess molar volume, V^E, as a function of the concentration of glycol in ethanol at $T = 288.15$ K and $T = 318.15$ K: ■, □, ethylene glycol dimethyl ether; ◆, ◇, diethylene glycol dimethyl ether; ▲, △, triethylene glycol dimethyl ether; ●, ○, tetraethylene glycol dimethyl ether; —, - - -, Redlich–Kister equation.

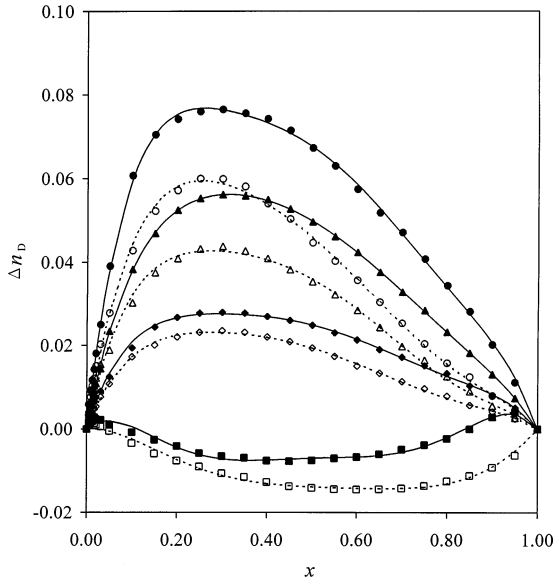

Figure 2. Experimentally derived refractive indices, Δn_D, as a function of the concentration of glycol in ethanol at $T = 288.15$ K and $T = 318.15$ K: ■, □, ethylene glycol dimethyl ether; ◆, ◇, diethylene glycol dimethyl ether; ▲, △, triethylene glycol dimethyl ether; ●, ○, tetraethylene glycol dimethyl ether; —, - - -, Redlich–Kister equation.

Table 5. Experimental Densities, ρ, and Refractive Indices, n_D, for Binary Mixtures at 318.15 K

x	ρ/g·cm^{-3}	n_D	x	ρ/g·cm^{-3}	n_D	x	ρ/g·cm^{-3}	n_D
			(x)Ethylene Glycol Dimethyl Ether + (1 − x)Ethanol					
0.0000	0.7679	1.3509	0.1500	0.7863	1.3552	0.6000	0.8215	1.3634
0.0045	0.7685	1.3510	0.2000	0.7915	1.3565	0.6499	0.8241	1.3640
0.0086	0.7690	1.3511	0.2500	0.7963	1.3576	0.7000	0.8266	1.3646
0.0125	0.7696	1.3512	0.3000	0.8007	1.3586	0.7499	0.8290	1.3652
0.0165	0.7701	1.3513	0.3500	0.8048	1.3596	0.7999	0.8312	1.3657
0.0205	0.7707	1.3515	0.4000	0.8087	1.3605	0.8500	0.8334	1.3661
0.0305	0.7720	1.3518	0.4500	0.8122	1.3613	0.9000	0.8354	1.3666
0.0500	0.7746	1.3524	0.5000	0.8155	1.3620	0.9499	0.8373	1.3669
0.1000	0.7807	1.3539	0.5500	0.8186	1.3628	1.0000	0.8392	1.3672
			(x)Diethylene Glycol Dimethyl Ether + (1 − x)Ethanol					
0.0000	0.7679	1.3509	0.1500	0.8151	1.3655	0.5999	0.8879	1.3877
0.0045	0.7696	1.3514	0.2000	0.8271	1.3692	0.6500	0.8928	1.3892
0.0085	0.7711	1.3518	0.2500	0.8378	1.3725	0.6999	0.8973	1.3905
0.0125	0.7726	1.3523	0.3000	0.8473	1.3754	0.7499	0.9015	1.3917
0.0165	0.7741	1.3528	0.3500	0.8558	1.3780	0.7999	0.9054	1.3929
0.0205	0.7756	1.3532	0.4000	0.8635	1.3803	0.8499	0.9090	1.3940
0.0305	0.7792	1.3543	0.4500	0.8705	1.3824	0.8998	0.9125	1.3950
0.0500	0.7860	1.3564	0.4999	0.8768	1.3843	0.9498	0.9157	1.3959
0.1000	0.8015	1.3612	0.5500	0.8826	1.3861	1.0000	0.9186	1.3968
			(x)Triethylene Glycol Dimethyl Ether + (1 − x)Ethanol					
0.0000	0.7679	1.3509	0.1500	0.8390	1.3741	0.6000	0.9288	1.4026
0.0045	0.7706	1.3517	0.2000	0.8552	1.3794	0.6500	0.9342	1.4043
0.0085	0.7731	1.3525	0.2500	0.8692	1.3839	0.7000	0.9390	1.4058
0.0125	0.7755	1.3533	0.3000	0.8814	1.3877	0.7500	0.9435	1.4072
0.0165	0.7780	1.3541	0.3500	0.8919	1.3910	0.7999	0.9475	1.4084
0.0205	0.7803	1.3548	0.4000	0.9011	1.3939	0.8499	0.9513	1.4096
0.0305	0.7860	1.3567	0.4499	0.9092	1.3965	0.8998	0.9548	1.4106
0.0500	0.7964	1.3602	0.5000	0.9164	1.3988	0.9498	0.9581	1.4116
0.1000	0.8197	1.3679	0.5500	0.9229	1.4008	1.0000	0.9611	1.4125
			(x)Tetraethylene Glycol Dimethyl Ether + (1 − x)Ethanol					
0.0000	0.7679	1.3509	0.1500	0.8607	1.3818	0.6000	0.9578	1.4128
0.0045	0.7719	1.3522	0.2000	0.8799	1.3881	0.6499	0.9630	1.4144
0.0085	0.7753	1.3533	0.2500	0.8957	1.3931	0.7000	0.9676	1.4159
0.0125	0.7787	1.3545	0.3000	0.9089	1.3973	0.7498	0.9719	1.4172
0.0165	0.7820	1.3556	0.3500	0.9202	1.4009	0.7999	0.9756	1.4184
0.0205	0.7853	1.3567	0.4000	0.9298	1.4040	0.8499	0.9791	1.4194
0.0305	0.7931	1.3593	0.4500	0.9382	1.4067	0.8997	0.9824	1.4204
0.0500	0.8071	1.3641	0.5000	0.9455	1.4090	0.9496	0.9853	1.4213
0.1000	0.8371	1.3741	0.5500	0.9520	1.4110	1.0000	0.9881	1.4221

Table 6. Coefficients and Standard Deviations, σ, of V^E and Δn_D for the Binary Mixtures in the Temperature Range 288.15−318.15 K

Y/unit	T/K	10^2a_0	10^2a_1	10^2a_2	10^2a_3	10^2a_4	$10^5\sigma$
		(x)Ethylene Glycol Dimethyl Ether + (1 − x)Ethanol					
V^E/cm^3·mol^{-1}	288.15	−91.181	16.432	39.649	24.770	−78.219	605
	298.15	−88.063	20.818	31.601	13.545	−56.285	337
	308.15	−83.619	23.191	23.446	−1.3110	−29.453	225
	318.15	−79.107	21.148	30.456	9.5017	−30.958	369
Δn_D	288.15	−2.7845	0.7396	−4.4033	1.3961	18.476	91
	298.15	−4.5988	−0.92115	−3.3140	−4.3815	6.6039	93
	308.15	−4.9354	−0.83996	−3.9137	−4.9467	6.3115	86
	318.15	−5.5278	−0.94144	−3.5553	−5.8077	3.5838	81
		(x)Diethylene Glycol Dimethyl Ether + (1 − x)Ethanol					
V^E/cm^3·mol^{-1}	288.15	−111.19	34.968	3.2271	36.574	−58.551	525
	298.15	−109.02	43.764	8.0194	10.595	−56.558	337
	308.15	−102.37	46.179	−7.9734	5.8396	−27.671	382
	318.15	−97.339	49.471	−6.0971	−5.6219	−17.180	351
Δn_D	288.15	9.9554	−5.4262	2.3063	−5.1204	11.646	101
	298.15	9.2635	−5.9937	1.8017	−4.0040	9.9423	58
	308.15	8.5504	−6.1568	1.1089	−4.2953	10.072	42
	318.15	7.7607	−6.3587	1.3473	−4.0294	8.4207	43
		(x)Triethylene Glycol Dimethyl Ether + (1 − x)Ethanol					
V^E/cm^3·mol^{-1}	288.15	−145.13	70.878	2.5646	66.224	−72.580	615
	298.15	−142.88	79.059	8.1409	39.986	−75.028	699
	308.15	−138.33	78.601	−23.192	39.278	−18.852	490
	318.15	−137.64	87.421	−16.763	14.482	−23.356	661
Δn_D	288.15	19.950	−12.662	6.1547	−7.3449	11.318	415
	298.15	18.533	−13.759	5.4270	−5.0967	7.1427	63
	308.15	17.125	−14.600	3.3565	−5.0864	10.971	123
	318.15	14.366	−11.920	1.0332	−9.7535	15.283	138
		(x)Tetraethylene Glycol Dimethyl Ether + (1 − x)Ethanol					
V^E/cm^3·mol^{-1}	288.15	−181.21	89.526	−43.538	86.654	−56.655	697
	298.15	−179.15	93.594	−52.437	70.402	−35.999	657
	308.15	−177.66	99.213	−51.962	63.934	−30.482	507
	318.15	−176.69	97.152	−46.420	61.557	−35.433	419
Δn_D	288.15	27.006	−14.552	9.8671	−19.689	27.662	84
	298.15	24.549	−16.922	5.9532	−15.443	29.082	105
	308.15	21.545	−18.168	8.0240	−15.887	23.008	96
	318.15	18.370	−18.434	7.4823	−10.421	15.284	119

$$\Delta n_D = n_D - (x_1 n_{D1} + x_2 n_{D2}) \quad (2)$$

where n_D, n_{D1}, and n_{D2} are the refractive index of the mixture and the refractive indices of pure components 1 and 2, respectively. The experimental densities and refractive indices of four binary mixtures $\{(x)CH_3(OCH_2CH_2)_\nu OCH_3 + (1 - x)C_2H_5OH\}$ for $\nu = 1-4$ at $T = (288.15, 298.15, 308.15, \text{and } 318.15)$ K and atmospheric pressure over the entire mole fraction range are presented in Tables 2−5.

In the system studied, excess molar volumes are negative and become more negative as the number of $-OCH_2CH_2-$ groups of the glycol increases through the whole range of mole fraction. Similar behavior can also be seen for mixtures of 1-propanol + ethylene glycol dimethyl ether, + diethylene glycol dimethyl ether, and + triethylene glycol dimethyl ether at 298.15 K.[2] The equimolar values of V^E vary from −0.20 cm^3·mol^{-1} to −0.45 cm^3·mol^{-1}. Figure 1 shows the excess molar volumes, V^E, as a function of mole fraction of glycol for the four systems at the temperatures 288.15 K and 318.15 K. Volume expansion is observed for the increase in temperature. However, the temperature has no significant effect on V^E for triethylene glycol dimethyl ether and tetraethylene glycol dimethyl ether in ethanol.

The values of Δn_D are positive for all of the systems over the entire range of composition except that small negative values were observed for the system ethylene glycol dimethyl ether. Figure 2 shows the deviations in refractive index, Δn_D, as a function of mole fraction of glycol for temperatures at 288.15 K and 318.15 K. The equimolar values of Δn_D vary from −0.0141 to 0.0673. There is a very obvious increase in the magnitudes of n_D and Δn_D as the number of $-OCH_2CH_2-$ groups increases in the glycol molecules. The increase in temperature leads to a lower value of Δn_D for the four systems studied.

The mixing functions V^E and Δn_D were represented mathematically by the following type of Redlich−Kister equation[14] for correlating the experimental data:

$$Y = x(1 - x)\sum_{i=0}^{p} a_i(2x - 1)^i \quad (3)$$

where Y refers to V^E/cm^3·mol^{-1} or Δn_D, x is the mole fraction of the glycol, and a_i are the coefficients. The values of coefficients a_i were determined by a multiple regression analysis based on the least-squares method and are summarized along with the standard deviations between the experimental and fitted values of the respective functions in Table 6. The standard deviation is defined by

$$\sigma = [\sum_{i=1}^{m}(Y_i^{\,\text{exp}} - Y_i^{\,\text{calc}})^2/(m - p)]^{1/2} \quad (4)$$

where m is the number of experimental points and p is the number of adjustable parameters. For the case of V^E, the σ values lie between 0.0022 cm^3·mol^{-1} and 0.0070 cm^3·mol^{-1} and the largest σ value corresponds to the triethylene glycol dimethyl ether + ethanol mixture at 298.15 K. For the case of Δn_D, the σ values lie

between 0.0004 and 0.0014 and the largest σ value corresponds to triethylene glycol dimethyl ether + ethanol at 318.15 K.

Literature Cited

(1) Thompson, C. M. *The Use of Plyalkylene Glycols in Sonar Transducers*; Navy Research Laboratory Report No. 8283; Washington, DC, February 1979.

(2) Pal, A.; Sharma, S. Excess Molar Volumes and Viscosities of 1-Propanol + Ethylene Glycol, + Ethylene Glycol Monomethyl, + Ethylene Glycol Dimethyl, + Diethylene Glycol Dimethyl, + Triethylene Glycol Dimethyl, + Diethylene Glycol Diethyl, and Diethylene Glycol Dibutyl Ethers at 298.15 K. *J. Chem. Eng. Data* **1998**, *43*, 532−536.

(3) Ruiz Holgado, M. E. F. de; Schaefer, C. R. de; Arancibia, E. L. Densities and Viscosities of Binary Mixtures of Polyethylene Glycol 350 Monomethyl Ether with *n*-Butanol and *n*-Pentanol and Tetraethylene Glycol Dimethyl Ethers with *n*-Propanol, *n*-Butanol, and *n*-Pentanol from 278.15 K to 318.15 K. *J. Chem. Eng. Data* **2002**, *47*, 144−148.

(4) Wallace, W. J.; Mathews, A. L. Densities, Refractive Indices, Molar Refractions, and Viscosities of Ethylene Glycol Dimethyl Ether-Water Solutions at 25 °C. *J. Chem. Eng. Data* **1963**, *8*, 496−498.

(5) Wallace, W. J.; Shephard, C. S.; Underwood, C. Densities, Refractive Indices, Molar Refractions, Viscosities, and Dielectric Constants of Triethylene Glycol Dimethyl Ether-Water Solutions at 25 °C. *J. Chem. Eng. Data* **1968**, *13*, 11−13.

(6) McGee, R. L.; Wallace, W. J.; Ratalczak, R. D. Densities, Viscosities, Refractive Indices, Molar Refractions of the Binary System Tetraethylene Glycol Dimethyl Ether-Water Solutions at 25 °C. *J. Chem. Eng. Data* **1983**, *28*, 305−307.

(7) Dethlefsen, C.; Hvidt, A. Densities and Derived Volume Fractions of Binary Mixtures; (an Ethylene Glycol Derivative + Water) at 298.15 K. *J. Chem. Thermodyn.* **1985**, *17*, 193−199.

(8) Riddick, A.; Bunger, W. B.; Sakano, T. K. *Organic Solvents, Physical Properties and Method of Purification*, 4th ed.; Wiley-Interscience: New York, 1986.

(9) Orge, B.; Iglesias, M.; Rodriguez, A.; Canosa, J. M.; Tojo, J. Mixing Properties of (Methanol, Ethanol, or 1-Propanol) with (*n*-Pentane, *n*-Hexane, *n*-Heptane and *n*-Octane) at 298.15 K. *Fluid Phase Equilib.* **1997**, *133*, 213−227.

(10) Gabaldón, C.; Martínez-Soria, V.; Marzal, P.; Montón, J. B. Isobaric Vapor-Liquid Equilibria for the Binary System 3-Methylpentane + Ethanol and for the Ternary System 2-Methyl-2-propanol + Ethanol + 3-Methylpentane at 101.3 kPa. *J. Chem. Eng. Data* **2000**, *45*, 882−886.

(11) Das, B.; Roy, M. N.; Hazra, D. K. Densities and Viscosities of Binary Aqueous Mixtures of Tetrahydrofuran and 1,2-Dimethoxyethane at 298, 308 and 318 K. *Indian J. Chem. Technol.* **1994**, *1*, 93−97.

(12) Tover, C. A.; Carballo, E.; Cerdeiriña, C. A.; Romaní, L. Excess Molar Volumes and Excess Molar Heat Capacities of Mixtures Containing (Mono and Poly) Ethers + Ethyl Acetate. *J. Chem. Eng. Data* **1997**, *42*, 1085−1089.

(13) Treszczanowicz, T. Application of the Flory and Sanchez-Lacombe Theories to the Excess Molar Volume of Ether + Hydrocarbon Systems. *Thermochim. Acta* **1990**, *160*, 253−266.

(14) Redlich, O.; Kister, A. T. Thermodynamics of Nonelectrolyte Solutions. Algebraic Representation of Thermodynamic Properties and the Classification of Solutions. *Ind. Eng. Chem.* **1948**, *40*, 345−348.

Received for review October 2, 2003. Accepted December 21, 2003.

JE0302304