Density and Viscosity of Mixtures of Alkoxypropanols with Ethanol at T = (298.15, 308.15, and 318.15) K

Su-Chen Ku, I-Hung Peng, and Chein-Hsiun Tu*

Department of Applied Chemistry, Providence University, Shalu 43301 Taiwan

Densities and viscosities were measured for the binary mixtures formed by 1-methoxy-2-propanol, 1-propoxy-2-propanol, 1-butoxy-2-propanol, dipropylene glycol methyl ether, dipropylene glycol propyl ether, and dipropylene glycol butyl ether with ethanol at T = (298.15, 308.15, and 318.15) K and atmospheric pressure over the whole concentration range. Densities were determined using a vibratingtube densimeter. Viscosities were measured with an automatic Ubbelohde capillary viscometer. The estimated uncertainties are less than $\pm 1 \times 10^{-4} \text{ g} \cdot \text{cm}^{-3}$ for density and $\pm 0.6\%$ for viscosity. Excess volumes V^{E} and deviations in viscosity $\Delta \eta$ for the mixtures were derived from the experimental data, and the computed results were fitted to the Redlich–Kister equation. Furthermore, McAllister's multibodyinteraction model is used to correlate the binary kinematic viscosities.

Introduction

Alkoxyalkanols are very interesting solvents having the ability to form intra- and intermolecular hydrogen bonds.¹ On the other hand, alcohols are the most well-known solvents with protic and self-associated properties. Upon mixing together, these mixtures might generate interesting properties due to specific interactions, hydrogen bond effects, etc.^{2–5} A detailed understanding of the effect of the simultaneous presence of the ether (-O-) and hydroxyl (-OH) groups in the same molecule on the excess thermodynamic properties and the corresponding behavior of alkoxyalkanols in mixtures with alcohols is important from both practical and fundamental viewpoints.

In the present paper we report density and viscosity data for six binary systems formed by 1-methoxy-2-propanol [CH₃OCH₂CH(OH)CH₃], 1-propoxy-2-propanol [C₃H₇OCH₂-CH(OH)CH₃], 1-butoxy-2-propanol [C₄H₉OCH₂CH(OH)-CH₃], dipropylene glycol methyl ether [CH₃OC₃H₆OC₃H₆-OH], dipropylene glycol propyl ether [C₃H₇OC₃H₆OC₃H₆OH], and dipropylene glycol butyl ether [C₄H₉OC₃H₆OC₃H₆OH] with ethanol (C₂H₅OH) at T = (298.15, 308.15, and 318.15)K and atmospheric pressure. The experimental data are used to calculate excess molar volumes V^{E} and deviations in viscosity $\Delta \eta$ of the mixtures. These results might be useful for the interpretation of the nature of interactions that occur in the liquid mixtures containing alkoxyalkanol with ethanol. The V^{E} and $\Delta \eta$ of the mixtures have been fitted to the Redlich-Kister equation, and the coefficients of the Redlich-Kister equation were determined. An attempt has also been made to correlate the kinematic viscosities with the McAllister equations. To the best of our knowledge, no literature results are available for these mixtures.

Experimental Section

The chemicals used were of analytical grade. 1-Methoxy-2-propanol (Tedia), 1-propoxy-2-propanol (Aldrich), 1-butoxy-2-propanol (TCI), dipropylene glycol methyl ether

(Tedia), dipropylene glycol propyl ether (Aldrich), dipropylene glycol butyl ether (Aldrich), and ethanol (Showa) were used directly without further purification. Dipropylene glycol propyl ether and dipropylene glycol butyl ether were received as mixtures of isomers. The gas chromatographic analysis of components showed that the major peak area exceeded 99.8% for ethanol, 1-methoxy-2-propanol, and dipropylene glycol methyl ether and 99.5% for 1-propoxy-2-propanol, 1-butoxy-2-propanol, dipropylene glycol propyl ether, and dipropylene glycol butyl ether. Liquids were dried over activated molecular sieves type 0.4 nm from Aldrich. Densities were measured with an Anton Paar DMA-58 vibrating-tube densimeter (Graz, Austria) with a stated uncertainty of $\pm 2 \times 10^{-5}$ g·cm⁻³. The temperature in the measuring cell was regulated to ± 0.01 K. Calibration was performed at atmospheric pressure periodically, in accordance with specifications, using deionized doubly distilled water and dry air. Precautions were taken to avoid evaporation losses and air dissolved during the experimental work. The uncertainty of the density measurements was estimated to be ${\,^<\!\pm1}$ \times 10^{-4} g·cm^{-3}. The excess molar volumes were calculated from densities, and the uncertainty was within $\pm 5 \times 10^{-2} \text{ cm}^3 \cdot \text{mol}^{-1}$.

The kinematic viscosities were determined with commercial Ubbelohde capillary viscometers (Schott-Geräte, Hofheim, Germany) of 0.53 and 0.63 mm diameter. The viscometer was kept in a Lauda D20 KP thermostat controlled to ± 0.01 K with a proportional-integral-differential regulator. A computer-controlled measuring system (Lauda, Lauda-Königshofen, Germany) with an uncertainty of ± 0.01 s was used for flow-time measurement. The range of the flow time for the liquids investigated is varied from 150 s to 550 s. The kinematic viscosity (ν) was then calculated from the relationship

$$\nu \equiv \eta / \rho = k(t - \theta) \tag{1}$$

where *t* is the flow time, η is the absolute viscosity, and *k* and θ are, respectively, the viscometer constant and the Hagenbach correction. The *k* values for several viscometers were provided by the manufacturer and checked by mea-

^{*} Corresponding author (e-mail chtu@pu.edu.tw).

Table 1. Experimental Densities (ρ), Dynamic Viscosities (η), and Excess Molar Volumes (V^{E}) for 1-Methoxy-2-propanol (1) + Ethanol (2)

	ρ	η	VE		ρ	η	VE		ρ	η	VE
<i>X</i> ₁	g·cm ⁻³	mPa∙s	cm ³ ·mol ⁻¹	<i>X</i> ₁	g·cm ⁻³	mPa∙s	cm ³ ·mol ⁻¹	<i>X</i> 1	g·cm ⁻³	mPa∙s	cm ³ ·mol ⁻¹
298.15 K											
0.0000	0.7852	1.087	0.00	0.3500	0.8510	1.369	-0.29	0.7000	0.8923	1.589	-0.24
0.0501	0.7968	1.128	-0.07	0.3999	0.8580	1.405	-0.30	0.7500	0.8969	1.610	-0.22
0.1000	0.8075	1.174	-0.13	0.4500	0.8646	1.440	-0.31	0.8002	0.9013	1.629	-0.18
0.1500	0.8175	1.215	-0.18	0.5000	0.8708	1.477	-0.30	0.8498	0.9054	1.647	-0.14
0.2000	0.8267	1.253	-0.22	0.5498	0.8766	1.508	-0.29	0.8999	0.9093	1.665	-0.10
0.2500	0.8353	1.297	-0.25	0.5998	0.8822	1.537	-0.29	0.9499	0.9131	1.677	-0.06
0.3003	0.8434	1.333	-0.28	0.6498	0.8873	1.564	-0.26	1.0000	0.9165	1.694	0.00
					308	3.15 K					
0.0000	0.7766	0.906	0.00	0.3500	0.8419	1.111	-0.30	0.7000	0.8828	1.263	-0.24
0.0501	0.7882	0.933	-0.07	0.3999	0.8489	1.138	-0.31	0.7500	0.8875	1.275	-0.22
0.1000	0.7988	0.964	-0.13	0.4500	0.8554	1.163	-0.31	0.8002	0.8918	1.289	-0.18
0.1500	0.8087	0.994	-0.19	0.5000	0.8616	1.188	-0.31	0.8498	0.8959	1.300	-0.14
0.2000	0.8178	1.025	-0.22	0.5498	0.8673	1.211	-0.30	0.8999	0.8998	1.308	-0.10
0.2500	0.8264	1.055	-0.26	0.5998	0.8729	1.230	-0.29	0.9499	0.9035	1.318	-0.06
0.3003	0.8345	1.081	-0.28	0.6498	0.8779	1.245	-0.27	1.0000	0.9069	1.329	0.00
					318	3.15 K					
0.0000	0.7678	0.761	0.00	0.3500	0.8326	0.909	-0.31	0.7000	0.8732	1.017	-0.25
0.0501	0.7793	0.779	-0.08	0.3999	0.8395	0.928	-0.32	0.7500	0.8778	1.029	-0.22
0.1000	0.7898	0.801	-0.14	0.4500	0.8460	0.947	-0.32	0.8002	0.8821	1.038	-0.19
0.1500	0.7997	0.822	-0.19	0.5000	0.8521	0.964	-0.32	0.8498	0.8861	1.048	-0.15
0.2000	0.8087	0.846	-0.23	0.5498	0.8579	0.979	-0.31	0.8999	0.8900	1.058	-0.10
0.2500	0.8172	0.866	-0.26	0.5998	0.8633	0.991	-0.30	0.9499	0.8937	1.068	-0.06
0.3003	0.8252	0.887	-0.29	0.6498	0.8684	1.004	-0.27	1.0000	0.8971	1.078	0.00

Table 2. Experimental Densities (ρ), Dynamic Viscosities (η), and Excess Molar Volumes (V^{E}) for 1-Propoxy-2-propanol (1) + Ethanol (2)

	ρ	η	VE		ρ	η	VE		ρ	η	$V^{\rm E}$
<i>X</i> ₁	g·cm ⁻³	mPa∙s	$cm^3 \cdot mol^{-1}$	<i>X</i> ₁	g·cm ⁻³	mPa∙s	cm ³ ·mol ⁻¹	<i>X</i> 1	g·cm ⁻³	mPa∙s	$cm^3 \cdot mol^{-1}$
					298	3.15 K					
0.0000	0.7852	1.087	0.00	0.3500	0.8415	1.716	-0.34	0.7000	0.8681	2.168	-0.26
0.0500	0.7967	1.180	-0.09	0.4000	0.8465	1.790	-0.35	0.7500	0.8707	2.219	-0.22
0.1000	0.8066	1.272	-0.16	0.4500	0.8511	1.862	-0.36	0.8000	0.8732	2.264	-0.18
0.1500	0.8153	1.363	-0.21	0.5000	0.8551	1.928	-0.35	0.8498	0.8753	2.307	-0.13
0.2000	0.8230	1.448	-0.26	0.5500	0.8588	1.998	-0.33	0.9000	0.8774	2.354	-0.08
0.2500	0.8299	1.534	-0.29	0.6000	0.8622	2.056	-0.32	0.9500	0.8794	2.369	-0.04
0.3000	0.8360	1.612	-0.32	0.6500	0.8653	2.113	-0.29	1.0000	0.8813	2.389	0.00
					308	3.15 K					
0.0000	0.7766	0.906	0.00	0.3500	0.8327	1.362	-0.37	0.7000	0.8591	1.674	-0.30
0.0500	0.7880	0.974	-0.09	0.4000	0.8377	1.417	-0.39	0.7500	0.8617	1.706	-0.27
0.1000	0.7979	1.041	-0.17	0.4500	0.8421	1.467	-0.39	0.8000	0.8640	1.734	-0.22
0.1500	0.8066	1.108	-0.23	0.5000	0.8462	1.513	-0.38	0.8498	0.8661	1.766	-0.17
0.2000	0.8143	1.171	-0.28	0.5500	0.8499	1.557	-0.38	0.9000	0.8682	1.790	-0.12
0.2500	0.8212	1.231	-0.32	0.6000	0.8532	1.602	-0.36	0.9500	0.8700	1.815	-0.06
0.3000	0.8273	1.288	-0.35	0.6500	0.8563	1.651	-0.33	1.0000	0.8718	1.822	0.00
					318	3.15 K					
0.0000	0.7678	0.761	0.00	0.3500	0.8236	1.105	-0.40	0.7000	0.8497	1.322	-0.33
0.0500	0.7791	0.813	-0.10	0.4000	0.8285	1.142	-0.41	0.7500	0.8523	1.345	-0.28
0.1000	0.7890	0.863	-0.18	0.4500	0.8330	1.177	-0.41	0.8000	0.8546	1.368	-0.24
0.1500	0.7977	0.911	-0.24	0.5000	0.8370	1.210	-0.42	0.8498	0.8568	1.389	-0.19
0.2000	0.8053	0.960	-0.30	0.5500	0.8406	1.241	-0.39	0.9000	0.8588	1.406	-0.14
0.2500	0.8121	1.005	-0.34	0.6000	0.8439	1.274	-0.38	0.9500	0.8606	1.414	-0.08
0.3000	0.8182	1.046	-0.37	0.6500	0.8470	1.297	-0.36	1.0000	0.8622	1.416	0.00

surement of the viscosities of pure water, ethanol, and heptane; the results at T = 298.15 K were, respectively, $\eta(H_2O) = 0.892$ [0.89025] mPa·s, $\eta(C_2H_5OH) = 1.087$ [1.0826] mPa·s, and $\eta(C_7H_{16}) = 0.393$ [0.3967] mPa·s. Literature values⁶ are in brackets. The value θ , which is dependent on the flow time and the size of the capillary, was taken from the tables supplied by the manufacturer. Triplicate measurements of flow times were reproducible within $\pm 0.04\%$. The uncertainty of the viscosity measurement was $<\pm 0.6\%$.

The densities and viscosities for the binary mixtures of 1-methoxy-2-propanol, 1-propoxy-2-propanol, 1-butoxy-2propanol, dipropylene glycol methyl ether, dipropylene glycol propyl ether, and dipropylene glycol butyl ether with ethanol were measured at T = (298.15, 308.15, and 318.15)K and atmospheric pressure. Samples were prepared by mass in a 50 cm³ Erlenmeyer flask provided with a joint stopper and transferred by syringe to prevent preferential evaporation, using a Mettler AB204 balance with an accuracy of $\pm 1 \times 10^{-4}$ g. The uncertainty in the mole fraction was believed to be $<\pm 1 \times 10^{-4}$. A set of 19 compositions with an increment of 0.05 mole fractions was prepared for each system. An average of at least three measurements was taken for each composition.

Results and Discussion

By considering the system consisting of pure component 1 (alkoxypropanol) and pure component 2 (ethanol), the

Table 3.	Experimental	Densities (ρ),	Dynamic V	iscosities (η)	, and Excess	Molar Volun	nes (<i>V</i> ^E) for 1	-Butoxy-2-prop	panol (1)
+ Ethan	ol (2)		-	-					

	ρ	η	VE		ρ	η	VE		ρ	η	$V^{\rm E}$
<i>X</i> ₁	g·cm ⁻³	mPa∙s	cm ³ ·mol ⁻¹	<i>X</i> ₁	g·cm ⁻³	mPa·s	cm ³ ·mol ⁻¹	<i>X</i> 1	g·cm ⁻³	mPa·s	cm ³ ·mol ⁻¹
					298	3.15 K					
0.0000	0.7852	1.087	0.00	0.3500	0.8406	1.918	-0.36	0.7000	0.8640	2.536	-0.28
0.0500	0.7971	1.229	-0.10	0.4000	0.8450	2.022	-0.36	0.7499	0.8662	2.608	-0.25
0.1000	0.8072	1.344	-0.17	0.4500	0.8491	2.120	-0.37	0.7998	0.8682	2.674	-0.20
0.1500	0.8159	1.462	-0.24	0.5000	0.8527	2.211	-0.36	0.8500	0.8700	2.737	-0.15
0.2000	0.8233	1.585	-0.28	0.5500	0.8560	2.305	-0.35	0.8998	0.8717	2.788	-0.10
0.2500	0.8299	1.705	-0.32	0.6000	0.8589	2.384	-0.34	0.9500	0.8733	2.841	-0.05
0.3000	0.8355	1.813	-0.34	0.6500	0.8615	2.469	-0.30	1.0000	0.8748	2.855	0.00
					308	3.15 K					
0.0000	0.7766	0.906	0.00	0.3500	0.8320	1.516	-0.38	0.7000	0.8552	1.935	-0.31
0.0500	0.7885	1.013	-0.10	0.4000	0.8364	1.589	-0.39	0.7499	0.8574	1.983	-0.27
0.1000	0.7986	1.103	-0.18	0.4500	0.8405	1.656	-0.40	0.7998	0.8594	2.035	-0.22
0.1500	0.8072	1.193	-0.25	0.5000	0.8441	1.724	-0.40	0.8500	0.8613	2.067	-0.18
0.2000	0.8146	1.279	-0.29	0.5500	0.8473	1.779	-0.38	0.8998	0.8629	2.099	-0.12
0.2500	0.8212	1.363	-0.34	0.6000	0.8502	1.841	-0.36	0.9500	0.8645	2.135	-0.06
0.3000	0.8269	1.442	-0.36	0.6500	0.8528	1.891	-0.34	1.0000	0.8659	2.142	0.00
					318	8.15 K					
0.0000	0.7678	0.761	0.00	0.3500	0.8230	1.220	-0.40	0.7000	0.8463	1.517	-0.33
0.0500	0.7797	0.846	-0.11	0.4000	0.8276	1.273	-0.42	0.7499	0.8484	1.550	-0.28
0.1000	0.7898	0.915	-0.19	0.4500	0.8316	1.321	-0.42	0.7998	0.8504	1.580	-0.24
0.1500	0.7984	0.982	-0.26	0.5000	0.8352	1.365	-0.42	0.8500	0.8523	1.609	-0.19
0.2000	0.8058	1.046	-0.31	0.5500	0.8383	1.409	-0.40	0.8998	0.8539	1.633	-0.13
0.2500	0.8124	1.108	-0.36	0.6000	0.8412	1.445	-0.38	0.9500	0.8554	1.647	-0.07
0.3000	0.8180	1.166	-0.38	0.6500	0.8439	1.490	-0.35	1.0000	0.8568	1.655	0.00

Table 4. Experimental Densities (ρ), Dynamic Viscosities (η), and Excess Molar Volumes (V^{E}) for Dipropylene Glycol Methyl Ether (1) + Ethanol (2)

	ρ	η	VE		ρ	η	$V^{\rm E}$		ρ	η	$V^{\rm E}$
<i>X</i> ₁	g•cm ^{−3}	mPa∙s	cm ³ ·mol ⁻¹	<i>X</i> ₁	g·cm ⁻³	mPa·s	cm ³ ·mol ⁻¹	<i>X</i> ₁	g·cm ⁻³	mPa∙s	$\overline{\text{cm}^3 \cdot \text{mol}^{-1}}$
298.15 K											
0.0000	0.7852	1.087	0.00	0.3500	0.8868	2.081	-0.43	0.7001	0.9302	3.001	-0.31
0.0500	0.8073	1.237	-0.14	0.4001	0.8952	2.216	-0.44	0.7500	0.9344	3.125	-0.27
0.1000	0.8257	1.385	-0.23	0.4500	0.9025	2.350	-0.43	0.8001	0.9383	3.241	-0.23
0.1501	0.8415	1.525	-0.29	0.5000	0.9092	2.485	-0.42	0.8497	0.9417	3.359	-0.17
0.2000	0.8552	1.661	-0.35	0.5497	0.9151	2.616	-0.34	0.8996	0.9450	3.472	-0.11
0.2501	0.8671	1.803	-0.38	0.6000	0.9207	2.744	-0.38	0.9498	0.9480	3.579	-0.05
0.3000	0.8775	1.941	-0.40	0.6497	0.9257	2.871	-0.36	1.0000	0.9510	3.691	0.00
					308	3.15 K					
0.0000	0.7766	0.906	0.00	0.3500	0.8780	1.623	-0.44	0.7001	0.9213	2.281	-0.33
0.0500	0.7986	1.014	-0.14	0.4001	0.8862	1.723	-0.44	0.7500	0.9254	2.365	-0.29
0.1000	0.8170	1.119	-0.23	0.4500	0.8936	1.820	-0.44	0.8001	0.9292	2.449	-0.23
0.1501	0.8328	1.218	-0.31	0.5000	0.9002	1.916	-0.43	0.8497	0.9327	2.531	-0.17
0.2000	0.8465	1.320	-0.37	0.5497	0.9062	2.006	-0.41	0.8996	0.9360	2.610	-0.12
0.2501	0.8583	1.421	-0.40	0.6000	0.9117	2.099	-0.38	0.9498	0.9390	2.686	-0.05
0.3000	0.8687	1.521	-0.42	0.6497	0.9167	2.192	-0.36	1.0000	0.9419	2.765	0.00
					318	3.15 K					
0.0000	0.7678	0.761	0.00	0.3500	0.8690	1.301	-0.45	0.7001	0.9123	1.796	-0.33
0.0500	0.7898	0.840	-0.14	0.4001	0.8772	1.379	-0.46	0.7500	0.9164	1.857	-0.29
0.1000	0.8082	0.920	-0.24	0.4500	0.8846	1.451	-0.45	0.8001	0.9202	1.922	-0.24
0.1501	0.8239	0.996	-0.32	0.5000	0.8913	1.525	-0.44	0.8497	0.9237	1.979	-0.17
0.2000	0.8375	1.073	-0.37	0.5497	0.8971	1.594	-0.41	0.8996	0.9270	2.036	-0.12
0.2501	0.8494	1.148	-0.42	0.6000	0.9026	1.662	-0.39	0.9498	0.9300	2.090	-0.06
0.3000	0.8597	1.225	-0.43	0.6497	0.9077	1.726	-0.37	1.0000	0.9329	2.147	0.00

molar excess volumes, $V^{\mathbb{E}}$, have been calculated from density data according to the equation

$$V^{\rm E} = (x_1 M_1 + x_2 M_2)/\rho - (x_1 M_1/\rho_1 + x_2 M_2/\rho_2)$$
(2)

where ρ is the density of the mixture and x_1 , ρ_1 , M_1 , x_2 , ρ_2 , and M_2 are the mole fractions, densities, and molecular weights of pure components 1 and 2, respectively. The deviation of the viscosity from the mole fraction average, $\Delta \eta$, is given by

$$\Delta \eta = \eta - (x_1 \eta_1 + x_2 \eta_2) \tag{3}$$

where η , η_1 , and η_2 are the dynamic viscosities of the

mixture and of pure components 1 and 2, respectively. The experimental densities, viscosities, and excess volumes for all of the systems are given in Tables 1-6.

For each of the mixtures studied, the $V^{\rm E}$ values are negative over the whole mole fraction range, symmetrical for mixtures with monoethers, and slightly skewed toward the region of high mole fraction of ethanol for mixtures with diethers as shown in Figure 1. The values of $V^{\rm E}$ at equimolar concentrations of the alkoxypropanols + ethanol mixtures follow the order 1-methoxy-2-propanol > 1-propoxy-2-propanol > 1-butoxy-2-propanol > 1-propoxy-2-propanol > 1-butoxy-2-propanol > dipropylene glycol methyl ether > dipropylene glycol propyl ether > dipropylene glycol butyl ether. The equimolar values of $V^{\rm E}$ are varied from -0.55 cm³·mol⁻¹ to -0.30 cm³·mol⁻¹. These

Table 5. Experimental Densities (ρ), Dynamic Viscosities (η), and Excess Molar Volumes (V^{E}) for Dipropylene Glycol Propyl Ether (1) + Ethanol (2)

	ρ	η	VE		ρ	η	VE		ρ	η	$V^{\rm E}$
<i>X</i> ₁	g·cm ⁻³	mPa·s	cm ³ ·mol ⁻¹	<i>X</i> ₁	g·cm ⁻³	mPa∙s	cm ³ ·mol ⁻¹	<i>X</i> 1	g·cm ⁻³	mPa∙s	cm ³ ·mol ⁻¹
					298	3.15 K					
0.0000	0.7852	1.087	0.00	0.3501	0.8734	2.322	-0.53	0.6996	0.9035	3.343	-0.39
0.0500	0.8067	1.270	-0.18	0.4000	0.8795	2.485	-0.55	0.7496	0.9062	3.475	-0.35
0.1000	0.8235	1.446	-0.25	0.4501	0.8848	2.643	-0.54	0.8000	0.9086	3.593	-0.28
0.1500	0.8372	1.621	-0.37	0.5000	0.8894	2.795	-0.52	0.8499	0.9109	3.704	-0.22
0.2000	0.8486	1.799	-0.43	0.5500	0.8936	2.942	-0.50	0.8999	0.9129	3.807	-0.15
0.2500	0.8582	1.994	-0.48	0.6000	0.8974	3.081	-0.49	0.9500	0.9147	3.896	-0.08
0.3000	0.8663	2.144	-0.51	0.6497	0.9006	3.218	-0.44	1.0000	0.9164	4.001	0.00
					308	3.15 K					
0.0000	0.7766	0.906	0.00	0.3501	0.8646	1.830	-0.55	0.6996	0.8947	2.550	-0.41
0.0500	0.7981	1.046	-0.18	0.4000	0.8706	1.944	-0.55	0.7496	0.8974	2.627	-0.36
0.1000	0.8148	1.181	-0.29	0.4501	0.8760	2.055	-0.55	0.8000	0.8998	2.702	-0.29
0.1500	0.8286	1.315	-0.38	0.5000	0.8806	2.163	-0.53	0.8499	0.9020	2.764	-0.23
0.2000	0.8400	1.446	-0.45	0.5500	0.8848	2.270	-0.52	0.8999	0.9040	2.839	-0.16
0.2500	0.8494	1.572	-0.49	0.6000	0.8886	2.367	-0.50	0.9500	0.9059	2.906	-0.09
0.3000	0.8576	1.706	-0.53	0.6497	0.8918	2.463	-0.45	1.0000	0.9075	2.986	0.00
					318	3.15 K					
0.0000	0.7678	0.761	0.00	0.3501	0.8557	1.468	-0.56	0.6996	0.8858	1.965	-0.42
0.0500	0.7892	0.872	-0.19	0.4000	0.8617	1.550	-0.57	0.7496	0.8885	2.020	-0.36
0.1000	0.8060	0.978	-0.30	0.4501	0.8671	1.631	-0.57	0.8000	0.8909	2.081	-0.30
0.1500	0.8197	1.081	-0.39	0.5000	0.8717	1.705	-0.55	0.8499	0.8931	2.131	-0.23
0.2000	0.8310	1.180	-0.46	0.5500	0.8760	1.777	-0.54	0.8999	0.8951	2.177	-0.17
0.2500	0.8405	1.278	-0.51	0.6000	0.8797	1.842	-0.52	0.9500	0.8969	2.215	-0.09
0.3000	0.8487	1.374	-0.55	0.6497	0.8828	1.905	-0.46	1.0000	0.8986	2.271	0.00

Table 6. Experimental Densities (ρ), Dynamic Viscosities (η), and Excess Molar Volumes (V^{E}) for Dipropylene Glycol Butyl Ether (1) + Ethanol (2)

	ρ	η	VE		ρ	η	$V^{\rm E}$		ρ	η	$V^{\rm E}$
<i>X</i> ₁	g·cm ⁻³	mPa∙s	cm ³ ·mol ⁻¹	<i>X</i> ₁	g·cm ⁻³	mPa∙s	cm ³ ·mol ⁻¹	<i>X</i> 1	g·cm ⁻³	mPa∙s	$cm^3 \cdot mol^{-1}$
					298	3.15 K					
0.0000	0.7852	1.087	0.00	0.3500	0.8707	2.562	-0.53	0.6998	0.8978	3.756	-0.40
0.0500	0.8068	1.300	-0.17	0.4001	0.8763	2.755	-0.54	0.7499	0.9001	3.899	-0.34
0.1000	0.8235	1.505	-0.28	0.4499	0.8811	2.940	-0.54	0.7999	0.9021	4.018	-0.26
0.1500	0.8369	1.717	-0.38	0.4999	0.8853	3.121	-0.52	0.8499	0.9040	4.147	-0.19
0.2000	0.8478	1.927	-0.45	0.5499	0.8890	3.292	-0.50	0.8997	0.9058	4.271	-0.13
0.2500	0.8568	2.135	-0.49	0.5997	0.8922	3.453	-0.47	0.9498	0.9073	4.386	-0.05
0.3000	0.8642	2.362	-0.50	0.6501	0.8952	3.608	-0.44	1.0000	0.9089	4.503	0.00
					308	3.15 K					
0.0000	0.7766	0.906	0.00	0.3500	0.8622	2.003	-0.55	0.6998	0.8892	2.821	-0.41
0.0500	0.7982	1.074	-0.17	0.4001	0.8677	2.140	-0.56	0.7499	0.8916	2.910	-0.35
0.1000	0.8149	1.227	-0.29	0.4499	0.8725	2.265	-0.56	0.7999	0.8936	2.998	-0.28
0.1500	0.8283	1.386	-0.39	0.4999	0.8767	2.390	-0.54	0.8499	0.8955	3.088	-0.22
0.2000	0.8391	1.541	-0.45	0.5499	0.8804	2.510	-0.52	0.8997	0.8973	3.158	-0.15
0.2500	0.8482	1.696	-0.51	0.5997	0.8837	2.622	-0.49	0.9498	0.8988	3.233	-0.07
0.3000	0.8558	1.858	-0.54	0.6501	0.8867	2.724	-0.46	1.0000	0.9003	3.313	0.00
					318	3.15 K					
0.0000	0.7678	0.761	0.00	0.3500	0.8533	1.597	-0.56	0.6998	0.8805	2.182	-0.42
0.0500	0.7894	0.896	-0.17	0.4001	0.8590	1.696	-0.58	0.7499	0.8828	2.240	-0.36
0.1000	0.8061	1.015	-0.30	0.4499	0.8638	1.790	-0.58	0.7999	0.8849	2.306	-0.30
0.1500	0.8195	1.137	-0.40	0.4999	0.8680	1.879	-0.55	0.8499	0.8868	2.363	-0.22
0.2000	0.8304	1.256	-0.47	0.5499	0.8717	1.956	-0.53	0.8997	0.8886	2.423	-0.16
0.2500	0.8394	1.369	-0.51	0.5997	0.8750	2.039	-0.50	0.9498	0.8902	2.466	-0.07
0.3000	0.8469	1.497	-0.54	0.6501	0.8779	2.114	-0.47	1.0000	0.8916	2.531	0.00

results show that the V^{E} value decreases as the alkyl chain end length or the number of $-\text{OC}_3\text{H}_6$ – groups in the glycol molecules increases. Similar behavior can also be seen in the work of Cobos et al.² for mixtures of alkoxyethanols with 1-butanol and in the work of Pal and Sharma³ for mixtures of alkoxyethanols with 1-propanol. The V^{E} values are very close between 1-propoxy-2-propanol and 1-butoxy-2-propanol and between dipropylene glycol propyl ether and dipropylene glycol butyl ether, which shows that each addition of a $-\text{CH}_2$ – group to the alkyl chain end in the glycol molecule decreases the V^{E} value but with less significant change. On the other hand, the volume contraction is observed for all of the systems from T = (298.15 to 318.15) K. Such a result can also be seen for mixtures of diethylene glycol dimethyl ether with ethyl acetate or methyl benzoate7 and mixtures of 2-ethoxyethanol with 1,2-dimethoxyethane. 8

Alkoxyethanols exist as an associated structure like alcohols in liquid state, and association may be formed from intramolcular hydrogen bonding between the ether (-O-) and hydroxyl (-OH) groups.^{9,10} The same association through intramolecular hydrogen bonds is expected to be formed for alkoxypropanols. The hydrogen bond of the self-associated alkoxypropanols can be broken, and new hydrogen bonds can be formed between alkoxypropanols and ethanol. The degrees of association through hydrogen bonding depend on such variables as chain length, temperature, and dilution by other substances. The dependence



Figure 1. Variation of excess molar volume V^{E} with mole fraction for alkoxypropanols (1) + ethanol (2) at 308.15 K: ×, 1-methoxy-2-propanol; \Diamond , 1-propoxy-2-propanol; \Box , 1-butoxy-2-propanol; \triangle , dipropylene glycol methyl ether; *, dipropylene glycol propyl ether; \bigcirc , dipropylene glycol butyl ether; \neg , Redlich–Kister equation.



Figure 2. Variation of viscosity deviations $\Delta \eta$ with mole fraction for alkoxypropanols (1) + ethanol (2) at 308.15 K: \bigcirc , dipropylene glycol butyl ether; *, dipropylene glycol propyl ether; \square , 1-butoxy-2-propanol; \diamondsuit , 1-propoxy-2-propanol; \triangle , dipropylene glycol methyl ether; ×, 1-methoxy-2-propanol; \neg , Redlich–Kister equation.

of V^E on both composition and temperature for the present mixtures may be explained as a balance between

Table 7. Coefficients of the Redlich–Kister Equation and Standard Deviations for V^{E} and $\Delta \eta$

Y E∕unit	<i>T</i> /K	$a_0 \cdot 10^2$	$a_1 \cdot 10^2$	$a_2 \cdot 10^2$	$a_3 \cdot 10^2$	$\sigma \cdot 10^4$
1	-Methox	y-2-propai	nol (1) +	Ethanol	(2)	
V ^E /cm ³ ⋅mol ⁻¹	298.15	-121.50	-20.15	-14.93		46
	308.15	-123.69	-21.38	-11.54		35
	318.15	-127.10	-24.24	-13.44		40
$\Delta \eta$ /mPa·s	298.15	33.94	-9.83	-4.96	10.59	15
,	308.15	28.12	-6.83	-11.28	3.34	11
	318.15	17.49	-0.65	-10.29	-2.55	9
1	-Propoxy	y-2-propar	nol (1) +	Ethanol	(2)	
V ^E /cm ³ ⋅mol ⁻¹	298.15	-138.80	-30.22	5.50	-37.18	27
	308.15	-154.49	-27.05	-6.53	-11.23	31
	318.15	-163.81	-28.96	-19.30		47
$\Delta \eta$ /mPa·s	298.15	75.94	-8.45	1.94	-31.36	67
•	308.15	61.77	-7.76	-3.63	-14.61	54
	318.15	48.43	0.53	-0.23	-25.42	45
1	l-Butoxy	-2-propan	ol (1) + 1	Ethanol ((2)	
V ^E /cm ³ ⋅mol ⁻¹	298.15	-145.50	-29.67	-14.27	-35.19	37
	308.15	-157.85	-28.40	-13.66	-22.62	41
	318.15	-165.41	-34.90	-20.59	-10.51	41
∆η/mPa•s	298.15	95.87	-8.25	14.30	-19.83	53
	308.15	78.08	-0.42	11.99	-10.76	41
	318.15	62.37	4.47	14.68	-10.53	37
Diprop	ylene Gl	ycol Meth	yl Ether	(1) + Et	hanol (2)	
V ^E /cm ³ ⋅mol ⁻¹	298.15	-168.15	-46.05	-29.27	-54.23	61
	308.15	-172.53	-46.49	-37.39	-60.79	47
	318.15	-175.78	-56.30	-41.00	-47.89	67
∆η/mPa•s	298.15	37.86	-12.24	6.41	12.01	20
	308.15	31.41	-9.13	-1.11	7.28	17
	318.15	27.51	-9.86	-2.89	6.39	16
Diprop	ylene G	lycol Prop	yl Ether	(1) + Eth	nanol (2)	
V ^E /cm ³ ⋅mol ⁻¹	298.15	-210.34	-60.16	-45.20	-55.15	85
	308.15	-214.63	-61.95	-57.95	-48.26	61
	318.15	-221.89	-65.83	-51.93	-49.34	82
∆η/mPa•s	298.15	100.12	-20.97	-16.41	0.17	40
	308.15	88.73	-12.11	-26.81	27.81	34
	318.15	75.79	6.52	-13.38		33
Diproi	ovlene G	lycol Buty	l Ether ((1) + Eth	anol (2)	
VE/cm ³ ·mol ⁻¹	298.15	-209.59	-58.26	-34.17	-87.66	68
	308.15	-217.64	-68.89	-41.26	-52.84	43
	318.15	-222.30	-71.56	-52.03	-47.10	49
$\Delta \eta$ /mPa·s	298.15	130.69	-21.83	-45.77		48
	308.15	113.41	-4.47	-31.58		42
	318.15	93.14	9.51	-22.51		46

positive contributions (hydrogen bond rupture, dispersive interactions between unlike molecules) and negative contributions (intermolecular dipolar interactions and geometrical fitting between components). The interactions between alkyoxpropanol and ethanol molecules lead to weak dispersion type and/or hydrogen bond effects, giving a negative contribution to V^{E} . The presence of the etheric oxygen (-O-) enhances the ability of the -OHgroup of the alkoxypropanol to form hydrogen bonds with ethanol molecules, leading to more negative V^{E} values for dipropylene glycol + ethanol mixtures than for propylene glycol + ethanol mixtures. The difference in V^{E} values between propylene glycol-containing and dipropylene glycol-containing mixtures is also the result of molecular size differences between the glycol molecules (i.e., at T = 308.15 K, V = 99.37 cm³·mol⁻¹ for 1-methoxy-2propanol and $V = 157.34 \text{ cm}^3 \cdot \text{mol}^{-1}$ for dipropylene glycol methyl ether). Again, due to the electron-donating inductive effect of the alkyl group, the strength of bonding with ethanol increases as the aliphatic chain length of the alkyoxpropanol in each homologous series increases, resulting in lower V^{E} values for the molecules with higher alkyl chain length.

The values of $\Delta \eta$ presented in Figure 2 are positive for all of the systems over the entire range of composition. The equimolar $\Delta \eta$ values of the alkoxypropanols + ethanol



Figure 3. Temperature dependence of (a) excess molar volume V^{E} and (b) viscosity deviation $\Delta \eta$ at equimolar composition (x = 0.5) for alkoxypropanols (1) + ethanol (2) at T = (298.15, 308.15, and 318.15) K: ×, 1-methoxy-2-propanol; \Diamond , 1-propoxy-2-propanol; \Box , 1-butoxy-2-propanol; \triangle , dipropylene glycol methyl ether; *, dipropylene glycol propyl ether; \bigcirc , dipropylene glycol butyl ether.

Table 8.	Parameters of McAllister's Three-Body and
Four-Bo	dy Interaction Model and Standard Deviations
for Kine	matic Viscosities

		three-	body	four-body					
			σ·10 ³				<i>σ</i> •10 ³		
<i>T</i> /K	а	b	$10^{-6} \text{ m}^2 \cdot \text{s}^{-1}$	а	b	с	$10^{-6} \text{ m}^2 \cdot \text{s}^{-1}$		
		1-Meth	oxy-2-propan	ol (1) +	Ethan	ol (2)			
298.15	1.841	1.698	3	1.827	1.774	1.594	2		
308.15	1.486	1.379	4	1.448	1.471	1.289	1		
318.15	1.195	1.137	4	1.167	1.206	1.067	1		
		1-Prop	oxy-2-propan	ol (1) +	Ethan	ol (2)			
298.15	2.626	2.371	i1 i1 i	2.684	2.386	2.081	9		
308.15	2.054	1.884	7	2.071	1.911	1.663	7		
318.15	1.640	1.528	7	1.653	1.531	1.368	7		
		1-Buto	xy-2-propand	ol (1) +	Ethano	d (2)			
298.15	3.030	2.889	25	3.253	2.633	2.497	17		
308.15	2.315	2.311	19	2.493	2.039	2.034	9		
318.15	1.833	1.872	14	1.961	1.641	1.662	5		
	Dipro	pylene	Glycol Methy	l Ether	(1) + H	Ethanol	(2)		
298.15	3.169	3.044	34	3.547	2.706	2.609	20		
308.15	2.498	2.315	11	2.676	2.224	1.969	6		
318.15	2.004	1.837	6	2.111	1.809	1.572	3		
	Dipro	pylene	Glycol Propy	l Ether	(1) + E	Ethanol	(2)		
298.15	3.694	3.864	ž 27	4.070	3.313	3.070	8		
308.15	2.818	3.054	17	3.053	2.636	2.432	9		
318.15	2.188	2.467	15	2.381	2.063	2.002	5		
	Dipr	opylene	Glycol Butyl	Ether	(1) + E	thanol	(2)		
298.15	4.095	4.649	Š 33	4.569	3.771	3.532	9		
308.15	3.103	3.620	26	3.444	2.897	2.805	7		
318.15	2.398	2.909	21	2.667	2.273	2.291	7		

mixtures follow the order dipropylene glycol butyl ether > dipropylene glycol propyl ether > 1-butoxy-2-propanol > 1-propoxy-2-propanol > dipropylene glycol methyl ether > 1-methoxy-2-propanol. The equimolar values of $\Delta \eta$ are varied from 0.045 mPa·s to 0.326 mPa·s. There is a very obvious increase in the magnitude of $\Delta \eta$ with the alkyl chain end length or the increase in the number of $-OC_3H_6$ -groups in the glycol molecules. A similar behavior can also be seen for the mixtures of alkoxyethanols with 1-propanol.³ The increase in temperature leads to a lower value. Figure 3 shows that the equimolar values of V^{E} or $\Delta \eta$ decrease as temperature increases for all of the systems studied.

The mixing functions V^{E} and $\Delta \eta$ were represented mathematically by the following form of the Redlich–Kister equation¹¹ for correlating the experimental data

$$Y = x_1(1 - x_1) \sum_{i=0}^{p} a_i (2x_1 - 1)^i$$
(4)

where *Y* refers to $V^{\text{E}}/\text{cm}^3 \cdot \text{mol}^{-1}$ or $\Delta \eta/\text{mPa} \cdot \text{s}$, x_1 is the mole fraction of alcohol, 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 7. The standard deviation is defined by

$$\sigma = \left[\sum_{i=1}^{m} (Y_i^{\text{exptl}} - Y_i^{\text{calcd}})^2 / (m-p)\right]^{1/2}$$
(5)

where *m* is the number of experimental points and *p* is the number of adjustable parameters. For the case of $V^{\rm E}$, the σ values lie between $3.1 \times 10^{-3} \, {\rm cm^3 \cdot mol^{-1}}$ and $8.2 \times 10^{-3} \, {\rm cm^3 \cdot mol^{-1}}$ and the largest σ value corresponds to dipropylene glycol propyl ether + ethanol mixture at 318.15 K. For the case of $\Delta \eta$, the σ values lie between 9×10^{-4} mPa·s and 6.7×10^{-3} mPa·s, and the largest σ value corresponds to 1-propoxy-2-propanol + ethanol at 298.15 K.

McAllister's multibody-interaction model¹² is widely used for correlating the kinematic viscosity of liquid mixtures with mole fraction. The three-body model is defined as

$$\ln \nu = x_1^{3} \ln \nu_1 + 3x_1^{2} x_2 \ln a + 3x_1 x_2^{2} \ln b + x_2^{3} \ln \nu_2 - \ln(x_1 + x_2 M_2/M_1) + 3x_1^{2} x_2 \ln[(2 + M_2/M_1)/3] + 3x_1 x_2^{2} \ln[(1 + 2M_2/M_1)/3] + x_2^{3} \ln(M_2/M_1)$$
(6)

and the four-body model is given by

$$\ln \nu = x_1^4 \ln \nu_1 + 4x_1^3 x_2 \ln a + 6x_1^2 x_2^2 \ln b + 4x_1 x_2^3 \ln c + x_2^4 \ln \nu_2 - \ln(x_1 + x_2 M_2 / M_1) + 4x_1^3 x_2 \ln[(3 + M_2 / M_1) / 4] + 6x_1^2 x_2^2 \ln[(1 + M_2 / M_1) / 2] + 4x_1 x_2^3 \ln[(1 + 3M_2 / M_1) / 4] + x_2^4 \ln(M_2 / M_1)$$
(7)

where ν is the kinematic viscosity of the mixture and x_1 , ν_1 , M_1 , x_2 , ν_2 , and M_2 are the mole fractions, kinematic viscosities, and molecular weights of pure components 1

and 2, respectively; *a*, *b*, and *c* are adjustable parameters that are characteristic of the system. In the above eqs 6 and 7, the coefficients *a*, *b*, and *c* have been calculated using the least-squares procedure. The estimated parameters of the viscosity equations and the standard deviations, σ , between the calculated and experimental values are given in Table 8. The standard deviation is defined by eq 5. It is observed that the four-body model of the McAllister equation correlates the mixture viscosity to a significantly higher degree of accuracy for all of the systems than does the three-body model. Furthermore, the values of the McAllister parameters have shown a decreasing tendency with rise in temperature. Generally, McAllister's models are adequate in correlation for those systems as evidenced by small standard deviations.

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