

Volumetric and Surface Properties of Aqueous Mixtures of Polyethers at $T = (298.15, 308.15, \text{ and } 318.15) \text{ K}$

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ABSTRACT: Density and surface tension for binary mixtures of diethylene glycol dimethyl ether, triethylene glycol dimethyl ether, and tetraethylene glycol dimethyl ether with water are measured over the whole concentration range at $T = (298.15, 308.15, \text{ and } 318.15) \text{ K}$ and atmospheric pressure. The experimental densities and surface tensions have been used to calculate excess molar volumes (V^E) and surface tension deviations ($\Delta\sigma$), respectively. While the excess molar volumes are compared with the existing literature data, surface tension measurements for these mixtures are reported for the first time. Molar surface energies and parachor have also been calculated from experimental surface tension data. Primary data on surface tension are fitted to a polynomial equation, whereas the V^E and $\Delta\sigma$ derived from densities and surface tensions are fitted to the Redlich–Kister type polynomial equation.

INTRODUCTION

The thermophysical properties of fluid mixtures depend markedly on the manner in which the pure constituents are associated with each other in the mixtures. The surface tension of mixtures is an important property for the design of contacting equipment, which is used to carry out chemical processes such as gas absorption.¹ The specific molecular interactions that occur on the surface and in the bulk region of liquid are characterized by surface tension.² Surface tension along with other thermodynamic properties is essential for practical and theoretical modeling of the liquid state of substances.^{3,4}

In the present paper, we report the densities and surface tensions of binary liquid mixtures comprising of polyethers (diethylene glycol dimethyl ether, triethylene glycol dimethyl ether, and tetraethylene glycol dimethyl ether) and water at $T = (298.15, 308.15, \text{ and } 318.15) \text{ K}$ over the whole concentration range. The polyethers used are one of the main components forming Selexol, a widely used solvent in natural gas sweetening, and is made of a mixture of poly(ethylene glycol) dimethyl ethers. Also, these can be used as inert solvents for reduction in organometallic reactions involving alkali metals and used as cosolvent in brakes fluids, adhesives, and paints and electrodeposition. Further, these polyethers are of interest to understand interactions of water with amphiphilic molecules.^{5,6} The surface tension for ethylene glycol dimethyl ether with water has been reported earlier.⁷ The excess molar volumes for the present mixtures chosen for the study have also been reported in literature^{8–12} at 298.15 K and different temperatures^{5,6} and are compared with the present data at 298.15 K. Surface properties for these mixtures are reported and discussed for the first time.

EXPERIMENTAL SECTION

Materials. Millipore grade water with conductivity $< 0.66 \cdot 10^{-8} \text{ S} \cdot \text{cm}^{-1}$ was used throughout this study. Diethylene glycol dimethyl ether (mass fraction > 0.985), triethylene glycol

dimethyl ether (mass fraction > 0.98), and tetraethylene glycol dimethyl ether (mass fraction > 0.97) were obtained from Merck-Schuchardt and were used without further purification. All of the liquids were kept in tightly sealed bottles to minimize the absorption of atmospheric moisture and CO_2 . Prior to use all of the liquids were dried over 0.4 nm molecular sieves and were partially degassed under vacuum. The densities and surface tensions of the pure components along with their literature values^{5,6,13–28} are reported in Table 1.

Apparatus and Procedure. The densities of the pure solvents and their binary mixtures were measured with an Anton Paar (model DMA 4500) vibrating-tube densimeter with a resolution of $5 \cdot 10^{-5} \text{ g} \cdot \text{cm}^{-3}$. A density check and an air/water adjustment were performed at 20 °C with doubly distilled, degassed water and with dry air at atmospheric pressure. The validation of the readings was done with double-distilled and degassed water, cyclopentane, propanol, benzene, bromobenzene, dimethyl sulfide, and *N,N*-dimethylformamide in the experimental temperature range. The temperature of the apparatus was controlled to within $\pm 0.01 \text{ K}$ by a built-in Peltier device, and the uncertainty corresponding to change in temperature of $\pm 0.01 \text{ K}$ is $\pm 0.0002 \%$. The accuracy in the density measurements was found to be $\pm 0.00002 \text{ g} \cdot \text{cm}^{-3}$. The overall uncertainty in comparison with literature data for the calibrating liquids and in the averaged density measurements of the binary mixtures is judged to be less than 0.002 %. The density values are repeatable to $3 \cdot 10^{-5} \text{ g} \cdot \text{cm}^{-3}$. The experimental uncertainty in the estimated excess molar volume is approximately $\pm 2 \cdot 10^{-3} \text{ cm}^3 \cdot \text{mol}^{-1}$. The uncertainty estimates do not include the effects of certain minor impurities that may be present in the solvents. The repeatability obtained with triplicate measurements on the same sample maintained inside the densimeter at

Received: July 20, 2010

Accepted: March 15, 2011

Published: March 22, 2011

Table 1. Experimental Densities (ρ) and Surface Tensions (σ) of the Pure Component Liquids Together with Literature Values

component	T/K	$\rho \cdot 10^3 / \text{kg} \cdot \text{m}^{-3}$		$\sigma / \text{mN} \cdot \text{m}^{-1}$				
		exptl	lit.	exptl	lit.			
diethylene glycol dimethyl ether	298.15	0.94001	0.9399 ¹³	24.56				
			0.9394 ¹⁴					
			0.9391 ¹⁵					
diethylene glycol dimethyl ether	308.15	0.93003	0.9285 ¹⁶	27.65				
			0.92868 ¹⁷					
			0.9186 ¹⁶					
triethylene glycol dimethyl ether	318.15	0.91999	0.9186 ¹⁶	23.44				
			0.9811 ¹⁵					
			0.98171 ¹⁸					
triethylene glycol dimethyl ether	298.15	0.98123	0.9811 ¹⁵	27.56				
			0.97115 ¹⁷					
			0.97126 ¹⁹					
triethylene glycol dimethyl ether	308.15	0.97171	0.97115 ¹⁷	28.48				
			0.97126 ¹⁹					
			0.9710 ²⁰					
tetraethylene glycol dimethyl ether	318.15	0.96219		27.83				
			298.15		1.00726	1.00665 ⁵	33.74	
						1.0063 ¹⁵		
tetraethylene glycol dimethyl ether	308.15	0.99798	1.00662 ²¹	32.45				
					0.99634 ¹⁷			
					0.99642 ²²			
water	318.15	0.98872		31.71				
			298.15		0.99705	0.99704 ⁶	71.37	71.35 ²⁵
						0.9970480 ²³		71.6 ²⁶
0.99706 ²⁴								
water	308.15	0.99406	0.9940359 ²³	70.08	70.41 ²⁴			
			0.99404 ²⁴		70.1 ²⁶			
			0.99023 ²⁴		68.78 ²⁴			
water	318.15	0.99025	0.99021 ²⁷	69.11	68.84 ²⁸			

constant temperature at different times during the course of present measurements is $1 \cdot 10^{-5} \text{ g} \cdot \text{cm}^{-3}$. The samples for density measurements were prepared by mass in the stoppered glass bottles. Surface tension measurements in both the pure liquids and their mixtures were carried out at different temperatures using a DataPhysics DCAT II automated tensiometer, which employs the Wilhelmy plate method. A wettable platinum blade with an area of 3.98 mm^2 (wetted length 40.20 mm) was immersed in solution and slowly withdrawn to measure the vertical force, which is related to the surface tension by ($\sigma = Fg/W$), where σ is the surface tension, F is the measured vertical force, g is the acceleration of gravity, and W is the perimeter of the blade. The measurements were performed by the titration method wherein the first component of the mixture was taken in the measurement cell (25 g) and the second component was added by mass in steps. Before each measurement, stirring was performed for about 5 min, and thereafter the mixture was kept for 5 min for equilibration. The resolution of the dynamic contact angle device used for surface tension measurements is $0.01 \text{ mN} \cdot \text{m}^{-1}$. The repeatability for the triplicate measurements done for the same sample was $\pm 0.03 \text{ mN} \cdot \text{m}^{-1}$. The uncertainty obtained in σ values is $< 0.3 \text{ mN} \cdot \text{m}^{-1}$. The uncertainty obtained in the $\Delta\sigma$ values is $\pm 0.4 \text{ mN} \cdot \text{m}^{-1}$. The uncertainty obtained for molar surface energy and parachor are found to be less than $0.3 \text{ N} \cdot \text{m} \cdot \text{mol}^{-1}$ and $0.4 (\text{mN} \cdot \text{m}^{-1})^{1/4} \text{ cm}^3 \cdot \text{mol}^{-1}$, respectively. The concentrations for the density and surface tension measurements

are different as both methods employed different methods and required different amount of solutions. The temperature of the measurement cell was controlled with a Julabo water thermostat within $\pm 0.1 \text{ K}$. Binary mixtures were prepared by mass, using an analytical balance with a precision of $\pm 0.0001 \text{ g}$ (Denver Instrument APX-200). The mole fraction of each mixture was obtained with an accuracy of $1 \cdot 10^{-4}$ from the measured masses of the components. All molar quantities were based on the IUPAC relative atomic mass table.²⁹

RESULTS AND DISCUSSION

Experimental densities, ρ , along with the excess molar volumes V^E for binary mixtures of polyethers (diethylene glycol dimethyl ether or triethylene glycol dimethyl ether or tetraethylene glycol dimethyl ether) and water at $T = (298.15, 308.15, \text{ and } 318.15) \text{ K}$ are listed in Table 2. Excess molar volumes were calculated from our measurements according to following equation

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

where x_1 and x_2 are mole fractions, M_1 and M_2 are molar masses, and ρ_1 and ρ_2 are the densities of pure components 1 and 2, respectively. ρ is the density of the binary mixtures.

Experimental results on surface tension σ , and surface tension deviations $\Delta\sigma$, at different temperatures are reported in Table 3. Values of σ were fitted to a polynomial type equation utilizing the

Table 2. Densities (ρ), and Excess Molar Volumes (V^E) for x Polyether + (1 - x) Water Mixtures at $T = (298.15, 308.15, \text{ and } 318.15) \text{ K}$

x	$\rho \cdot 10^3 / \text{kg} \cdot \text{m}^{-3}$			$V^E \cdot 10^6 / \text{m}^3 \cdot \text{mol}^{-1}$		
	$T/\text{K} = 298.15$	$T/\text{K} = 308.15$	$T/\text{K} = 318.15$	$T/\text{K} = 298.15$	$T/\text{K} = 308.15$	$T/\text{K} = 318.15$
x Diethylene Glycol Dimethyl Ether + (1 - x) Water						
0.0188	1.00255	0.99841	0.99430	-0.265	-0.264	-0.278
0.0543	1.00680	1.00143	0.99625	-0.679	-0.685	-0.710
0.1289	1.00243	0.99623	0.98910	-1.230	-1.27	-1.295
0.1903	0.99476	0.98730	0.97979	-1.461	-1.492	-1.537
0.3195	0.97875	0.97044	0.96172	-1.575	-1.619	-1.655
0.4068	0.97055	0.96172	0.95275	-1.535	-1.573	-1.615
0.4993	0.96315	0.95406	0.94464	-1.394	-1.434	-1.461
0.6210	0.95566	0.94587	0.93650	-1.155	-1.150	-1.201
0.7181	0.95074	0.94070	0.93128	-0.908	-0.886	-0.945
0.8097	0.94627	0.93634	0.92676	-0.580	-0.575	-0.625
0.9099	0.94233	0.93239	0.92258	-0.225	-0.225	-0.253
0.9551	0.94097	0.93105	0.92112	-0.090	-0.096	-0.109
x Triethylene Glycol Dimethyl Ether + (1 - x) Water						
0.0173	1.00622	1.00432	0.99853	-0.240	-0.285	-0.265
0.0914	1.01965	1.01626	1.00741	-0.989	-1.036	-1.077
0.1739	1.01724	1.01056	1.00145	-1.406	-1.452	-1.431
0.2731	1.00997	1.00113	0.99210	-1.538	-1.565	-1.601
0.3468	1.004700	0.99527	0.98606	-1.560	-1.561	-1.589
0.4515	0.99825	0.98866	0.97925	-1.312	-1.365	-1.404
0.5727	0.99240	0.98292	0.97334	-1.135	-1.110	-1.080
0.6451	0.98970	0.98017	0.97059	-0.955	-0.930	-0.903
0.7766	0.98598	0.97639	0.96682	-0.635	-0.610	-0.590
0.8679	0.98402	0.97451	0.96492	-0.415	-0.410	-0.391
0.8977	0.98345	0.97395	0.96434	-0.343	-0.340	-0.321
0.9699	0.98195	0.97246	0.96291	-0.120	-0.125	-0.118
x Tetraethylene Glycol Dimethyl Ether + (1 - x) Water						
0.0142	1.01113	1.00656	1.00129	-0.260	-0.249	-0.238
0.0747	1.03525	1.02726	1.01904	-1.063	-1.016	-0.975
0.1452	1.03672	1.02767	1.01851	-1.502	-1.441	-1.386
0.2309	1.03130	1.02201	1.01258	-1.649	-1.590	-1.531
0.2974	1.02641	1.01712	1.00772	-1.587	-1.535	-1.482
0.4065	1.02020	1.01092	1.00156	-1.381	-1.338	-1.294
0.5085	1.01634	1.00706	0.99773	-1.172	-1.136	-1.100
0.5863	1.01423	1.00492	0.99558	-1.016	-0.983	-0.949
0.6788	1.01216	1.00283	0.99348	-0.812	-0.783	-0.750
0.8139	1.00947	1.00017	0.99083	-0.434	-0.417	-0.391
0.8540	1.00876	0.99947	0.99015	-0.311	-0.298	-0.277
0.9569	1.00743	0.99816	0.98889	-0.044	-0.042	-0.035

method of least-squares with each point weighted equally.

$$\sigma = \sum_{i=0} A_i x_1^i \quad (2)$$

The coefficients A_i for the correlation of σ -concentration data evaluated using least-squares method are given in Table 4 along with the resulting standard deviations.

The surface tension deviations $\Delta\sigma$ from mole fraction average were calculated from the relationship

$$\Delta\sigma = \sigma - (x_1\sigma_1 - x_2\sigma_2) \quad (3)$$

where σ is the surface tension of the mixture, x_1 and x_2 are the mole fractions, and σ_1 and σ_2 are the surface tension of the pure components 1 and 2, respectively.

The calculated values of V^E and $\Delta\sigma$ of the binary mixtures were fitted to a Redlich-Kister³⁰ type polynomial equation

$$Y(x) = x_1 x_2 \sum_{i=0}^n A_i (x_1 - x_2)^i \quad (4)$$

where $Y(x) = V^E / \text{cm}^3 \cdot \text{mol}^{-1}$ and $\Delta\sigma / \text{mN} \cdot \text{m}^{-1}$. The coefficients A_i for the correlation of $Y(x)$ -concentration data were

Table 3. Surface Tension (σ), Surface Tension Deviations ($\Delta\sigma$), Surface Energies (E_a), and Parachor (P) for x Polyether + (1 - x) Water Liquid Mixtures at $T = (298.15, 308.15, \text{ and } 318.15) \text{ K}$

x_1	σ	$\Delta\sigma$	$E_a \cdot 10^2$	P
	$\text{mN} \cdot \text{m}^{-1}$	$\text{mN} \cdot \text{m}^{-1}$	$\text{N} \cdot \text{m} \cdot \text{mol}^{-1}$	$(\text{mN} \cdot \text{m}^{-1})^{1/4} \text{cm}^3 \cdot \text{mol}^{-1}$
x Diethylene Glycol Dimethyl Ether + (1 - x) Water				
$T/\text{K} = 298.15$				
0.0000	71.37	0.00	49.62	53
0.0047	49.27	-21.88	34.91	49
0.0141	44.11	-26.60	32.41	51
0.0279	42.26	-27.80	32.66	54
0.0456	39.85	-29.38	32.72	58
0.0874	35.99	-31.29	33.55	69
0.1184	31.62	-34.21	32.01	75
0.1582	30.69	-33.27	34.13	86
0.2241	30.45	-30.43	38.71	104
0.3191	29.90	-26.54	44.50	132
0.4283	28.69	-22.63	49.41	162
0.5164	28.08	-19.12	53.38	187
0.6493	27.90	-13.08	60.19	225
0.7841	26.77	-7.89	64.37	262
0.8737	26.29	-4.78	67.38	287
0.9228	25.69	-1.88	68.01	299
0.9704	25.19	-0.76	68.71	311
1.0000	24.56	0.00	68.20	318
$T/\text{K} = 308.15$				
0.0000	70.08	0.00	48.82	52
0.0014	53.47	-16.55	37.46	49
0.0038	50.51	-19.41	35.74	49
0.0085	47.12	-22.60	33.97	50
0.0142	44.72	-24.76	32.96	51
0.0279	41.30	-27.59	32.02	54
0.0457	38.99	-29.15	32.14	58
0.0875	33.65	-32.72	31.51	68
0.1200	32.57	-32.42	33.25	77
0.1602	31.09	-32.19	34.90	87
0.2265	29.75	-30.72	38.19	105
0.3217	29.19	-27.24	43.86	133
0.4305	28.79	-23.02	50.02	164
0.5179	28.41	-19.69	54.44	189
0.6498	28.30	-14.21	61.50	228
0.7831	27.70	-9.15	67.03	267
0.8744	27.58	-5.44	71.22	294
0.9165	27.54	-3.61	73.13	306
0.9645	27.43	-1.73	75.08	320
1.0000	27.65	0.00	77.33	331
$T/\text{K} = 318.15$				
0.0000	69.11	0.00	48.27	52
0.0015	55.76	-13.28	39.19	50
0.0038	51.77	-17.17	36.72	50
0.0081	48.33	-20.41	44.55	73
0.0135	45.61	-22.88	33.61	51
0.0269	41.95	-25.93	32.50	54

Table 3. Continued

x_1	σ	$\Delta\sigma$	$E_a \cdot 10^2$	P
	$\text{mN} \cdot \text{m}^{-1}$	$\text{mN} \cdot \text{m}^{-1}$	$\text{N} \cdot \text{m} \cdot \text{mol}^{-1}$	$(\text{mN} \cdot \text{m}^{-1})^{1/4} \text{cm}^3 \cdot \text{mol}^{-1}$
0.0444	39.33	-27.75	32.39	58
0.0857	34.62	-30.58	32.38	68
0.1091	28.86	-35.27	28.77	72
0.1560	26.65	-35.34	29.78	83
0.2194	25.34	-33.75	32.27	100
0.3174	24.45	-30.16	36.72	127
0.4248	24.26	-25.45	42.13	157
0.5110	24.18	-21.59	46.31	182
0.6513	23.87	-15.50	52.29	221
0.7915	23.64	-9.32	57.96	261
0.8844	23.50	-5.24	61.53	288
0.9137	23.48	-3.92	62.68	296
0.9547	23.46	-2.01	64.29	308
1.0000	23.44	0.00	66.03	321
x Triethylene Glycol Dimethyl Ether + (1 - x) Water				
$T/\text{K} = 298.15$				
0.0000	71.37	0.00	49.62	53
0.0012	53.35	-17.97	37.34	49
0.0024	51.27	-19.99	36.12	49
0.0029	49.07	-22.17	34.66	49
0.0036	48.59	-22.62	34.45	49
0.0043	47.60	-23.58	33.88	49
0.0206	40.60	-29.87	31.38	53
0.0375	38.88	-30.85	32.44	59
0.0695	36.20	-32.13	34.26	70
0.0905	33.99	-33.42	34.58	77
0.1223	33.06	-32.95	37.08	88
0.1630	32.87	-32.00	41.08	104
0.2911	32.23	-25.75	52.36	153
0.3517	31.66	-24.30	56.65	176
0.4658	31.16	-19.80	64.90	220
0.5830	30.50	-15.33	72.14	264
0.6590	30.09	-12.41	76.42	293
0.7279	29.54	-9.94	79.55	318
0.8210	29.05	-6.35	84.07	352
0.8823	28.52	-4.19	86.21	374
0.9461	28.04	-1.88	88.44	397
1.0000	27.56	0.00	89.94	416
$T/\text{K} = 308.15$				
0.0000	70.08	0.00	48.82	52
0.0009	53.01	-17.03	37.11	49
0.0017	50.04	-19.97	35.19	49
0.0026	47.96	-22.01	33.89	49
0.0039	45.41	-24.51	32.31	49
0.0109	41.72	-27.91	30.79	50
0.0218	40.14	-29.03	31.26	54
0.0353	38.28	-30.33	31.70	58
0.0882	36.04	-30.37	36.50	78
0.1214	34.06	-30.97	38.25	89
0.1767	33.08	-29.65	42.94	110
0.2497	32.48	-27.21	49.23	138
0.2497	31.82	-24.11	48.23	137

Table 3. Continued

x_1	σ		$E_a \cdot 10^2$	P	
	$\text{mN} \cdot \text{m}^{-1}$	$\Delta\sigma$ $\text{mN} \cdot \text{m}^{-1}$	$\text{N} \cdot \text{m} \cdot \text{mol}^{-1}$	$(\text{mN} \cdot \text{m}^{-1})^{1/4} \text{cm}^3 \cdot \text{mol}^{-1}$	
0.3400	31.44	-21.41	55.59	172	
0.4141	30.89	-17.26	60.67	201	
0.5272	30.74	-15.06	69.06	245	
0.5837	30.15	-10.08	71.81	266	
0.7176	29.76	-6.07	80.00	318	
0.8234	29.38	-4.46	85.73	358	
0.9458	28.74	-1.99	91.22	403	
1.0000	28.48	0.00	93.55	424	
$T/K = 318.15$					
0.0000	69.11	0.00	48.27	52	
0.0014	51.81	-17.24	36.47	49	
0.0021	47.47	-21.55	33.54	49	
0.0028	46.10	-22.89	32.70	49	
0.0039	44.63	-24.32	31.84	49	
0.0100	41.37	-27.33	43.74	86	
0.0212	39.06	-29.17	30.43	54	
0.034	37.85	-29.86	31.28	58	
0.0543	35.26	-31.61	31.72	65	
0.0791	32.67	-33.58	32.22	73	
0.0849	32.50	-33.19	32.70	75	
0.0917	32.42	-32.83	33.37	77	
0.1220	32.27	-31.40	36.48	89	
0.1848	32.14	-29.34	42.74	113	
0.2728	31.26	-26.59	49.73	147	
0.3289	31.05	-24.49	54.28	169	
0.3776	30.83	-22.69	57.95	188	
0.4688	30.30	-19.46	64.11	223	
0.6611	29.59	-12.23	76.28	298	
0.7234	29.40	-9.85	79.94	322	
0.8102	28.99	-6.68	84.34	355	
0.8562	28.68	-5.09	86.26	372	
0.8915	28.30	-4.01	87.22	385	
1.0000	27.83	0.00	92.02	425	
x Tetraethylene Glycol Dimethyl Ether + (1 - x) Water					
$T/K = 298.15$					
0.0000	71.37	0.00	49.62	53	
0.0016	50.16	-21.15	35.25	49	
0.0020	48.89	-22.40	34.45	49	
0.0026	47.04	-24.23	33.28	49	
0.0031	46.37	-24.88	32.91	49	
0.0092	43.11	-27.91	31.82	51	
0.0174	41.23	-29.49	31.98	54	
0.0283	40.10	-30.21	33.07	59	
0.0570	39.54	-29.69	37.52	72	
0.0746	38.88	-29.91	39.75	80	
0.1026	38.65	-28.63	43.88	94	
0.1497	37.66	-28.08	49.59	116	
0.2264	36.29	-26.56	57.82	153	
0.2862	35.79	-24.81	64.26	182	
0.4268	35.09	-20.22	78.41	251	
0.5414	34.92	-16.08	89.50	308	
0.6144	34.46	-13.79	95.17	343	

Table 3. Continued

x_1	σ		$E_a \cdot 10^2$	P	
	$\text{mN} \cdot \text{m}^{-1}$	$\Delta\sigma$ $\text{mN} \cdot \text{m}^{-1}$	$\text{N} \cdot \text{m} \cdot \text{mol}^{-1}$	$(\text{mN} \cdot \text{m}^{-1})^{1/4} \text{cm}^3 \cdot \text{mol}^{-1}$	
0.7870	34.20	-7.56	109.70	428	
0.8286	34.19	-5.99	113.20	449	
0.9196	33.91	-2.86	119.70	493	
1.0000	33.74	0.00	125.40	532	
$T/K = 308.15$					
0.0000	70.08	0.00	48.82	52	
0.0014	51.00	-27.17	35.90	49	
0.0023	46.99	-19.03	33.25	49	
0.0032	45.45	-23.00	32.36	49	
0.0040	44.21	-24.51	31.64	49	
0.0090	42.87	-25.72	30.05	47	
0.0175	39.90	-29.52	31.07	54	
0.0275	39.08	-29.96	32.21	58	
0.0539	38.34	-29.71	36.05	71	
0.0715	37.36	-30.03	37.91	79	
0.0990	37.28	-29.08	42.03	92	
0.1478	35.51	-29.01	46.78	115	
0.2212	34.95	-26.81	55.39	150	
0.3074	34.22	-24.29	64.20	192	
0.4252	33.85	-20.23	75.94	250	
0.5523	33.58	-15.72	87.62	313	
0.6404	33.32	-12.66	94.92	356	
0.7835	33.05	-7.55	106.40	427	
0.8140	32.88	-6.57	108.30	441	
0.9479	32.64	-1.77	118.10	507	
1.0000	32.45	0.00	121.40	532	
$T/K = 318.15$					
0.0000	69.11	0.00	48.27	52	
0.0013	58.46	-10.60	41.20	51	
0.0019	54.20	-14.84	38.35	50	
0.0024	51.29	-17.73	36.42	50	
0.0033	47.59	-21.40	34.00	49	
0.0098	42.27	-26.47	31.51	51	
0.0187	40.41	-28.02	31.81	55	
0.0314	40.39	-27.52	34.14	61	
0.0584	38.25	-28.68	36.89	73	
0.0748	37.24	-29.07	38.51	81	
0.1022	36.50	-28.79	41.85	94	
0.1482	35.37	-28.20	46.93	116	
0.2219	33.81	-27.00	54.00	151	
0.3152	33.30	-24.02	63.71	197	
0.4328	32.94	-19.98	75.11	255	
0.5259	32.75	-16.69	83.56	301	
0.5974	32.47	-14.30	89.30	336	
0.7667	32.22	-8.22	103.00	420	
0.8249	32.05	-6.21	107.10	448	
0.9324	31.94	-2.29	115.20	501	
1.0000	31.71	0.00	119.40	533	

obtained by fitting the equations to the experimental values with a least-squares method are given in Table 5 along with standard deviations δ . The standard deviation was calculated by

$$\delta = \left[\sum_1^n (Y(x)_{\text{exptl}} - Y(x)_{\text{calcd}})^2 / (n - m) \right]^{1/2} \quad (5)$$

where n and m are the number of experimental points and parameters, respectively.

Molar surface energies E_a and parachor P , have also been calculated from experimental surface tensions and densities with following relationships

$$E_a = \sigma(M/\rho)^{2/3} \quad (6)$$

Table 4. Standard Deviations (δ) and Parameters $A_i/\text{mN}\cdot\text{m}^{-1}$ in eq 2 for Surface Tension ($\sigma/\text{mN}\cdot\text{m}^{-1}$)

T/K	A_0	A_1	A_2	A_3	A_4	δ $\text{mN}\cdot\text{m}^{-1}$
x Diethylene Glycol Dimethyl Ether + $(1-x)$ Water						
298.15	47.36	-171.63	537.74	-672.74	289.09	1.55
308.15	49.30	-208.86	687.18	-89.78	396.78	2.25
318.15	51.83	-239.31	704.13	-847.68	356.96	4.44
x Triethylene Glycol Dimethyl Ether + $(1-x)$ Water						
298.15	49.06	-209.78	758.04	-1053.21	489.58	2.59
308.15	47.09	-161.74	545.72	-729.97	331.22	2.93
318.15	45.89	-202.89	803.88	-1197.42	592.27	2.54
x Tetraethylene Glycol Dimethyl Ether + $(1-x)$ Water						
298.15	46.62	-113.77	394.41	-548.04	259.46	2.22
308.15	45.28	-122.78	426.13	-578.91	265.59	2.47
318.15	49.64	-193.37	691.99	-958.13	448.02	4.29

Table 5. Standard Deviations (δ) and Parameters $A_i/\text{m}^3\cdot\text{mol}^{-1}$ or $A_i/\text{mN}\cdot\text{m}^{-1}$ in eq 4

$Y(x)$	T/K	A_0	A_1	A_2	A_3	A_4	δ
x Diethylene Glycol Dimethyl Ether + $(1-x)$ Water							
$V^E \cdot 10^6/\text{m}^3\cdot\text{mol}^{-1}$	298.15	-5.601	3.156	-2.694	3.753		0.009
	308.15	-5.699	3.637	-2.647	3.128		0.013
	318.15	-5.854	3.449	-3.017	3.512		0.010
$\Delta\sigma/\text{mN}\cdot\text{m}^{-1}$	298.15	47.39	-172.67	541.48	-686.28	297.18	1.55
	308.15	49.30	-209.01	688.18	-895.64	397.83	2.25
	318.15	51.26	-269.15	871.56	-1121.26	495.55	2.31
x Triethylene Glycol Dimethyl Ether + $(1-x)$ Water							
$V^E \cdot 10^6/\text{m}^3\cdot\text{mol}^{-1}$	298.15	-5.035	4.084	-4.038	1.411		0.030
	308.15	-5.114	4.424	-2.799	1.453	-2.659	0.016
	318.15	-5.153	4.866	-2.397	0.975	-3.127	0.024
$\Delta\sigma/\text{mN}\cdot\text{m}^{-1}$	298.15	49.09	-212.56	777.11	-1089.73	510.55	2.60
	308.15	47.10	-161.74	545.73	-729.97	331.22	2.93
	318.15	45.87	-202.23	801.04	-1193.21	590.22	2.58
x Tetraethylene Glycol Dimethyl Ether + $(1-x)$ Water							
$V^E \cdot 10^6/\text{m}^3\cdot\text{mol}^{-1}$	298.15	-4.759	4.011	-5.092	5.590		0.005
	308.15	-4.615	3.926	-4.797	5.217		0.005
	318.15	-4.465	3.828	-4.475	5.020		0.004
$\Delta\sigma/\text{mN}\cdot\text{m}^{-1}$	298.15	46.28	-113.48	393.97	-548.07	259.70	2.27
	308.15	45.28	-122.78	426.13	-578.91	265.59	2.47
	318.15	49.64	-193.16	690.75	-956.17	447.13	4.29

$$P = M\sigma^{1/4}/\rho \quad (7)$$

where other symbols have their usual meanings. These values are also reported in Table 3.

From Figures 1 to 3, it is observed that excess molar volumes for polyether (1) + water (2) binary liquid mixtures show negative deviations over whole concentration range at all temperatures. The magnitude of excess molar volume decreases with the increase in the polar headgroup of the polyether, that is, the

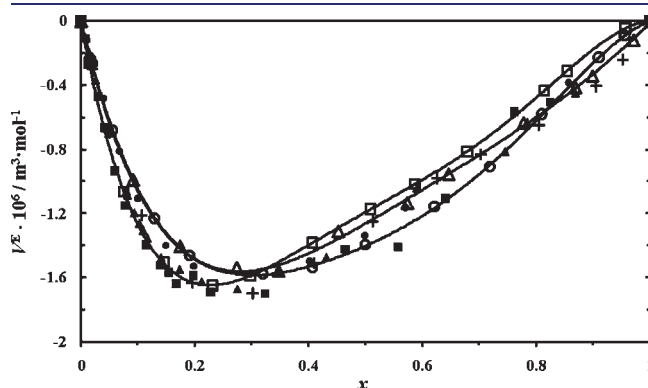


Figure 1. Excess molar volumes V^E for \circ , x diethylene glycol dimethyl ether + $(1-x)$ water; \bullet , ref 8, x diethylene glycol dimethyl ether + $(1-x)$ water; \triangle , x triethylene glycol dimethyl ether + $(1-x)$ water; \blacktriangle , ref 9, x triethylene glycol dimethyl ether + $(1-x)$ water; \square , x tetraethylene glycol dimethyl ether + $(1-x)$ water; \blacksquare , ref 10, x tetraethylene glycol dimethyl ether + $(1-x)$ water; $+$, ref 5, x tetraethylene glycol dimethyl ether + $(1-x)$ water at 298.15 K. Smooth curves have been drawn from polynomial curve fitting.

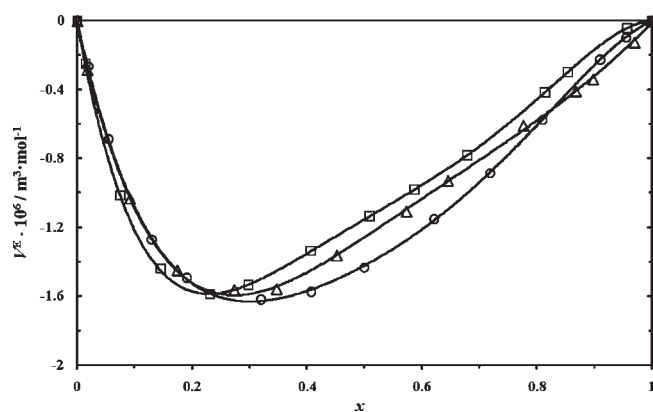


Figure 2. Excess molar volumes V^E for \circ , x diethylene glycol dimethyl ether + $(1-x)$ water; \triangle , x triethylene glycol dimethyl ether + $(1-x)$ water; \square , x tetraethylene glycol dimethyl ether + $(1-x)$ water at 308.15 K. Smooth curves have been drawn from polynomial curve fitting.

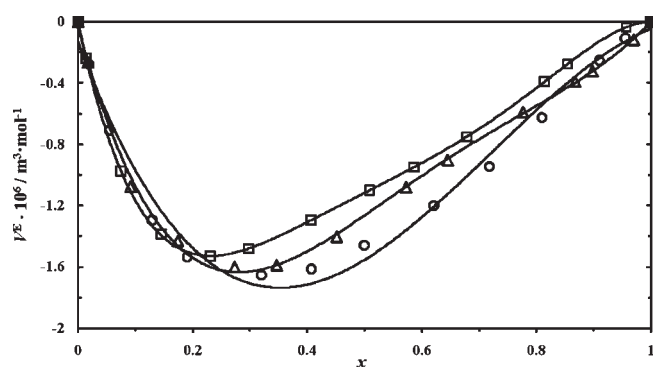


Figure 3. Excess molar volumes V^E for \circ , x diethylene glycol dimethyl ether + $(1-x)$ water; \triangle , x triethylene glycol dimethyl ether + $(1-x)$ water; \square , x tetraethylene glycol dimethyl ether + $(1-x)$ water at 318.15 K. Smooth curves have been drawn from polynomial curve fitting.

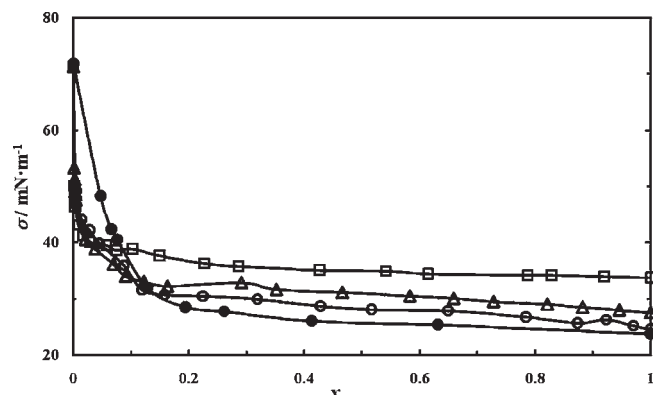


Figure 4. Experimental surface tension σ for \bullet , ref 7, x ethylene glycol dimethyl ether + $(1-x)$ water; \circ , x diethylene glycol dimethyl ether + $(1-x)$ water; \triangle , x triethylene glycol dimethyl ether + $(1-x)$ water; \square , x tetraethylene glycol dimethyl ether + $(1-x)$ water at 298.15 K. The solid lines are a guide for the eye.

presence of diethylene glycol units $[\text{CH}_2\text{CH}_2\text{O}]$ in the glyme chain lowers the excess molar volume. The negative values of V^E

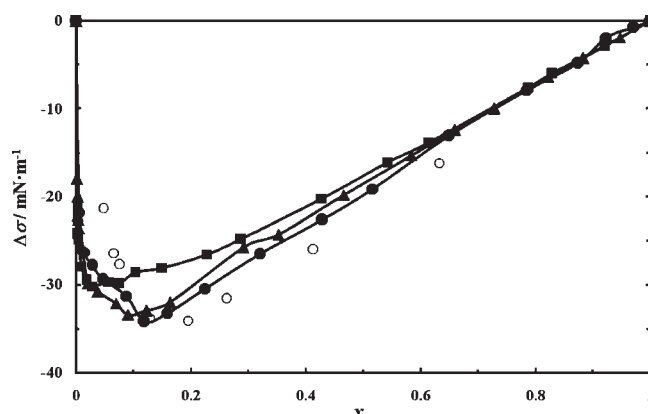


Figure 5. Surface tension deviations $\Delta\sigma$ for \circ , ref 7, x ethylene glycol dimethyl ether + $(1-x)$ water; \bullet , x diethylene glycol dimethyl ether + $(1-x)$ water; \triangle , x triethylene glycol dimethyl ether + $(1-x)$ water; \blacksquare , x tetraethylene glycol dimethyl ether + $(1-x)$ water at 298.15 K. The solid lines are a guide for the eye.

suggest a strong chemical or specific interaction between the unlike components which is maximum in diethylene glycol dimethyl ether–water mixture. For comparison we have shown the excess molar volumes calculated from densities reported earlier^{5,8–10} for these binary mixtures. The difference in the values may be due to the method of measurements and purity of samples.

Figure 4 shows that the surface tension σ for the binary liquid mixtures decreases with the increase in the concentration of polyether. Surface tension of the binary mixtures follows the order: ethylene glycol dimethyl ether⁷ < diethylene glycol dimethyl ether < triethylene glycol dimethyl ether < tetraethylene glycol dimethyl ether. This sequence shows that the surface tension increases with the increase in the polar headgroup in the polyether. Surface tension deviations, $\Delta\sigma$, values at all of the studied temperatures are reported in Table 3. The values of $\Delta\sigma$ at 298.15 K are shown in Figure 5. The values are negative over the whole concentration range for all binary liquid mixtures and show a sharp minimum in the water-rich region. It shows maximum deviations for x ethylene glycol dimethyl ether + $(1-x)$ water mixture, and the magnitude decreases with increase in the number of polar head groups in polyether.

The surface energy E_a and parachor P are calculated using eqs 6 and 7 at studied temperatures for all binary liquid mixtures and are reported in Table 3. Both values increase with the increase in the concentration of polyether in liquid mixtures at all temperatures. Also the values for the mixtures increase at all temperatures as we shift from diethylene glycol dimethyl ether to triethylene glycol dimethyl ether to tetraethylene glycol dimethyl ether.

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ACKNOWLEDGMENT

M.S. and A.K. are thankful to the director of CSMCRI for permitting experimental measurements at the SMC Division of CSMCRI as a part of summer training program.

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