

Density, Viscosity, and Refractive Index for Water + 2-Butoxyethanol and + 2-(2-Butoxyethoxy)ethanol at Various Temperatures

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Density, viscosity, and refractive index for the binary systems water + 2-butoxyethanol and water + 2-(2-butoxyethoxy)ethanol have been measured at the temperatures ranging from (283.15 to 323.15) K at atmospheric pressure. The excess molar volume and deviations of viscosity and refractive index from a mole fraction average of these binary mixtures were correlated by the Redlich–Kister equation.

Introduction

The homologous series of nonionic surfactant poly(oxyethylene) alcohol $\text{CH}_3(\text{CH}_2)_{i-1}(\text{OCH}_2\text{CH}_2)_j\text{OH}$, abbreviated by C_iE_j hereafter, is extensively used both in industrial and in fundamental research applications. In our laboratory, we have been extensively working on the phase behavior and the wetting behavior for systems of the types water + C_iE_j and water + C_iE_j + oil.^{1–18} In this study, density, viscosity, and refractive index measurements were performed on two binary systems: water + 2-butoxyethanol (C_4E_1) and water + 2-(2-butoxyethoxy)ethanol (C_4E_2). To the best of our knowledge, there are neither viscosity nor refractive index measurements for the systems water + C_4E_1 and water + C_4E_2 available in the literature. The density of the water + C_4E_2 system increases with the increase in the mole fraction of C_4E_2 in the very dilute region, and after reaching a maximum the density then decreases monotonically along with a further increase in the mole fraction of C_4E_2 . However, there is no such maximum density behavior at the very dilute region for the water + C_4E_1 system. As a comparison, the water + C_6E_2 system was also studied to determine if there is a maximum density behavior at the very dilute region. Finally, all of the excess molar volume and deviations of the viscosity and refractive index from a mole fraction average of these binary mixtures were correlated by the Redlich–Kister equation.

Experimental Section

The surfactant 2-butoxyethanol (C_4E_1) of 99 % + purity was purchased from Riedel-de Haën. The surfactant 2-(2-butoxyethoxy)ethanol (C_4E_2) of 99 % + purity was purchased from Aldrich Chemical Corporation. The nonionic short chain surfactant diethylene glycol monohexyl ether (C_6E_2) of 98 % purity was a product of Merck Chemical Co. The surfactant C_6E_2 was fractionally distilled under a reduced pressure until a purity of > 99.5 % was attained as determined by gas chromatography (China Chromatography GC9800, Taiwan). Water was purified by double-distillation and then followed by a PURELAB (Maxima, Elga) purification system with the resistivity always better than $18.2 \text{ M}\Omega \cdot \text{cm}$.

Viscosity measurements were performed in an Ubbelohde suspended-level glass-capillary viscometer supplied by Schott-Gerate (Hofheim a. Ts., Germany) along with a Schott-Gerate

Table 1. Comparison of the Experimental Results and Literature Data of Densities, ρ , and Refractive Indices, n_D , of C_4E_1

T K	ρ $\text{g} \cdot \text{cm}^{-3}$		n_D	
	exptl	lit.	exptl	lit.
293.15	0.90118	0.9003 ^a	1.4196	1.4193 ^a
313.15	0.88421	0.883775 ^b		

^a From ref 21. ^b From ref 22.

Table 2. Comparison of the Experimental Results and Literature Data of Densities, ρ , Viscosities, η , and Refractive Indices, n_D , of C_4E_2

T K	ρ $\text{g} \cdot \text{cm}^{-3}$		η $\text{mPa} \cdot \text{s}$		n_D	
	exptl	lit.	exptl	lit.	exptl	lit.
293.15	0.95416	0.95281 ^a 0.95387 ^c 0.95688 ^d 0.952196 ^e 0.9522 ^f 0.9529 ^b	5.8597	5.84 ^b	1.4312	1.4320 ^a
303.15	0.94574	0.94535 ^c 0.943743 ^e 0.9435 ^b 0.9438 ^f	4.3229	4.23 ^b		
313.15	0.93735	0.9359 ^b 0.9353 ^f	3.2955	3.22 ^b		
323.15	0.92885	0.9266 ^{f,b}	2.5805	2.51 ^b		

^a From ref 23. ^b From ref 28. ^c From ref 24. ^d From ref 25. ^e From ref 26. ^f From ref 27.

automatic measuring unit model AVS-310 (Hofheim a. Ts., Germany). The temperature was kept constant within ± 0.005 K by a homemade computer-controlled water-bath thermostat.⁴ The uncertainty of the time for flow measurements of Schott-Gerate AVS-310 was within ± 0.01 s. At least six measurements were performed for each composition and temperature, and the results were determined by averaging over these six measurements. According to the variation of our experimental results of flow times, the estimated uncertainty in the kinematic viscosity measurements was less than 0.33 %. All of the solutions were prepared by mass with an uncertainty of less than 0.1 % from the reported compositions.

The kinematic viscosity was related to the flow time as

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$$\nu = At + \frac{B}{t} \quad (1)$$

where constants A and B were determined by calibration. Four pure components, water, octane, decane, and 2-methyl-2-butanol, were used to calibrate the Ubbelohde viscometer by measuring the flow times of the above fluids at five different temperatures: (283.15, 293.15, 303.15, 313.15, and 323.15) K. All of the kinematic viscosities of these calibration fluids were adopted from literature,^{19,20} and the linear regression analysis of eq 1 yielded constants A and B with a standard deviation always better than 0.0017 mPa·s for every Ubbelohde viscometer used in this study.

Since the absolute viscosity, η , is defined by $\eta = \nu\rho$, the density of a mixture should be measured to determine its viscosity, η . Densities were measured with a vibrating tube density meter (Anton-Paar DMA-58, Austria) equipped with a thermostat with stability within ± 0.01 K. The calibration of the density meter was carried out with water (purified) and dry air at each temperature under atmospheric pressure. The uncertainty of the density measurements was ± 0.00002 g·cm⁻³. The mixtures were prepared by mass with an uncertainty of ± 0.00001 g. The refractive indices were measured by using an Abbe refractometer (Type 3T, Atago, Japan) under D-rays of wavelength 589.3 nm. This Abbe refractometer was connected to a thermostat circulator (Thermo Haake K-10 and DC-30, Germany) with stability within ± 0.01 K to maintain its

Table 3. Experimental Densities, Viscosities, and Refractive Indices for the Binary (1 - x) H₂O + x C₄E₁ System at T = (283.15, 293.15, 303.15, 313.15, and 323.15) K

x	T/K				
	283.15	293.15	303.15	313.15	323.15
	$\rho/\text{g}\cdot\text{cm}^{-3}$				
0.00000	0.99970	0.99820	0.99565	0.99221	0.98804
0.10030	0.97552	0.96912	0.96259	0.95566	<i>a</i>
0.20000	0.95751	0.95015	0.94262	0.93480	0.92683
0.30000	0.94528	0.93750	0.92957	0.92147	0.91323
0.40000	0.93577	0.92776	0.91960	0.91130	0.90287
0.50000	0.92869	0.92054	0.91216	0.90378	0.89522
0.60000	0.92316	0.91496	0.90660	0.89814	0.88956
0.70000	0.91870	0.91049	0.90202	0.89357	0.88496
0.79990	0.91501	0.90678	0.89830	0.88984	0.88126
0.90000	0.91208	0.90380	0.89530	0.88683	0.87823
1.00000	0.90949	0.90118	0.89268	0.88421	0.87560
	$\eta/\text{mPa}\cdot\text{s}$				
0.00000	1.3087	1.0028	0.7983	0.6543	0.5492
0.10030	5.4889	3.7909	2.7721	2.1258	<i>a</i>
0.20000	7.1068	4.8544	3.4832	2.5836	1.9792
0.30000	7.4150	5.0794	3.6402	2.6979	2.0537
0.40000	7.2339	4.9945	3.5939	2.6720	2.0385
0.50000	6.8300	4.7608	3.4481	2.5828	1.9810
0.60000	6.3522	4.4755	3.2718	2.4647	1.9007
0.70000	5.8575	4.1720	3.0787	2.3369	1.8133
0.79990	5.3597	3.8645	2.8791	2.2047	1.7213
0.90000	4.8846	3.5598	2.6793	2.0683	1.6287
1.00000	4.4600	3.2878	2.4995	1.9459	1.5430
	n_D				
0.00000	1.3337	1.3330	1.3319	1.3306	1.3290
0.10030	1.3785	1.3766	1.3740	1.3712	<i>a</i>
0.20000	1.3965	1.3942	1.3912	1.3878	1.3839
0.30000	1.4061	1.4036	1.4003	1.3966	1.3925
0.40000	1.4118	1.4091	1.4056	1.4018	1.3976
0.50000	1.4156	1.4128	1.4092	1.4052	1.4010
0.60000	1.4182	1.4153	1.4116	1.4075	1.4032
0.70000	1.4199	1.4170	1.4132	1.4090	1.4047
0.79990	1.4212	1.4182	1.4143	1.4101	1.4058
0.90000	1.4221	1.4191	1.4152	1.4110	1.4066
1.00000	1.4226	1.4196	1.4157	1.4114	1.4070

^a The sample falls in two-phase coexistence region.

Table 4. Experimental Densities, Viscosities, and Refractive Indices for the Binary (1 - x) H₂O + x C₄E₂ System at T = (283.15, 293.15, 303.15, 313.15, and 323.15) K

x	T/K				
	283.15	293.15	303.15	313.15	323.15
	$\rho/\text{g}\cdot\text{cm}^{-3}$				
0.00000	0.99970	0.99820	0.99565	0.99221	0.98804
0.10000	1.00167	0.99455	0.98721	0.97973	0.97195
0.20000	0.99263	0.98471	0.97663	0.96847	0.96010
0.29990	0.98544	0.97727	0.96897	0.96058	0.95190
0.40000	0.97951	0.97127	0.96291	0.95451	0.94589
0.50000	0.97490	0.96663	0.95827	0.94982	0.94129
0.60000	0.97146	0.96317	0.95474	0.94632	0.93775
0.70000	0.96877	0.96045	0.95205	0.94362	0.93503
0.79980	0.96662	0.95825	0.94980	0.94134	0.93280
0.89990	0.96458	0.95618	0.94772	0.93934	0.93080
1.00000	0.96257	0.95416	0.94574	0.93735	0.92885
	$\eta/\text{mPa}\cdot\text{s}$				
0.00000	1.3087	1.0028	0.7983	0.6543	0.5492
0.10000	8.6445	5.6843	3.9740	2.9143	2.2162
0.20000	12.3561	7.9858	5.4816	3.9425	2.9429
0.29990	13.3196	8.6369	5.9297	4.2587	3.1732
0.40000	13.0650	8.5504	5.9126	4.2704	3.1954
0.50000	12.3588	8.1827	5.7132	4.1614	3.1332
0.60000	11.4863	7.7076	5.4416	3.9975	3.0333
0.70000	10.5782	7.2031	5.1442	3.8159	2.9180
0.79980	9.7483	6.7269	4.8575	3.6376	2.8037
0.89990	9.0379	6.3093	4.6010	3.4737	2.6968
1.00000	8.3013	5.8597	4.3229	3.2955	2.5805
	n_D				
0.00000	1.3337	1.3330	1.3319	1.3306	1.3290
0.10000	1.3916	1.3894	1.3871	1.3842	1.3808
0.20000	1.4111	1.4083	1.4057	1.4022	1.3982
0.29990	1.4204	1.4174	1.4146	1.4109	1.4067
0.40000	1.4255	1.4224	1.4194	1.4157	1.4113
0.50000	1.4286	1.4254	1.4224	1.4185	1.4141
0.60000	1.4307	1.4274	1.4243	1.4204	1.4159
0.70000	1.4323	1.4289	1.4258	1.4219	1.4173
0.79980	1.4334	1.4299	1.4268	1.4227	1.4182
0.89990	1.4342	1.4307	1.4275	1.4234	1.4188
1.00000	1.4347	1.4312	1.4281	1.4240	1.4194

temperature at a prescribed value with uncertainty of ± 0.1 K. The uncertainty of refractive index measurements was ± 0.0002 .

Results and Discussion

The comparison of measured density, refractive index, and viscosity of C₄E₁ and C₄E₂ with literature values is shown in

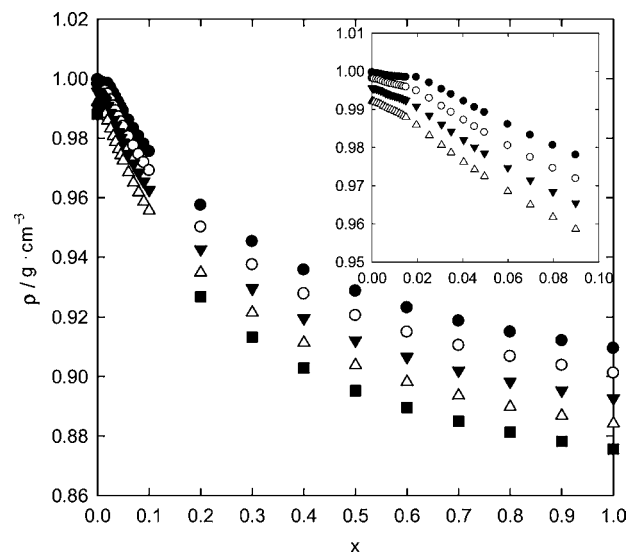


Figure 1. Variation of the density for (1 - x) H₂O + x C₄E₁ at: ●, 283.15 K; ○, 293.15 K; ▼, 303.15 K; △, 313.15 K; ■, 323.15 K.

Table 5. Experimental Densities for the Binary $(1 - x) \text{H}_2\text{O} + x \text{C}_4\text{E}_1$ System and $(1 - x) \text{H}_2\text{O} + x \text{C}_4\text{E}_2$ System in a Very Dilute Region ($x < 0.09$) at $T = (283.15, 293.15, 303.15, \text{ and } 313.15) \text{ K}$

T/K					T/K				
x	283.15	293.15	303.15	313.15	x	283.15	293.15	303.15	313.15
$\rho/\text{g}\cdot\text{cm}^{-3}$					$\rho/\text{g}\cdot\text{cm}^{-3}$				
C_4E_1									
0.0000	0.99970	0.99820	0.99565	0.99221	0.01317	0.99855	0.99616	0.99285	0.98865
0.00050	0.99962	0.99813	0.99557	0.99212	0.01401	0.99849	0.99602	0.99263	0.98837
0.00100	0.99953	0.99801	0.99546	0.99202	0.01499	0.99849	0.99591	0.99238	0.98801
0.00201	0.99943	0.99789	0.99529	0.99180	0.01959	0.99845	0.99490	0.99079	0.98595
0.00300	0.99937	0.99778	0.99512	0.99158	0.02529	0.99700	0.99294	0.98838	0.98321
0.00399	0.99924	0.99760	0.99489	0.99131	0.03070	0.99531	0.99088	0.98603	0.98066
0.00500	0.99906	0.99734	0.99459	0.99098	0.03495	0.99394	0.98928	0.98422	0.97871
0.00601	0.99889	0.99711	0.99427	0.99064	0.04047	0.99216	0.98722	0.98199	0.97624
0.00699	0.99886	0.99697	0.99406	0.99036	0.04524	0.99059	0.98550	0.98012	0.97425
0.00801	0.99880	0.99683	0.99386	0.99011	0.04961	0.98923	0.98399	0.97847	0.97250
0.00896	0.99872	0.99670	0.99369	0.98986	0.05991	0.98608	0.98054	0.97475	0.96852
0.00998	0.99868	0.99657	0.99350	0.98960	0.06979	0.98328	0.97749	0.97148	0.96502
0.01102	0.99864	0.99643	0.99330	0.98931	0.07979	0.98063	0.97461	0.96838	0.96177
0.01209	0.99859	0.99630	0.99309	0.98899	0.08979	0.97805	0.97187	0.96546	0.95867
C_4E_2									
0.00000	0.99970	0.99820	0.99565	0.99221	0.01492	1.00427	1.00144	0.99766	0.99362
0.00199	1.00020	0.99859	0.99587	0.99268	0.02056	1.00574	1.00203	0.99751	0.99305
0.00300	1.00041	0.99879	0.99601	0.99286	0.02380	1.00636	1.00220	0.99718	0.99261
0.00498	1.00105	0.99920	0.99631	0.99328	0.02697	1.00666	1.00211	0.99700	0.99219
0.00617	1.00143	0.99948	0.99653	0.99343	0.03015	1.00678	1.00194	0.99661	0.99164
0.00706	1.00175	0.99968	0.99667	0.99351	0.03953	1.00653	1.00104	0.99523	0.98979
0.00794	1.00200	0.99988	0.99681	0.99362	0.06038	1.00513	0.99881	0.99228	0.98616
0.00892	1.00232	1.00011	0.99695	0.99366	0.07987	1.00342	0.99664	0.98968	0.98324
0.00993	1.00265	1.00034	0.99707	0.99371					

Tables 1 and 2, respectively. A reasonable agreement was found among our experimental results and literature data.^{21–28}

The experimental results of densities, viscosities, and refractive indices for two binary systems: $(1 - x)$ water + $x \text{C}_4\text{E}_1$ and $(1 - x)$ water + $x \text{C}_4\text{E}_2$ as a function of mole fraction of C_iE_j , x , at temperatures ranging from (283.15 to 323.15) K are given in Tables 3 and 4, respectively. Note that the lower critical solution temperature (LCST) of the water + C_4E_1 system is 322.15 K and that the system exhibits liquid–liquid coexistence when the system temperature is above its LCST.²⁹ Therefore, the water + C_4E_1 system of $x = 0.10030$ at 323.15 K falls into the two-liquid phase coexistence region, and no data of density, viscosity, and refractive index are reported in Table 3.

The variation of viscosity as a function of the mole fraction x under the condition of a fixed temperature consistently exhibits a maximum viscosity around $x = 0.3$ for both systems, as shown in Tables 3 and 4. On the other hand, the refractive index increases monotonically along with an increase in the mole fraction x for both systems.

Figure 1 shows the variation of density of the water + C_4E_1 system at five different temperatures: (283.15, 293.15, 303.15, 313.15, and 323.15) K. The density of the water + C_4E_1 system decreases monotonically along with an increase in the mole fraction x . Note that the density exhibits a linear behavior at the very dilute region ($x < 0.02$), as shown in the inset of Figure 1. These density data at the very dilute region ($x < 0.08$) of the water + C_4E_1 system are listed in Table 5. There is a transition of slope from a slower one to a steeper one around $x = 0.02$ for the density at each temperature. The transition point shifts toward a smaller mole fraction x as the temperature increases, as shown in inset of Figure 1. As the temperature increases, the linear behavior at dilute regions ($x < 0.02$) becomes steeper, and the difference between the two slopes before and after the transition point becomes smaller. This observation is consistent with that of Wicczorek (1991).³⁰

Figure 2 shows the variation of density of the water + C_4E_2 system at five different temperatures. The density of the water

+ C_4E_2 mixture increases along with an increase in the mole fraction x of C_4E_2 in the very dilute C_4E_2 region, as shown in the inset of Figure 2. These density data in the very dilute region ($x < 0.09$) of the water + C_4E_2 system are also listed in Table 5. After reaching a maximum, the density then decreases monotonically along with a further increase in the mole fraction x . It should be noted that the peak maximum diminishes and shifts toward a smaller concentration as the temperature increases. This observation is consistent with that of Wicczorek (1996).³¹ A similar behavior of maximum density with composition for dilute ethanol solutions was also observed in the ethanol + water system.³²

It is interesting to note that the variation of density as a function of mole fraction at the very dilute region for the water + C_4E_1 system is different from that for the water + C_4E_2

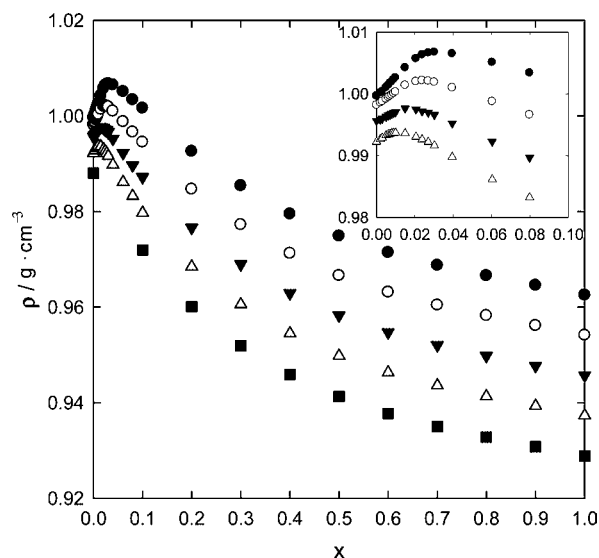


Figure 2. Variation of the density for $(1 - x) \text{H}_2\text{O} + x \text{C}_4\text{E}_2$ at: ●, 283.15 K; ○, 293.15 K; ▼, 303.15 K; △, 313.15 K; ■, 323.15 K.

Table 6. Experimental Densities for the Binary (1 - x) H₂O + x C₆E₂ System at T = (283.15, 288.15, 293.15, 303.15, and 313.15) K

x	T/K				
	283.15	288.15	293.15	303.15	313.15
	$\rho/\text{g}\cdot\text{cm}^{-3}$				
0.00000	0.99970	0.99910	0.99820	0.99565	0.99221
0.00050	0.99968	0.99908	0.99819	0.99564	0.99226
0.00075	0.99967	0.99906	0.99817	0.99559	0.99223
0.00100	0.99966	0.99907	0.99817	0.99558	0.99218
0.00118	0.99970	0.99909	0.99817	0.99557	0.99211
0.00135	0.99976	0.99914	0.99820	0.99558	0.99203
0.00150	0.99984	0.99917	0.99816	0.99551	0.99194
0.00164	0.99986	0.99918	0.99809	a	a
0.00196	0.99987	0.99915	a	a	a
0.00225	0.99988	0.99908	a	a	a
0.01501	0.99590	a	a	a	a
0.01996	0.99471	a	a	a	a
0.02493	0.99353	a	a	a	a
0.03004	0.99245	a	a	a	a
0.03536	0.99113	a	a	a	a
0.03996	0.99010	a	a	a	a
0.04496	0.98911	a	a	a	a
0.05010	0.98812	0.98554	a	a	a
0.05911	0.98643	0.98376	a	a	a
0.06985	0.98469	0.98201	0.97928	a	a
0.07977	0.98320	0.98024	0.97723	a	a
0.08835	0.98202	0.97892	0.97577	a	a
0.09988	0.98051	0.97740	0.97398	a	a
0.13322	0.97663	0.97314	0.96958	0.96238	a
0.20290	0.97018	0.96649	0.96268	0.95504	0.94726
0.28563	0.96436	0.96042	0.95652	0.94866	0.94071
0.35968	0.96018	0.95618	0.95221	0.94422	0.93621
0.45289	0.95583	0.95180	0.94782	0.93982	0.93176
0.54262	0.95240	0.94839	0.94440	0.93642	0.92833
0.67721	0.94833	0.94425	0.94024	0.93225	0.92421
0.82702	0.94513	0.94105	0.93703	0.92905	0.92102
1.00000	0.94209	0.93805	0.93406	0.92608	0.91817

^a The sample falls in two-phase coexistence region.

system. The system water + C₆E₂ was also studied. The experimental results of densities for the water + C₆E₂ system as a function of mole fraction of C₆E₂, x, at temperatures ranging from (283.15 to 313.15) K are given in Table 3. The LCST of the water + C₆E₂ system is 283.94 K.⁹ Hence, there are certain compositions that are in the two-phase coexistence region in Table 6, and thus no density is reported.

Figure 3 shows the variation of density of the water + C₆E₂ system at five different temperatures: (283.15, 288.15, 293.15,

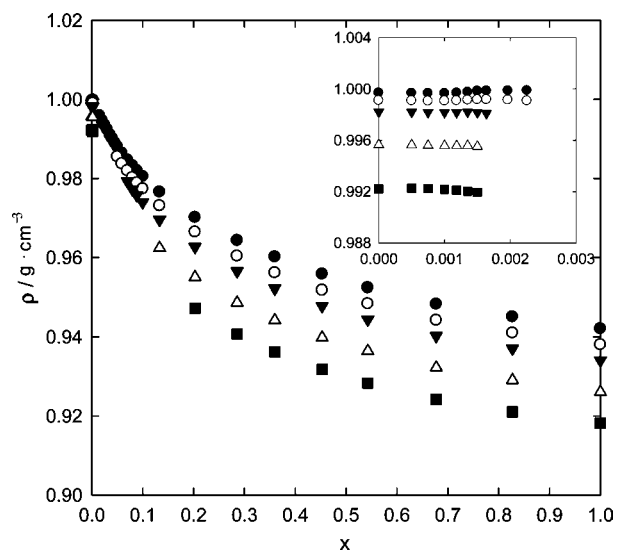


Figure 3. Variation of the density for (1 - x) H₂O + x C₆E₂ at: ●, 283.15 K; ○, 288.15 K; ▼, 293.15 K; △, 303.15 K; ■, 313.15 K.

Table 7. Correlated Results of the Adjustable Parameters and Standard Deviations (σ) of the Redlich–Kister Equation of V_m^E for Three Binary Systems, Water + C₄E₁, + C₄E₂, and + C₆E₂, at Various Temperatures

T	a	b	c	d	σ
K	cm ³ ·mol ⁻¹	cm ³ ·mol ⁻¹	cm ³ ·mol ⁻¹	cm ³ ·mol ⁻¹	cm ³ ·mol ⁻¹
H ₂ O + C ₄ E ₁					
283.15	-2.60640	1.71017	-1.29484	0.76928	0.0085
293.15	-2.47296	1.60346	-1.13305	0.51104	0.0064
303.15	-2.36801	1.55705	-1.00317	0.35452	0.0068
313.15	-2.26177	1.50573	-0.89719	0.19320	0.0070
323.15	-2.17616	1.50576	-0.79855	-0.08819	0.0082
H ₂ O + C ₄ E ₂					
283.15	-3.32905	2.19370	-2.73627	1.17025	0.0131
293.15	-3.20012	2.00491	-2.42647	0.92392	0.0104
303.15	-3.06560	1.86534	-2.14428	0.75645	0.0086
313.15	-2.92463	1.76951	-1.96621	0.54546	0.0076
323.15	-2.78592	1.62764	-1.77972	0.48900	0.0065
H ₂ O + C ₆ E ₂					
283.15	-3.25932	1.84878	-0.87031	0.01605	0.0070
288.15	-3.16767	1.85698	-0.74221	-0.19349	0.0050
293.15	-3.08476	1.78763	-0.61578	-0.20798	0.0063
303.15	-2.93596	1.68911	-0.46363	-0.49361	0.0063
313.15	-2.75008	1.64348	-0.29298	-0.55773	0.0047

Table 8. Correlated Results of the Adjustable Parameters and Standard Deviations (σ) of the Redlich–Kister Equation of the Viscosity Deviations for Two Binary Systems, Water + C₄E₁ and + C₄E₂, at Various Temperatures

T	a	b	c	d	σ
K	mPa·s	mPa·s	mPa·s	mPa·s	mPa·s
H ₂ O + C ₄ E ₁					
283.15	15.64883	-15.25780	14.89720	-10.05377	0.0303
293.15	10.36026	-9.77227	9.87024	-7.00191	0.0240
303.15	7.11436	-6.54793	7.09367	-5.43326	0.0222
313.15	5.03532	-4.46492	5.38131	-4.64798	0.0274
323.15	3.69598	-3.43048	3.65556	-2.60478	0.0103
H ₂ O + C ₄ E ₂					
283.15	30.23531	-31.85409	23.62673	-7.77839	0.0679
293.15	18.98673	-19.22530	15.09837	-5.89514	0.0309
303.15	12.57189	-12.33945	10.30201	-4.79681	0.0160
313.15	8.69193	-8.30557	7.41565	-4.01141	0.0119
323.15	6.22185	-5.82824	5.53845	-3.36133	0.0114

Table 9. Correlated Results of the Adjustable Parameters and Standard Deviations (σ) of the Redlich–Kister Equation of the Refractive Index Deviations for Two Binary Systems, Water + C₄E₁ and + C₄E₂, at Various Temperatures

T/K	a	b	c	d	σ
H ₂ O + C ₄ E ₁					
283.15	0.14706	-0.10891	0.13659	-0.12242	0.0008
293.15	0.14334	-0.10657	0.13205	-0.11874	0.0008
303.15	0.13893	-0.10382	0.12695	-0.11257	0.0008
313.15	0.13428	-0.10034	0.12265	-0.10791	0.0007
323.15	0.13069	-0.10356	0.10132	-0.06593	0.0003
H ₂ O + C ₄ E ₂					
283.15	0.17323	-0.13814	0.19920	-0.18895	0.0014
293.15	0.16878	-0.13516	0.19356	-0.18329	0.0013
303.15	0.16538	-0.13267	0.18855	-0.17898	0.0013
313.15	0.16086	-0.12825	0.18242	-0.17560	0.0013
323.15	0.15553	-0.12422	0.17571	-0.16879	0.0012

303.15, and 313.15) K. The density of the water + C₆E₂ system decreases almost monotonically along with an increase in the mole fraction x, as shown in Figure 3. However, the density remains almost constant at the low concentration region, x < 0.003, as shown in the inset of Figure 3.

The excess molar volume, V_m^E , of the binary H₂O + C_iE_j systems can be calculated from the densities of the pure components and the density of binary mixtures. The experimental results of the excess molar volumes exhibit negative

deviations from the ideal behavior at all of the investigated temperatures.

Viscosity and refractive index deviations of the binary $\text{H}_2\text{O} + \text{C}_i\text{E}_j$ systems can be calculated by

$$\delta y = y - (x \cdot y_{\text{C}_i\text{E}_j}^{\text{pure}} + (1 - x) \cdot y_{\text{H}_2\text{O}}^{\text{pure}}) \quad (2)$$

where δy stands for the mole fraction deviation in the property y , and $y = \eta$ or n_D . Both of the experimental results of the viscosity and refraction index deviations exhibit positive deviations from the ideal behavior at all of the investigated temperatures.

The experimental results of the excess molar volume, viscosity deviation, and refractive index deviation for each temperature were correlated as a function of mole fraction x by the Redlich–Kister equation³³ as the following.

$$\theta = x(1 - x)[a + b(2x - 1) + c(2x - 1)^2 + d(2x - 1)^3] \quad (3)$$

where $\theta = V_m^E$ or δy .

The least-squared regression analysis was applied to correlate the experimental results of the excess molar volume, viscosity deviation, and refractive index deviation to determine the adjustable parameters a , b , c , and d in eq 3. The results of the correlated parameters and fitting coefficients for the excess molar volume, viscosity deviation, and refractive index deviations are given in Tables 7, 8, and 9, respectively. The agreement between the experimental and the calculated deviations (or excess molar volumes) is excellent. Note that all of the density data at the very dilute region (all of the data in the insets of Figures 1, 2, and 3) are not included to perform the least-squared regression analysis to avoid putting too much weight at the very dilute region.

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