Volumetric and Viscometric Properties of Methanol, Ethanol, Propan-2-ol, and 2-Methylpropan-2-ol with a Synthetic C_{6+} Mixture from 298.15 K to 318.15 K

Chein-Hsiun Tu,* Hsu-Chen Ku, Wen-Fang Wang, and Yi-Ting Chou

Department of Applied Chemistry, Providence University, Shalu, 43301 Taiwan

Densities and viscosities were measured for the systems of methanol, ethanol, propan-2-ol, and 2-methylpropan-2-ol separately with a synthetic C_{6+} mixture at temperatures from 298.15 K to 318.15 K and atmospheric pressure. The synthetic C_{6+} is a five-component hydrocarbon mixture. Densities were determined using a vibrating-tube densimeter. Viscosities were measured with an automatic Ubbelohde capillary viscometer. The estimated uncertainties are less than ±0.0004 $g\cdot cm^{-3}$ for density and ±0.8% for viscosity. By considering the six-component mixture as a pseudobinary system, excess volumes and viscosity deviations as a function of mole fraction average were derived, and the computed results were fitted to the Redlich−Kister equation.

Introduction

The reformulation of gasoline includes certain oxygenated compounds such as alcohols and ethers. These are commonly methanol, ethanol, propanol, and butanols, as well as methyl *tert*-butyl ether (MTBE), ethyl *tert*-butyl ether (ETBE), and *tert*-amyl methyl ether (TAME). These oxygenated compounds are added to improve the octane rating and pollution-reducing capability of gasoline, and there is an increasing interest in the thermodynamic behavior of these components in a hydrocarbon mixture.[1−6]

To gain some more understanding of all the phenomena occurring in these mixtures, we measured the densities and viscosities of methanol, ethanol, propan-2-ol, and 2-methylpropan-2-ol separately with a synthetic C_{6+} mixture in the temperature interval of 298.15 K to 318.15 K at atmospheric pressure. The synthetic C_{6+} mixture is used as a simulated gasoline and contains hexane, heptane, 3-methylpentane, methylcyclohexane, and *p*-xylene. By considering the C_{6+} mixture as a pseudopure component, the experimental data are used to calculate excess molar volumes and viscosity deviations from the mole fraction average. These results are used to qualitatively discuss the nature of interactions of the C_{6+} mixtures in the presence of alcohols. The excess quantities have been fitted to the Redlich−Kister equation[7] to estimate the coefficients.

Experimental Section

The chemicals used were of analytical grade and obtained from Fisher, Tedia, and Merck. All alcohols were dried over molecular sieves (Aldrich, 0.3 nm), and all chemicals were used without further purification. The purity of all chemicals was checked by gas chromatography. In all cases chemicals with a purity greater than 99.6 mass % were used for the experimental investigations. The purity of solvents was further ascertained by comparing their densities, viscosities, and refractive indices at 298.15 K, which agreed reasonably with the corresponding literature values[8] (Table 1). Refractive indices, n_D, of pure chemicals were measured with a digital refractometer RX-5000 (ATAGO, Tokyo, Japan), with an uncertainty of ±0.000 01 units.

Solutions of different composition were prepared by mass in a 50-cm^3 Erlenmeyer flask provided with a joint stopper, using a Mettler AB204 balance with an uncertainty of ±0.1 mg. The uncertainty in the mole fraction is 1×10^{-4}. Densities were measured by using a DMA-58 vibrating-tube densimeter (Anton-Paar, Graz, Austria) with a stated uncertainty of ±0.000 02 $g\cdot cm^{-3}$. The temperature in the measuring cell was regulated to ±0.01 K. The uncertainty of the density measurements was less than ±0.0004 $g\cdot cm^{-3}$.

The kinematic viscosities were determined with commercial Ubbelohde capillary viscometers (SCHOTT-GERÄTE, Hofheim, Germany) of 0.36, 0.47, 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 250 s to 600 s. The kinematic viscosity (ν) was then calculated from the following relationship

$$\nu \equiv \eta/\rho = k(t - \theta) \qquad (1)$$

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 constants k for several viscometers were provided by the manufacturer and checked by measurement of the viscosities of pure water, acetone, ethanol, and benzene.[8−11] The value θ, which is dependent on the flow time and the size of capillary, was taken from the tables supplied by the manufacturer. Triplicate measurements of flow times were reproducible within ±0.04%. The uncertainty of the viscosity measurement was less than ±0.8%.

The densities and viscosities of the alcohol + C_{6+} mixtures were measured at temperatures from 298.15 K to 318.15 K and atmospheric pressure. The alcohols

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

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

	ρ/g·cm^{-3}		η/mPa·s		n_D	
	this work	lit.[8]	this work	lit.[8]	this work	lit.[8]
methanol	0.786 68	0.786 37	0.547	0.5513	1.326 85	1.326 52
ethanol	0.785 30	0.784 93	1.087	1.0826	1.359 48	1.359 41
propan-2-ol	0.781 20	0.781 26	2.063	2.0436	1.375 17	1.375 2
2-methylpropan-2-ol	0.780 80	0.781 2	4.432	4.438	1.384 86	1.385 2
3-methylpentane	0.659 60	0.659 76	0.291	0.2942	1.373 99	1.373 86
hexane	0.654 93	0.654 84	0.302	0.307	1.372 51	1.372 26
heptane	0.679 47	0.679 46	0.393	0.3967	1.385 37	1.385 11
methylcyclohexane	0.764 91	0.765 06	0.686	0.685	1.420 96	1.420 58
p-xylene	0.856 54	0.856 61	0.597	0.605	1.493 06	1.493 25

Table 2. Experimental Densities (ρ), Viscosities (η), and Excess Volumes (V^E) for Methanol (1) + C_{6+} (2)

x_1	ρ g·cm^{-3}	η mPa·s	V^E cm^3·mol^{-1}	x_1	ρ g·cm^{-3}	η mPa·s	V^E cm^3·mol^{-1}
298.15 K							
0.0000	0.7304	0.443	0.0000	0.7999	0.7568	0.531	0.3698
0.0507	0.7306	0.442	0.1249	0.8499	0.7616	0.534	0.3289
0.1007	0.7312	0.442	0.1930	0.9000	0.7679	0.538	0.2552
0.1598	0.7320	0.445	0.2488	0.9499	0.7760	0.542	0.1438
0.2004	0.7326	0.447	0.2844	1.0000	0.7866	0.547	0.0000
308.15 K							
0.0000	0.7217	0.400	0.0000	0.5501	0.7327	0.449	0.4811
0.0507	0.7217	0.399	0.1695	0.5999	0.7348	0.456	0.4818
0.1007	0.7222	0.398	0.2464	0.6501	0.7372	0.460	0.4755
0.1598	0.7229	0.398	0.3101	0.7000	0.7400	0.463	0.4627
0.2004	0.7235	0.399	0.3492	0.7499	0.7434	0.464	0.4365
0.2504	0.7244	0.403	0.3797	0.7999	0.7473	0.465	0.4061
0.3003	0.7254	0.409	0.4107	0.8499	0.7522	0.466	0.3550
0.3505	0.7266	0.416	0.4345	0.9000	0.7585	0.467	0.2666
0.4003	0.7279	0.425	0.4472	0.9499	0.7666	0.470	0.1512
0.4504	0.7293	0.435	0.4605	1.0000	0.7772	0.473	0.0000
0.5002	0.7309	0.442	0.4694				
318.15 K							
0.0000	0.7128	0.361	0.0000	0.5501	0.7232	0.406	0.5429
0.0507	0.7126	0.361	0.2027	0.5999	0.7253	0.410	0.5354
0.1007	0.7131	0.359	0.2855	0.6501	0.7277	0.411	0.5219
0.1598	0.7137	0.359	0.3602	0.7000	0.7305	0.411	0.5105
0.2004	0.7143	0.359	0.4068	0.7499	0.7338	0.411	0.4825
0.2504	0.7151	0.361	0.4431	0.7999	0.7377	0.410	0.4463
0.3003	0.7161	0.366	0.4791	0.8499	0.7427	0.410	0.3748
0.3505	0.7172	0.372	0.4998	0.9000	0.7489	0.411	0.2874
0.4003	0.7184	0.381	0.5171	0.9499	0.7569	0.411	0.1643
0.4504	0.7198	0.396	0.5302	1.0000	0.7676	0.413	0.0000
0.5002	0.7214	0.401	0.5359				

Table 3. Experimental Densities (ρ), Viscosities (η), and Excess Volumes (V^E) for Ethanol (1) + C_{6+} (2)

x_1	ρ g·cm^{-3}	η mPa·s	V^E cm^3·mol^{-1}	x_1	ρ g·cm^{-3}	η mPa·s	V^E cm^3·mol^{-1}
298.15 K							
0.0000	0.7304	0.443	0.0000	0.5501	0.7472	0.603	0.3134
0.0502	0.7312	0.444	0.0845	0.6000	0.7498	0.637	0.3031
0.1003	0.7322	0.446	0.1476	0.6500	0.7527	0.671	0.2866
0.1500	0.7331	0.453	0.2192	0.7000	0.7559	0.722	0.2687
0.2002	0.7343	0.473	0.2627	0.7499	0.7594	0.768	0.2427
0.2503	0.7356	0.483	0.2927	0.7999	0.7633	0.815	0.2180
0.3000	0.7372	0.488	0.3072	0.8499	0.7678	0.871	0.1784
0.3500	0.7388	0.506	0.3223	0.9000	0.7728	0.926	0.1298
0.4001	0.7406	0.526	0.3272	0.9497	0.7785	1.004	0.0729
0.4501	0.7427	0.549	0.3261	1.0000	0.7853	1.087	0.0000
0.5000	0.7448	0.578	0.3222				
308.15 K							
0.0000	0.7217	0.400	0.0000	0.5501	0.7381	0.520	0.3722
0.0502	0.7223	0.393	0.1311	0.6000	0.7408	0.547	0.3523
0.1003	0.7232	0.398	0.2012	0.6500	0.7437	0.578	0.3345
0.1500	0.7240	0.402	0.2898	0.7000	0.7470	0.612	0.3978
0.2002	0.7252	0.409	0.3370	0.7499	0.7505	0.640	0.2763
0.2503	0.7265	0.418	0.3669	0.7999	0.7544	0.685	0.2427
0.3000	0.7280	0.430	0.3854	0.8499	0.7589	0.727	0.1956
0.3500	0.7297	0.443	0.3982	0.9000	0.7640	0.779	0.1444
0.4001	0.7315	0.459	0.4006	0.9497	0.7698	0.834	0.0807
0.4501	0.7335	0.480	0.3927	1.0000	0.7766	0.906	0.0000
0.5000	0.7357	0.503	0.3823				
318.15 K							
0.0000	0.7128	0.361	0.0000	0.5501	0.7289	0.457	0.4302
0.0502	0.7132	0.357	0.1641	0.6000	0.7316	0.476	0.4033
0.1003	0.7140	0.358	0.2532	0.6500	0.7345	0.504	0.3791
0.1500	0.7147	0.361	0.3654	0.7000	0.7378	0.526	0.3416
0.2002	0.7159	0.366	0.4119	0.7499	0.7413	0.553	0.3175
0.2503	0.7172	0.373	0.4407	0.7999	0.7453	0.584	0.2721
0.3000	0.7187	0.381	0.4594	0.8499	0.7499	0.620	0.2187
0.3500	0.7204	0.392	0.4707	0.9000	0.7551	0.658	0.1547
0.4001	0.7222	0.404	0.4698	0.9497	0.7610	0.704	0.0836
0.4501	0.7243	0.425	0.4529	1.0000	0.7678	0.761	0.0000
0.5000	0.7265	0.439	0.4421				

investigated were commonly used as additives in gasoline, that is, methanol and ethanol, or have been more extensively tested as possible fuel additive candidates, for example, propan-2-ol and 2-methylpropan-2-ol. The synthetic C_{6+} is a five-component hydrocarbon mixture which was prepared in our laboratory to simulate an unleaded gasoline and consists of 15.0 mol % hexane, 15.1 mol % heptane, 15.1 mol % 3-methylpentane, 41.0 mol % methylcyclohexane, and 13.8 mol % *p*-xylene. This mixture has an average molecular weight of 95.98 and a refractive index of 1.410 26 at 298.15 K. An average of at least three measurements was taken for each composition.

Results and Discussion

By considering the multicomponent mixture as a pseudobinary system consisting of pure component 1 (alcohol) and pseudopure component 2 (C_{6+}), where component 2 is a five-component mixture, the molar excess volumes, V^E, have been calculated from density data according to the equation

$$V^E = (x_1M_1 + x_2M_2)/\rho - (x_1M_1/\rho_1 + x_2M_2/\rho_2) \qquad (2)$$

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 fraction, density, and molecular weight of alcohol and C_{6+}, respectively. The deviation of the viscosity from the mole fraction average is given by

$$\Delta\eta = \eta - (x_1\eta_1 + x_2\eta_2) \qquad (3)$$

where η, η_1, and η_2 are the absolute viscosities of the mixture and the absolute viscosities of alcohol and C_{6+}, respectively. The experimental densities, viscosities, and excess volumes for all of the systems are given in Tables 2−5.

In the system studied, excess molar volumes are positive over the entire mole fraction range and increase with a rise in temperature for all of the mixtures. In the methanol + C_{6+} system there is an immiscibility region observed at 298.15 K. Such a result can also be seen in the work of Orge et al.[3,5] for methanol + *n*-alkane binary mixtures. The experimental V^E values are also graphically represented

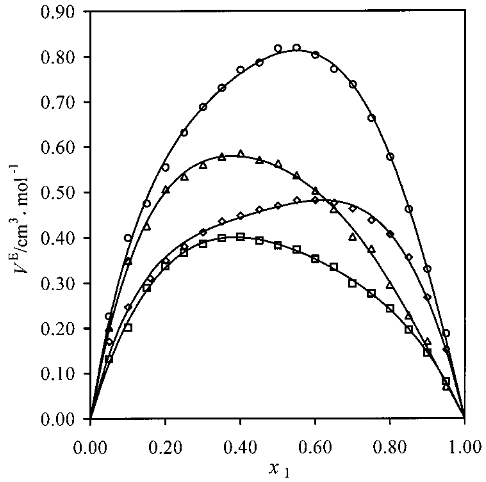

Figure 1. Variation of excess molar volume with mole fraction for alcohol (1) + C_{6+} (2) at 308.15 K: (◇) methanol; (□) ethanol; (△) propan-2-ol; (○) 2-methylpropan-2-ol; (—) Redlich−Kister.

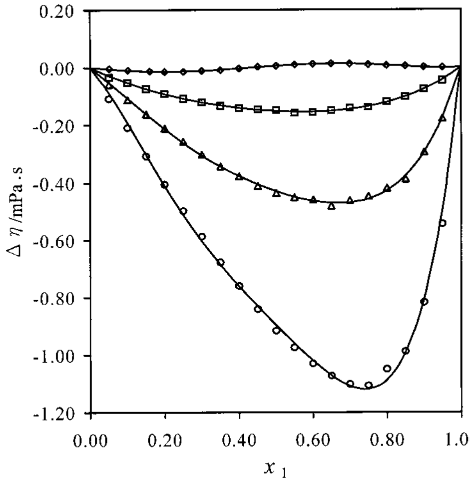

Figure 2. Variation of viscosity deviation with mole fraction for alcohol (1) + C_{6+} (2) at 308.15 K: (◇) methanol; (□) ethanol; (△) propan-2-ol (1); (○) 2-methylpropan-2-ol; (—) Redlich−Kister.

Table 4. Experimental Densities (ρ), Viscosities (η), and Excess Volumes (V^E) for Propan-2-ol (1) + C_{6+} (2)

x_1	ρ	η	V^E	x_1	ρ	η	V^E
	g·cm^{-3}	mPa·s	cm^3·mol^{-1}		g·cm^{-3}	mPa·s	cm^3·mol^{-1}
			298.15 K				
0.0000	0.7304	0.443	0.0000	0.5500	0.7487	0.681	0.4036
0.0500	0.7312	0.445	0.1411	0.6002	0.7514	0.751	0.3774
0.1005	0.7320	0.451	0.2691	0.6496	0.7541	0.817	0.3534
0.1501	0.7332	0.460	0.3408	0.7000	0.7573	0.918	0.3101
0.2001	0.7346	0.480	0.3904	0.7499	0.7606	1.013	0.2664
0.2502	0.7360	0.486	0.4323	0.7995	0.7641	1.133	0.2291
0.3000	0.7378	0.504	0.4480	0.8500	0.7680	1.265	0.1726
0.3500	0.7396	0.527	0.4578	0.9000	0.7720	1.473	0.1318
0.4000	0.7416	0.555	0.4599	0.9499	0.7765	1.742	0.0650
0.4501	0.7438	0.591	0.4427	1.0000	0.7813	2.064	0.0000
0.5000	0.7461	0.632	0.4320				
			308.15 K				
0.0000	0.7217	0.400	0.0000	0.5500	0.7391	0.582	0.5361
0.0500	0.7222	0.397	0.2010	0.6002	0.7419	0.632	0.5023
0.1005	0.7229	0.402	0.3489	0.6496	0.7447	0.666	0.4618
0.1501	0.7241	0.410	0.4247	0.7000	0.7480	0.744	0.4012
0.2001	0.7252	0.418	0.5062	0.7499	0.7512	0.815	0.3742
0.2502	0.7268	0.429	0.5340	0.7995	0.7549	0.900	0.2946
0.3000	0.7285	0.443	0.5595	0.8500	0.7589	0.989	0.2266
0.3500	0.7302	0.460	0.5784	0.9000	0.7631	1.140	0.1690
0.4000	0.7322	0.483	0.5844	0.9499	0.7679	1.314	0.0702
0.4501	0.7344	0.506	0.5702	1.0000	0.7727	1.550	0.0000
0.5000	0.7366	0.539	0.5624				
			318.15 K				
0.0000	0.7128	0.361	0.0000	0.5500	0.7296	0.487	0.6276
0.0500	0.7131	0.358	0.2422	0.6002	0.7324	0.522	0.5827
0.1005	0.7137	0.362	0.4103	0.6496	0.7352	0.557	0.5448
0.1501	0.7148	0.366	0.5036	0.7000	0.7385	0.610	0.4794
0.2001	0.7160	0.373	0.5707	0.7499	0.7419	0.661	0.4121
0.2502	0.7174	0.382	0.6375	0.7995	0.7455	0.728	0.3528
0.3000	0.7190	0.392	0.6687	0.8500	0.7496	0.793	0.2745
0.3500	0.7207	0.404	0.6976	0.9000	0.7538	0.903	0.2018
0.4000	0.7227	0.422	0.6859	0.9499	0.7585	1.019	0.1061
0.4501	0.7249	0.438	0.6709	1.0000	0.7637	1.181	0.0000
0.5000	0.7271	0.461	0.6595				

Table 5. Experimental Densities (ρ), Viscosities (η), and Excess Volumes (V^E) for 2-Methylpropan-2-ol (1) + C_{6+} (2)

x_1	ρ	η	V^E	x_1	ρ	η	V^E
	g·cm^{-3}	mPa·s	cm^3·mol^{-1}		g·cm^{-3}	mPa·s	cm^3·mol^{-1}
			298.15 K				
0.0000	0.7304	0.443	0.0000	0.5500	0.7489	0.773	0.7731
0.0499	0.7311	0.449	0.2025	0.5998	0.7514	0.839	0.7646
0.1000	0.7324	0.463	0.3180	0.6500	0.7541	0.936	0.7354
0.1500	0.7338	0.478	0.3991	0.7000	0.7570	1.061	0.6999
0.2000	0.7353	0.496	0.4752	0.7498	0.7603	1.237	0.6289
0.2501	0.7369	0.519	0.5475	0.8001	0.7638	1.468	0.5402
0.3000	0.7386	0.546	0.6130	0.8500	0.7676	1.791	0.4279
0.3500	0.7404	0.573	0.6628	0.8997	0.7717	2.289	0.2997
0.4002	0.7423	0.606	0.7053	0.9500	0.7761	3.062	0.1645
0.4502	0.7444	0.646	0.7277	1.0000	0.7808	4.432	0.0000
0.5001	0.7465	0.696	0.7611				
			308.15 K				
0.0000	0.7217	0.400	0.0000	0.5500	0.7393	0.644	0.8186
0.0499	0.7223	0.402	0.2264	0.5998	0.7418	0.698	0.8022
0.1000	0.7231	0.411	0.3991	0.6500	0.7445	0.766	0.7715
0.1500	0.7246	0.424	0.4743	0.7000	0.7473	0.848	0.7370
0.2000	0.7260	0.438	0.5548	0.7498	0.7504	0.953	0.6626
0.2501	0.7275	0.456	0.6309	0.8001	0.7538	1.122	0.5764
0.3000	0.7292	0.478	0.6878	0.8500	0.7576	1.293	0.4612
0.3500	0.7310	0.497	0.7303	0.8997	0.7615	1.573	0.3293
0.4002	0.7329	0.525	0.7700	0.9500	0.7658	1.960	0.1867
0.4502	0.7349	0.554	0.7856	1.0000	0.7706	2.614	0.0000
0.5001	0.7370	0.591	0.8171				
			318.15 K				
0.0000	0.7128	0.361	0.0000	0.5500	0.7295	0.548	0.8541
0.0499	0.7130	0.362	0.3003	0.5998	0.7319	0.584	0.8365
0.1000	0.7138	0.368	0.4715	0.6500	0.7345	0.631	0.7991
0.1500	0.7151	0.378	0.5570	0.7000	0.7372	0.688	0.7560
0.2000	0.7164	0.390	0.6508	0.7498	0.7403	0.761	0.6790
0.2501	0.7179	0.403	0.7147	0.8001	0.7436	0.844	0.5862
0.3000	0.7195	0.419	0.7710	0.8500	0.7472	0.955	0.4717
0.3500	0.7213	0.435	0.8002	0.8997	0.7511	1.117	0.3297
0.4002	0.7231	0.455	0.8366	0.9500	0.7552	1.343	0.1854
0.4502	0.7251	0.479	0.8528	1.0000	0.7598	1.699	0.0000
0.5001	0.7271	0.507	0.8704				

as a function of alcohol mole fraction for 308.15 K in Figure 1. The values of V^E at equimolar concentrations follow the order ethanol < methanol < propan-2-ol < 2-methylpropan-2-ol.

The increase in temperature leads to a higher value of $\Delta\eta$ for all of the mixtures. The values of $\Delta\eta$ are almost zero for the system methanol + C_{6+} and are negative for other systems. The experimental values of $\Delta\eta$ for 308.15 K are graphically presented in Figure 2. The $\Delta\eta$ values become more negative with an increase in size of the alcohol molecules. However, sharp maxima are not observed for ethanol or propan-2-ol + C_{6+} mixtures. The values of $\Delta\eta$ at equimolar concentrations follow the order methanol > ethanol > propan-2-ol > 2-methylpropan-2-ol. The temperature dependence of V^E and $\Delta\eta$ at equimolar concentrations for all of the systems studied is shown in Figure 3. It can be seen that the equimolar values of both V^E and $\Delta\eta$ increase as temperature increases for all of the systems.

In the present investigation, alcohols are strongly self-associated through hydrogen bonding, with degrees of association depending on such variables as chain length, the position of the OH group, temperature, and dilution

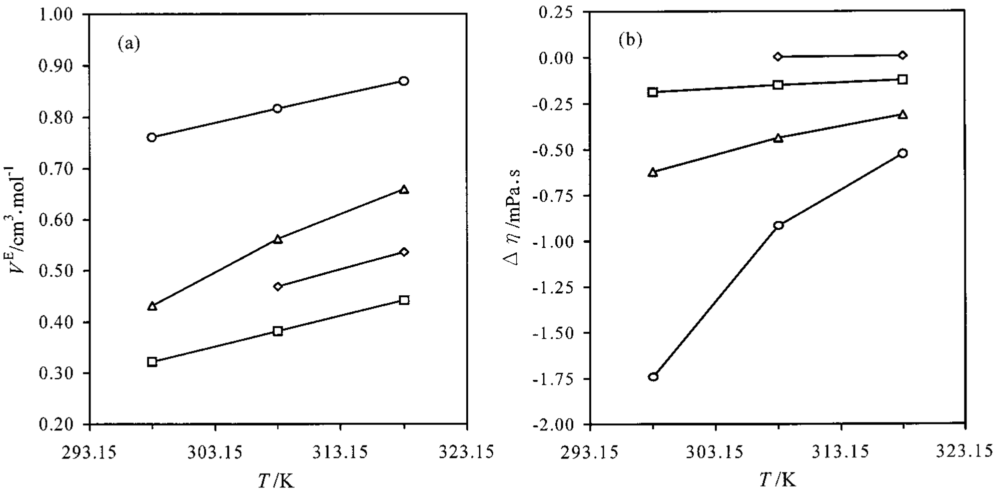

Figure 3. Temperature dependence of excess molar volume (a) and viscosity deviation (b) at equimolar composition ($x = 0.5$) for alcohol (1) + C_{6+} (2): (◇) methanol; (□) ethanol; (△) propan-2-ol; (○) 2-methylpropan-2-ol.

Table 6. Coefficients of the Redlich−Kister Equation and Standard Deviations for V^E and $\Delta\eta$

Y^E/unit	T/K	$a_0 \times 10^2$	$a_1 \times 10^2$	$a_2 \times 10^2$	$a_3 \times 10^2$	σ
		Methanol (1) + C_{6+} (2)				
V^E/cm^3·mol^{-1}	298.15	142.56	−61.94	168.63	36.44	0.0060
	308.15	186.67	−40.43	144.43	39.51	0.0090
	318.15	212.19	−29.72	155.85	45.15	0.0115
$\Delta\eta$/mPa·s	298.15	−1.17	−14.51	−6.57	9.89	0.0002
	308.15	2.00	−16.65	−11.61	14.77	0.0010
	318.15	2.90	−16.84	−11.09	15.94	0.0012
		Ethanol (1) + C_{6+} (2)				
V^E/cm^3·mol^{-1}	298.15	129.33	28.42	50.05	−17.54	0.0037
	308.15	153.61	49.42	71.35	−1.19	0.0050
	318.15	177.65	63.98	94.77	23.70	0.0066
$\Delta\eta$/mPa·s	298.15	−75.39	16.95	−8.91	9.72	0.0043
	308.15	−60.97	13.45	−17.17	−4.86	0.0023
	318.15	−48.85	7.61	−14.71	8.85	0.0015
		Propan-2-ol + C_{6+}				
	298.15	171.25	79.76	64.81	21.57	0.0047
	308.15	221.90	76.18	78.65	78.80	0.0086
	318.15	260.57	101.71	97.01	59.26	0.0104
$\Delta\eta$/mPa·s	298.15	−245.50	131.41	−107.42	91.77	0.0088
	308.15	−171.68	85.98	−80.09	68.03	0.0067
	318.15	−122.92	62.50	−48.52	30.95	0.0044
		2-Methylpropan-2-ol (1) + C_{6+} (2)				
V^E/cm^3·mol^{-1}	298.15	302.64	−74.05	54.60	128.76	0.0092
	308.15	322.34	−49.04	103.29	127.07	0.0108
	318.15	341.62	−19.91	140.80	165.89	0.0143
$\Delta\eta$/mPa·s	298.15	−679.61	529.66	−706.04	646.45	0.0469
	308.15	−358.86	259.95	−304.38	255.69	0.0204
	318.15	−204.73	133.53	−162.58	140.23	0.0100

by other substances. The C_{6+} mixture does not exhibit this property because it has no hydrogen atoms having that ability. The observed V^E or $\Delta\eta$ may be discussed in terms of several opposing effects. Some authors[12−14] explain both the composition and temperature dependence of V^E or $\Delta\eta$ of 1-alkanol + alkane mixtures as a balance between positive contributions (hydrogen bond rupture and dispersive interactions between unlike molecules) and negative contributions (dipole−dipole interactions and geometrical fitting between components). In addition, the dilution of dipoles affects V^E considerably and Marsh[15] showed the evidence of this effect for nitromethane + and nitroethane + each of several nonpolar liquids.

The mixing functions V^E and $\Delta\eta$ were represented mathematically by the following type of the Redlich−Kister equation[1] for correlating the experimental data

$$Y = x_1(1 - x_1)\sum_{i=0}^{3} a_i(2x_1 - 1)^i \tag{4}$$

where Y refers to V^E/cm^3·mol^{-1} or $\Delta\eta$/mPa·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 6. The standard deviation is defined by

$$\sigma = [\sum_{i=1}^{m}(Y_i^{\text{exp}} - Y_i^{\text{calc}})^2/(m - p)]^{1/2} \tag{5}$$

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 0.0037 cm^3·mol^{-1} and 0.0143 cm^3·mol^{-1} and the largest σ value corresponds to a 2-methylpropan-2-ol + C_{6+} mixture at 318.15 K. For the case of $\Delta\eta$, the σ values lie between 0.0002 mPa·s and 0.0469 mPa·s and the largest σ value corresponds to a 2-methylpropan-2-ol + C_{6+} mixture at 298.15 K.

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