Density and Viscosity Studies of Binary Mixtures of Acetonitrile with Methanol, Ethanol, Propan-1-ol, Propan-2-ol, Butan-1-ol, 2-Methylpropan-1-ol, and 2-Methylpropan-2-ol at (298.15, 303.15, 308.15, and 313.15) K

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Densities and viscosities have been measured for the binary mixtures of acetonitrile with linear and brached alkanols (C_1-C_4) over the entire composition range at (298.15, 303.15, 308.15, and 313.15) K. The experimental density (ρ) and viscosity (η) values were used to calculate the excess molar volume (V^E) and viscosity deviation ($\Delta\eta$). The effects of chain length and branching of alkanols on V^E and $\Delta\eta$ values have been discussed. The V^E and $\Delta\eta$ values are fitted to a Redlich−Kister equation.

Introduction

The thermodynamic and transport properties of liquid and liquid mixtures (Kim and Marsh, 1988) have been used to understand the molecular interactions between the components of the mixture and also for engineering applications concerning heat transfer, mass transfer, and fluid flow. The density and viscosity data of binary liquid mixtures are important from practical and theoretical points of view, to understand liquid theory. Acetonitrile, alkanols, and their binary mixtures find applications as solvent in chemistry and modern technology (Barthel et al., 1983). A survey of the literature shows that there are very few reports on the density and viscosity measurements of acetonitrile + alkanols (Sandhu et al., 1986, Paez and Contreras 1989; Saha et al.; 1995). We present here results of V^E and $\Delta\eta$ for binary mixtures of acetonitrile with alkanols (C_1-C_4) at various temperatures.

Experimental Section

Even though the purity of the substance is not a crucial factor in V^E measurements, it is very important for viscosity measurements. Therefore, all chemicals were used after purification. Acetonitrile (E. Merck, India, 99.5% pure) was treated with saturated aqueous solution of sodium carbonate and subsequently disilled over P_2O_5. Water was removed by azeotropic distillation, which improved the purity of acetonitrile slightly. The final purification was obtained by fractional distillation (Riddick et al., 1986). Alkanols (E. Merck, India, 99.7% pure) were dried by refluxing over fused calcium oxide for 5 h and then distilled fractionally two to three times (Riddick et al., 1986). Purity of the solvents (>99.7%) after purification was ascertained by GLC and constancy of their boiling temperatures during final distillations and also by comparing their densities and viscosities with the corresponding literature values at 298.15, 303.15, 308.15, and 313.15 K (Table 1). The procedure adopted for preparation of binary liquid mixtures is same as reported earlier (Nikam et al., 1997). Mixtures of acetonitrile with alkanols were prepared by mass, using a Mettler balance (Switzerland, model AE-240), in airtight stoppered glass bottles with a precision of ±0.01 mg, and every care was taken to avoid evaporation and contamination during the mixing process. The possible error in mole fraction is estimated to be less than 1×10^{-4}.

A double-arm pycnometer with a bulb of 15 cm^3 and a capillary of an internal diameter of about 1 mm was used to measure densities, (ρ), of binary liquid mixtures (Nikam and Sawant, 1997). The pycnometer was calibrated by using conductivity water (conductivity less than 1×10^{-6}) with 0.997 05, 0.995 65, 0.994 03, and 0.992 21 g·cm^{-3} as its densities at 298.15, 303.15, 308.15, and 313.15 K (Riddick et al., 1986), respectively. The pycnometer filled with air bubble free liquids was kept in a transparent-walled bath with a thermal stability of ±0.01 K, as checked by means of a calibrated thermometer, for 10−15 min to attain thermal equilibrium. The density values were reproducible within $\pm 5 \times 10^{-5}$ g·cm^{-3}.

The viscosity of the binary liquid mixtures was measured using a suspended level Ubbelohde viscometer (capacity 30 cm^3), calibrated with conductivity water using 0.8902, 0.7972, 0.7190, and 0.6526 mPa.s as its viscosities at 298.15, 303.15, 308.15, and 313.15K (Riddick et al., 1986), respectively. A thoroughly cleaned and perfectly dried viscometer, filled with experimental liquid, was placed exactly vertical in a trasparent water thermostat having thermal stability of ±0.01 K. After thermal stability was attained, the flow times of the liquids were recorded with a digital stopwatch correct to ±0.01 s. At least three repetitions of each data set reproducible to ±0.05 s were obtained, and the results were averaged. Since all flow times were greater than 300 s, and capillary radius (0.5 mm) was far less than its length (50−60 mm), the kinetic energy and end corrections, respectively, were found to be negligible. The viscosity, η, of the liquids was calcuated by

$$\frac{\eta}{\eta_w} = \frac{\rho \cdot t}{\rho_w \cdot t_w} \tag{1}$$

where ρ, ρ_w and t, t_w refer to the density and flow times of the experimental liquids and water, respectively. The accuracy in the viscosity measurements was ±0.1%.

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Table 1. Comparison of Densities (ρ) and Viscosities (η) of Pure Liquids at Different Temperatures

	$\rho \times 10^{-3}$/(kg·m^{-3})		η/(mPa·s)		$\rho \times 10^{-3}$/(kg·m^{-3})		η/(mPa·s)	
liquid	exptl	lit.	exptl	lit.	exptl	lit.	exptl	lit
		298.15 K				303.15 K		
methanol	0.786 66	0.786 37[a]	0.554	0.5513[a]	0.781 96	0.781 70[a]	0.515	0.5143[a]
		0.786 64[b]		0.553[b]		0.781 96[b]		0.5136[b]
		308.15 K				313.15 K		
	0.777 71	0.777 03[a]	0.482	0.476[a]	0.772 21	0.772 36[a]	0.452	0.448[a]
				0.4793[b]		0.772 6[b]		0.4481[b]
		298.15 K				303.15 K		
ethanol	0.784 97	0.784 93[a]	1.083	1.0826[a]	0.780 68	0.780 66[a]	0.987	0.987[a,b]
		0.785 09[b]		1.0826[b]		0.780 8[b]		
		308.15 K				313.15 K		
	0.776 41	0.776 39[a]	0.893	0.903[a]	0.772 13	0.772 12[a]	0.814	0.823[a]
				0.902[b]		0.772 1[b]		0.826[b]
		298.15 K				303.15 K		
propan-1-ol	0.799 58	0.799 60[a]	1.967	1.943[a]	0.795 48	0.795 65[a]	1.705	1.725[a,b]
		0.799 75[b]		1.9430[b]		0.795 7[b]		
		308.15 K				313.15 K		
	0.791 38	0.791 58[a]	1.500	1.463[a]	0.787 37	0.788 69[a]	1.336	1.314[a]
				1.537[b]		0.7883[b]		1.340[b]
		298.15 K				303.15 K		
propan-2-ol	0.781 23	0.781 26[a]	2.052	2.0436[a]	0.776 95	0.777 16[a]	1.779	1.767[a]
		308.15 K				313.15 K		
	0.772 46	0.773 06[a]	1.542	1.5405[a]	0.767 98	0.768 96[a]	1.336	1.3143[a]
				1.536[b]		0.7683[b]		1.340[b]
		298.15 K				303.15 K		
butan-1-ol	0.805 76	0.805 75[a]	2.571	2.571[a,b]	0.802 01	0.801 95[a]	2.271	2.271[a]
		0.806 0[b]				0.802 2[b]		2.263[b]
		308.15 K				313.15 K		
	0.798 21	0.798 15[a]	1.981	2.1885[a]	0.794 32	0.794 35[a]	1.692	1.8898[a]
				2.000[b]		0.7946[b]		1.7734[b]
		298.15 K				303.15 K		
2-methylpropan-1-ol	0.798 30	0.797 80[a]	3.332	3.333[a,b]	0.794 31	0.794 00[a]	2.842	3.2835[a]
		0.798 2[b]				0.793 8[b]		2.8466[b]
		308.15 K				313.15 K		
	0.790 26	0.790 20[a]	2.426	2.7210[a]	0.786 13	0.786 40[a]	2.080	2.2500[a]
				2.445[b]		0.785 8[b]		2.112[b]
		298.15 K				303.15 K		
2-methylpropan-2-ol	0.781 14	0.781 20[a]	4.439	4.438[a,b]	0.775 51	0.774 5[a]	3.378	3.378[a]
		0.781 2[b]				0.775 70[b]		3.390[b]
		308.15 K				313.15 K		
	0.770 46	0.770 24[a]	2.589	2.9397[a]	0.765 01	0.764 96[a]	2.047	2.237[a]
				2.644[b]		0.764 9[b]		2.1037[b]
		298.15 K				303.15 K		
acetonitrile	0.776 2	0.776 49[a]	0.342	0.341[a]	0.770 80	0.771 25[a]	0.326	0.324[a]
								0.328[c]
		308.15 K				313.15 K		
	0.765 18	0.765 86[a]	0.306	0.314[c]	0.759 42	0.760 47[a]	0.291	0.2974[d]

[a] Riddick et al. (1986). [b] TRC Tables (1996). [c] Moumouzias and Ritzoutis (1996). [d] Paze and Contreras (1989).

Results and Discussion

The experimental density (ρ) values given in Table 2 have been used to calculate the excess molar volume, V^E, using the following equation

$$V^E/(\text{cm}^3\cdot\text{mol}^{-1}) = \frac{M_1x_1 + M_2x_2}{\rho_{mix}} - \frac{M_1x_1}{\rho_1} - \frac{M_2x_2}{\rho_2} \quad (2)$$

where ρ_{mix} is the density of the mixture and M_1, M_2, x_1, x_2, ρ_1, ρ_2 are the molecular weight, mole fraction, and density of pure components 1 and 2, respectively. Excess volumes calculated from eq 2 are listed in Table 2. The results of V^E were fitted to a polynomial of the type

$$V^E/(\text{cm}^3\cdot\text{mol}^{-1}) = x_1x_2\sum_{i=0}^{m} a_i(x_2 - x_1)^i \quad (3)$$

where m is the number of coefficients a_i. In each case, the optimum number of coefficients is ascertained from an examination of the variation in standard deviation, σ, as given by

$$\sigma = [\sum(X_{obs} - X_{cal})^2/(n - m)]^{1/2} \quad (4)$$

where n is the total number of data points and m is the number of coefficients considered. The coefficients and standard deviation for V^E as computed from eqs 3 and 4, respectively, are presented in Table 3.

The viscosity deviations, $\Delta\eta$, are obtained by

$$\Delta\eta = \eta_{mix} - x_1\eta_1 - x_2\eta_2 \quad (5)$$

where η_{mix} is the viscosity of the mixture and x_1, x_2 and η_1, η_2 are the mole fraction and viscosity of pure components 1 and 2, respectively.

The coefficients, a_i, and standard deviation, σ, for $\Delta\eta$ as obtained from equations similar to eqs 3 and 4 are listed in Table 3. A comparison is made of observed excess molar volumes of acetonitrile with methanol, ethanol, propan-1-

Table 2. Density, ρ, Viscosity, η, and Excess Molar Volumes, V^E, for Acetonitrile (1) + Alkanols (2) at T = (298.15, 303.15, 308.15, and 313.15 K)

x_1	$\rho \times 10^{-3}$/(kg·m^{-3})	V^E/(cm^3·mol^{-1})	η/(mPa·s)	x_1	$\rho \times 10^{-3}$/(kg·m^{-3})	V^E/(cm^3·mol^{-1})	η/(mPa·s)	x_1	$\rho \times 10^{-3}$/(kg·m^{-3})	V^E/(cm^3·mol^{-1})	η/(mPa·s)
Acetonitrile (1) + Methanol (2)											
298.15 K											
0.0000	0.786 66		0.554	0.3423	0.785 34	−0.165	0.394	0.7574	0.779 68	−0.089	0.344
0.0798	0.786 59	−0.052	0.504	0.4384	0.784 17	−0.162	0.373	0.8754	0.777 95	−0.046	0.343
0.1633	0.786 48	−0.105	0.462	0.5393	0.782 85	−0.150	0.359	1.0000	0.776 22		0.342
0.2507	0.786 06	−0.143	0.424	0.6455	0.781 33	−0.125	0.349				
303.15 K											
0.0000	0.781 96		0.515	0.3423	0.780 05	−0.150	0.370	0.7574	0.774 21	−0.078	0.328
0.0798	0.781 78	−0.051	0.470	0.4384	0.778 85	−0.149	0.351	0.8754	0.772 54	−0.043	0.326
0.1633	0.781 46	−0.097	0.432	0.5393	0.777 43	−0.135	0.338	1.0000	0.770 80		0.326
0.2507	0.780 94	−0.133	0.398	0.6455	0.775 81	−0.107	0.329				
308.15 K											
0.0000	0.777 71		0.482	0.3423	0.774 63	−0.137	0.348	0.7574	0.768 60	−0.070	0.308
0.0798	0.776 70	−0.044	0.440	0.4384	0.773 34	−0.135	0.330	0.8754	0.766 90	−0.037	0.307
0.1633	0.776 28	−0.088	0.404	0.5393	0.771 84	−0.120	0.318	1.0000	0.765 18		0.306
0.2507	0.775 73	−0.128	0.373	0.6455	0.770 29	−0.100	0.312				
313.15 K											
0.0000	0.772 21		0.452	0.3423	0.769 14	−0.125	0.330	0.7574	0.762 92	−0.065	0.293
0.0798	0.771 71	−0.044	0.416	0.4384	0.767 80	−0.125	0.314	0.8754	0.761 18	−0.034	0.292
0.1633	0.771 03	−0.080	0.384	0.5393	0.766 27	−0.112	0.304	1.0000	0.759 42		0.291
0.2507	0.770 22	−0.110	0.354	0.6455	0.764 68	−0.095	0.297				
Acetonitrile (1) + Ethanol (2)											
298.15 K											
0.0000	0.784 97		1.083	0.4279	0.780 61	0.060	0.506	0.8179	0.777 00	0.066	0.370
0.1107	0.783 86	0.017	0.850	0.5288	0.779 57	0.071	0.458	0.9099	0.776 54	0.038	0.354
0.2192	0.782 76	0.032	0.693	0.6267	0.778 57	0.080	0.414	1.0000	0.776 22		0.342
0.3249	0.781 69	0.046	0.584	0.7236	0.777 62	0.084	0.392				
303.15 K											
0.0000	0.780 68		0.987	0.4279	0.775 64	0.077	0.473	0.8179	0.771 61	0.081	0.349
0.1107	0.779 39	0.022	0.779	0.5288	0.774 48	0.089	0.428	0.9099	0.771 11	0.046	0.336
0.2192	0.778 09	0.044	0.642	0.6267	0.773 39	0.096	0.391	1.0000	0.770 80		0.326
0.3249	0.776 85	0.062	0.545	0.7236	0.772 39	0.096	0.366				
308.15 K											
0.0000	0.776 41		0.893	0.4279	0.770 53	0.100	0.444	0.8179	0.766 00	0.099	0.333
0.1107	0.774 66	0.046	0.715	0.5288	0.769 27	0.109	0.405	0.9099	0.765 51	0.055	0.317
0.2192	0.773 27	0.065	0.589	0.6267	0.768 07	0.114	0.377	1.0000	0.765 18		0.306
0.3249	0.771 88	0.084	0.499	0.7236	0.766 92	0.115	0.347				
313.15 K											
0.0000	0.772 13		0.814	0.4279	0.765 38	0.127	0.417	0.8179	0.760 39	0.111	0.316
0.1107	0.769 93	0.070	0.656	0.5288	0.763 96	0.131	0.380	0.9099	0.759 73	0.068	0.301
0.2192	0.768 37	0.090	0.542	0.6267	0.762 63	0.135	0.352	1.0000	0.759 42		0.291
0.3249	0.766 81	0.110	0.467	0.7236	0.761 37	0.133	0.331				
Acetonitrile (1) + Propan-1-ol (2)											
298.15 K											
0.0000	0.799 58		1.967	0.4939	0.789 35	0.058	0.615	0.8539	0.780 39	0.029	0.391
0.1388	0.796 94	0.024	1.295	0.5945	0.786 97	0.059	0.522	0.9294	0.778 26	0.016	0.365
0.2787	0.794 08	0.044	0.922	0.6887	0.784 70	0.050	0.463	1.0000	0.776 22		0.342
0.3856	0.781 79	0.053	0.747	0.7735	0.782 53	0.041	0.421				
303.15 K											
0.0000	0.795 48		1.705	0.4939	0.784 44	0.081	0.574	0.8539	0.775 07	0.040	0.374
0.1388	0.792 64	0.029	1.166	0.5945	0.781 90	0.083	0.498	0.9294	0.772 86	0.024	0.352
0.2787	0.789 57	0.055	0.842	0.6887	0.779 50	0.073	0.436	1.0000	0.770 80		0.326
0.3856	0.787 08	0.071	0.695	0.7735	0.777 26	0.059	0.399				
308.15 K											
0.0000	0.791 38		1.500	0.4939	0.779 38	0.109	0.530	0.8539	0.769 61	0.050	0.355
0.1388	0.788 22	0.044	1.053	0.5945	0.776 77	0.103	0.465	0.9294	0.767 33	0.028	0.334
0.2787	0.784 88	0.078	0.769	0.6887	0.774 24	0.091	0.413	1.0000	0.765 18		0.306
0.3856	0.782 18	0.099	0.634	0.7735	0.771 89	0.074	0.380				
313.15 K											
0.0000	0.787 37		1.382	0.4939	0.774 36	0.134	0.496	0.8539	0.764 08	0.058	0.341
0.1388	0.783 74	0.072	0.983	0.5945	0.771 61	0.124	0.433	0.9294	0.761 66	0.034	0.320
0.2787	0.780 10	0.114	0.706	0.6887	0.768 94	0.108	0.390	1.0000	0.759 42		0.291
0.3856	0.777 31	0.127	0.587	0.7735	0.766 51	0.084	0.362				
Acetonitrile (1) + Propan-2-ol (2)											
298.15 K											
0.0000	0.781 23		2.052	0.4939	0.777 35	0.156	0.541	0.8541	0.776 26	0.070	0.343
0.1399	0.780 08	0.061	1.254	0.5942	0.776 70	0.163	0.482	0.9295	0.776 23	0.034	0.342
0.2679	0.779 14	0.098	0.846	0.6871	0.776 32	0.148	0.419	1.0000	0.776 22		0.342
0.3855	0.778 20	0.132	0.660	0.7736	0.776 29	0.107	0.372				

Table 2 (Continued)

x_1	$\rho \times 10^{-3}$/(kg·m^{-3})	V^E/(cm^3·mol^{-1})	η/(mPa·s)	x_1	$\rho \times 10^{-3}$/(kg·m^{-3})	V^E/(cm^3·mol^{-1})	η/(mPa·s)	x_1	$\rho \times 10^{-3}$/(kg·m^{-3})	V^E/(cm^3·mol^{-1})	η/(mPa·s)
					303.15 K						
0.0000	0.776 95		1.779	0.4939	0.772 34	0.181	0.502	0.8541	0.770 88	0.084	0.327
0.1399	0.775 65	0.065	1.114	0.5942	0.771 48	0.195	0.450	0.9295	0.770 84	0.041	0.326
0.2679	0.774 51	0.110	0.758	0.6871	0.770 95	0.181	0.394	1.0000	0.770 80		0.326
0.3855	0.773 37	0.152	0.599	0.7736	0.770 92	0.131	0.356				
					308.15 K						
0.0000	0.772 46		1.542	0.4939	0.767 14	0.205	0.465	0.8541	0.765 26	0.102	0.311
0.1399	0.770 94	0.076	0.995	0.5942	0.766 13	0.221	0.417	0.9295	0.765 20	0.051	0.309
0.2679	0.769 60	0.129	0.687	0.6871	0.765 44	0.211	0.370	1.0000	0.765 18		0.306
0.3855	0.768 25	0.179	0.546	0.7736	0.765 27	0.161	0.331				
					313.15 K						
0.0000	0.767 98		1.336	0.4939	0.761 81	0.237	0.427	0.8541	0.759 54	0.120	0.296
0.1399	0.766 16	0.093	0.889	0.5942	0.760 73	0.247	0.389	0.9295	0.759 46	0.059	0.294
0.2679	0.764 61	0.154	0.623	0.6871	0.759 98	0.230	0.348	1.0000	0.759 42		0.291
0.3855	0.763 11	0.206	0.500	0.7736	0.759 64	0.182	0.317				
					Acetonitrile (1) + Butan-1-ol (2)						
					298.15 K						
0.0000	0.805 76		2.571	0.5462	0.792 69	0.088	0.605	0.8784	0.781 42	0.039	0.387
0.1671	0.802 31	0.042	1.475	0.6436	0.789 69	0.087	0.484	0.9420	0.778 80	0.020	0.348
0.3110	0.799 01	0.066	1.029	0.7303	0.786 76	0.082	0.441	1.0000	0.776 22		0.342
0.4362	0.795 77	0.084	0.770	0.8082	0.783 99	0.066	0.403				
					303.15 K						
0.0000	0.802 01		2.271	0.5462	0.787 95	0.115	0.566	0.8784	0.776 15	0.052	0.367
0.1671	0.798 28	0.053	1.336	0.6436	0.784 81	0.110	0.457	0.9420	0.773 46	0.025	0.327
0.3110	0.794 69	0.089	0.937	0.7303	0.781 79	0.098	0.408	1.0000	0.770 80		0.326
0.4362	0.791 23	0.110	0.706	0.8082	0.778 90	0.078	0.381				
					308.15 K						
0.0000	0.798 21		1.981	0.5462	0.783 04	0.148	0.535	0.8784	0.770 65	0.069	0.347
0.1671	0.794 14	0.070	1.204	0.6436	0.779 67	0.145	0.431	0.9420	0.767 89	0.034	0.314
0.3110	0.790 21	0.119	0.849	0.7303	0.776 50	0.129	0.391	1.0000	0.765 18		0.306
0.4362	0.786 55	0.140	0.650	0.8082	0.773 55	0.099	0.361				
					313.15 K						
0.0000	0.794 32		1.692	0.5462	0.777 98	0.185	0.487	0.8784	0.765 05	0.085	0.332
0.1671	0.789 78	0.100	1.071	0.6436	0.774 48	0.176	0.423	0.9420	0.762 16	0.045	0.301
0.3110	0.785 53	0.161	0.777	0.7303	0.771 16	0.155	0.384	1.0000	0.759 42		0.291
0.4362	0.781 67	0.180	0.598	0.8082	0.768 00	0.125	0.346				
					Acetonitrile (1) + 2-Methylpropan-1-ol (2)						
					298.15 K						
0.0000	0.798 30		3.332	0.5476	0.787 81	0.133	0.692	0.8784	0.779 86	0.050	0.395
0.1676	0.795 46	0.062	1.788	0.6442	0.785 62	0.126	0.567	0.9420	0.778 07	0.022	0.371
0.3118	0.792 77	0.102	1.186	0.7304	0.783 55	0.110	0.483	1.0000	0.776 22		0.342
0.4373	0.790 20	0.126	0.870	0.8083	0.781 70	0.078	0.434				
					303.15 K						
0.0000	0.794 31		2.842	0.5476	0.783 05	0.151	0.634	0.8784	0.774 59	0.060	0.376
0.1676	0.791 20	0.075	1.582	0.6442	0.780 78	0.137	0.532	0.9420	0.772 72	0.026	0.362
0.3118	0.788 29	0.122	1.064	0.7304	0.778 55	0.122	0.455	1.0000	0.770 80		0.326
0.4373	0.785 54	0.149	0.793	0.8083	0.776 58	0.088	0.411				
					308.15 K						
0.0000	0.790 26		2.426	0.5476	0.778 16	0.170	0.586	0.8784	0.769 15	0.070	0.358
0.1676	0.796 90	0.085	1.389	0.6442	0.775 73	0.155	0.494	0.9420	0.767 20	0.030	0.344
0.3118	0.783 72	0.143	0.962	0.7304	0.773 39	0.136	0.428	1.0000	0.765 18		0.306
0.4373	0.780 78	0.172	0.725	0.8083	0.771 27	0.100	0.390				
					313.15 K						
0.0000	0.786 13		2.080	0.5476	0.773 17	0.189	0.548	0.8784	0.763 64	0.075	0.342
0.1676	0.782 47	0.100	1.232	0.6442	0.770 50	0.180	0.461	0.9420	0.761 57	0.032	0.324
0.3118	0.779 10	0.160	0.869	0.7304	0.768 01	0.158	0.405	1.0000	0.759 42		0.291
0.4373	0.775 97	0.190	0.664	0.8083	0.765 79	0.177	0.373				
					Acetonitrile (1) + 2-Methylpropan-2-ol (2)						
					298.15 K						
0.0000	0.781 14		4.439	0.5471	0.777 15	0.186	0.660	0.8784	0.776 29	0.068	0.394
0.1675	0.779 42	0.138	1.925	0.6446	0.776 84	0.160	0.552	0.9421	0.776 25	0.033	0.376
0.3117	0.778 20	0.205	1.187	0.7300	0.776 63	0.128	0.476	1.0000	0.776 22		0.342
0.4368	0.777 58	0.204	0.863	0.8084	0.776 37	0.103	0.428				
					303.15 K						
0.0000	0.775 51		3.378	0.5471	0.771 47	0.201	0.604	0.8784	0.770 87	0.066	0.375
0.1675	0.773 70	0.153	1.606	0.6446	0.771 17	0.175	0.511	0.9421	0.770 83	0.032	0.359
0.3117	0.772 47	0.223	1.035	0.7300	0.771 01	0.140	0.446	1.0000	0.770 80		0.326
0.4368	0.771 86	0.223	0.756	0.8084	0.770 95	0.100	0.404				

Table 2 (Continued)

x_1	$\rho \times 10^{-3}$/(kg·m^{-3})	V^E/(cm^3·mol^{-1})	η/(mPa·s)	x_1	$\rho \times 10^{-3}$/(kg·m^{-3})	V^E/(cm^3·mol^{-1})	η/(mPa·s)	x_1	$\rho \times 10^{-3}$/(kg·m^{-3})	V^E/(cm^3·mol^{-1})	η/(mPa·s)
					308.15 K						
0.0000	0.770 46		2.589	0.5471	0.765 88	0.234	0.553	0.8784	0.765 25	0.055	0.357
0.1675	0.768 48	0.168	1.359	0.6446	0.765 54	0.204	0.474	0.9421	0.765 21	0.036	0.342
0.3117	0.767 13	0.245	0.909	0.7300	0.765 39	0.161	0.418	1.0000	0.765 18		0.306
0.4368	0.766 40	0.250	0.680	0.8084	0.765 33	0.115	0.382				
					313.15 K						
0.0000	0.765 01		2.047	0.5471	0.760 08	0.259	0.509	0.8784	0.759 49	0.081	0.340
0.1675	0.762 87	0.185	1.158	0.6446	0.759 72	0.226	0.442	0.9421	0.759 45	0.039	0.330
0.3117	0.761 44	0.268	0.805	0.7300	0.759 63	0.174	0.394	1.0000	0.759 42		0.291
0.4368	0.760 66	0.274	0.615	0.8084	0.759 57	0.124	0.362				

Table 3. Parameters and Standard Deviations, σ, of Eqs 3 and 4 for Acetonitrile + Alkanols

system		temp/K	a_0	a_1	a_2	a_3	a_4	a_5	σ
acetonitrile + methanol	V^E/(cm^3·mol^{-1})	298.15	−0.6384	0.3374	0.0932	−0.2396			0.0030
		303.15	−0.5684	0.3414	0.0281	−0.2374			0.0011
		308.15	−0.5239	0.3493	0.0591	−0.2835			0.0042
		313.15	−0.4800	0.2463	0.0448	−0.0999			0.0017
	$\Delta\eta$/(mPa·s)	298.15	−0.3382	0.1427	0.0077	−0.0086			0.0011
		303.15	−0.3140	0.1283	0.0178	−0.0042			0.0007
		308.15	−0.2871	0.1279	0.0094	−0.0161			0.0007
		313.15	−0.2593	0.1203	0.0346	−0.0630			0.0009
acetonitrile + ethanol	V^E/(cm^3·mol^{-1})	298.15	0.2826	0.2623	0.0639	−0.1302			0.0026
		303.15	0.3526	0.2502	0.0727	−0.0614			0.0024
		308.15	0.4288	0.2719	0.2355	−0.2247			0.0039
		313.15	0.5070	0.2231	0.4080	−0.2514			0.0030
	$\Delta\eta$/(mPa·s)	298.15	−0.9727	0.5108	−0.2173	0.0592			0.0026
		303.15	−0.8660	0.4041	−0.2066	0.1255			0.0021
		308.15	−0.7466	0.4386	−0.1519	−0.0649			0.0029
		313.15	−0.6557	0.3943	−0.1426	−0.0604			0.0018
acetonitrile + propan-1-ol	V^E/(cm^3·mol^{-1})	298.15	0.2338	0.0155	−0.0289	0.0212			0.0016
		303.15	0.3214	0.0557	−0.0573	0.0363			0.0024
		308.15	0.4253	0.0159	−0.0672	0.0425			0.0020
		313.15	0.5237	−0.1058	0.0394	0.0616			0.0029
	$\Delta\eta$/(mPa·s)	298.15	−2.1786	1.2510	−0.8416	0.5497			0.0026
		303.15	−1.7885	0.9575	−0.5281	0.4173			0.0041
		308.15	−1.5127	0.8247	−0.3074	0.2387			0.0031
		313.15	−1.4060	0.8091	−0.1211	0.0846			0.0067
acetonitrile + propan-2-ol	V^E/(cm^3·mol^{-1})	298.15	0.6213	0.2197	−0.1586	−0.3113			0.0048
		303.15	0.7336	0.3310	−0.2223	−0.4067			0.0058
		308.15	0.8451	0.3959	−0.1968	−0.4548			0.0054
		313.15	0.9572	0.3764	−0.1574	−0.4405			0.0024
	$\Delta\eta$/(mPa·s)	298.15	−2.6382	1.7568	−1.2686	0.2933			0.0095
		303.15	−2.2318	1.5067	−0.9927	0.1001			0.0097
		308.15	−1.8767	1.2407	−0.7153	−0.0079			0.0096
		313.15	−1.5740	1.0381	−0.4900	−0.1280			0.0084
acetonitrile + butan-1-ol	V^E/(cm^3·mol^{-1})	298.15	0.3526	0.1538	−0.0010	−0.1841			0.0030
		303.15	0.4591	0.1236	−0.0491	−0.0960			0.0015
		308.15	0.5954	0.1421	−0.0429	−0.0886			0.0024
		313.15	0.7498	0.0537	0.0226	0.0056			0.0027
	$\Delta\eta$/(mPa·s)	298.15	−3.1558	1.2269	−1.2857	3.6089	0.0182	−3.0874	0.0093
		303.15	−2.7308	0.9664	−1.2511	3.7764	0.6637	−4.0668	0.0073
		308.15	−2.2384	0.8314	−1.4876	3.1652	1.5633	−3.8880	0.0061
		313.15	−1.8970	1.5628	1.0611	−5.2485	−3.3131	9.2771	0.0082
acetonitrile + 2-methylpropan-1-ol	V^E/(cm^3·mol^{-1})	298.15	0.5306	0.1309	−0.1347	−0.2071			0.0017
		303.15	0.6079	0.0766	−0.1283	−0.1325			0.0028
		308.15	0.6960	0.0495	−0.1582	−0.0710			0.0034
		313.15	0.7797	0.1291	−0.1240	−0.2909			0.0043
	$\Delta\eta$/(mPa·s)	298.15	−4.2879	2.6966	−2.1774	1.4361			0.0049
		303.15	−3.5459	2.1002	−1.5735	1.2743			0.0048
		308.15	−2.8930	1.6366	−1.2467	1.1923			0.0042
		313.15	−2.3683	1.3361	−0.9408	0.8921			0.0038
acetonitrile + 2-methylpropan-2-ol	V^E/(cm^3·mol^{-1})	298.15	0.7967	−0.3415	0.0421	0.1398			0.0045
		303.15	0.8689	−0.3976	0.0046	0.1015			0.0039
		308.15	0.9878	−0.3794	−0.0356	0.0498			0.0034
		313.15	1.0855	−0.4247	−0.0510	0.0564			0.0042
	$\Delta\eta$/(mPa·s)	298.15	−6.6026	4.8819	−3.7552	2.9569	−2.4997	1.8094	0.0061
		303.15	−4.6639	3.3694	−3.0674	2.0462	−0.5079	0.6191	0.0063
		308.15	−3.3645	2.2312	−1.8109	1.4546			0.0054
		313.15	−2.4674	1.4776	−1.0835	1.1654			0.0066

ol and butan-1-ol at 303.15 K with those reported in the literature (Sandhu et al., 1986). It is seen that the fitted equation agress with the current data and with the data of Sandhu et al. (1986) within experimental error.

Excess molar volumes are positive for mixtures of acetonitrile with all alkanols except methanol (Figure 1). The V^E values at equimolar concentrations of acetonitrile and 1-alkanols follow the order methanol < 1-propanol <

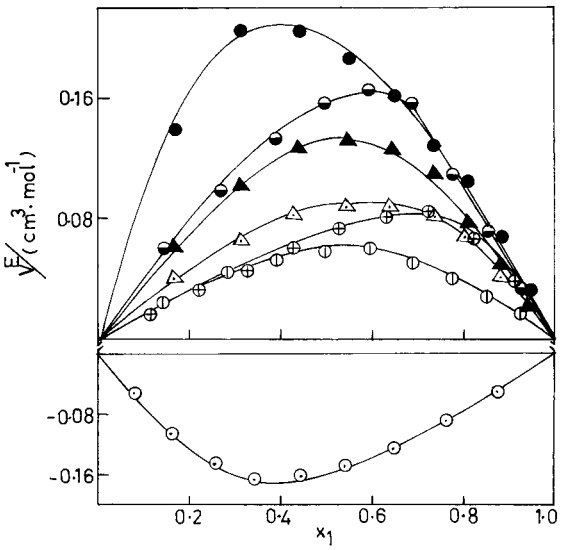

Figure 1. Excess molar volumes, V^E, a$^+$ 298.15 K for x_1 acetonitrile + $(1 - x_1)$ alkanols: (⊙) methanol; (⊕) ethanol; (Φ) propan-1-ol; (◒) propan-2-ol; (◬) butan-1-ol; (▲) 2-methylpropan-1-ol; (●) 2-methylpropan-2-ol.

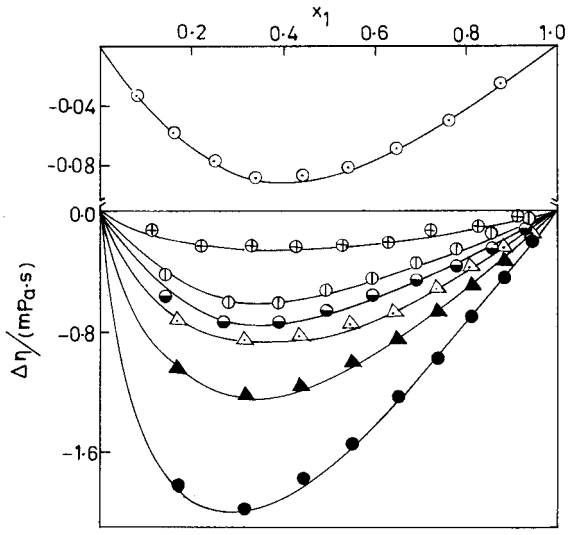

Figure 2. $\Delta\eta$ values at 298.15 K for x_1 acetonitrile + $(1 - x_1)$ alkanols: (⊙) methanol; (⊕) ethanol; (Φ) propan-1-ol; (◒) propan-2-ol; (◬) butan-1-ol; (▲) 2-methylpropan-1-ol; (●) 2-methylpropan-2-ol.

ethanol < l-butanol. Similar observations are made by Sandhu et al. (1986). The V^E values of acetonitrile with secondary (2-propanol, 2-butanol) and tertiary (*tert*-butyl alcohol) alkanols are larger than those corresponding to primary alkanols (l-propanol, l-butanol).

Treszczanowicz et al. (1981) suggested that V^E is the resultant of contributions from physical chemical and structural effects.

The negative V^E values of acetonitrile methanol mixtures can be attributed to interstitial accommodation of acetonitrile molecules in the H-bonded network of methanol which outweighs the positive V^E owing to physical interactions and breaking up of methanol clusters in the presence of acetonitrile molecules. Acetonitrile favors dipole−dipole interactions due to its high dipole moment (3.92 D). The positive V^E values for mixtures of acetonitrile with ethanol, propan-1-ol, propan-2-ol, butan-1-ol, 2-methylpropan-1-ol and 2-methylpropan-2-ol can be ascribed to dominance of disruption of H-bonds between alkanols over dipole−dipole interactions between alkanol (C_2−C_4) and acetonitrile molecules. The increase in V^E with increase in chain length of 1-alkanols implies that dipole−dipole interaction is weaker in higher alkanols owing to their decreased polarizabilities (Mecke 1950) with increase of chain length.

The effect of interaction between the two components becomes more and more sterically hindered when the alkyl group in the alkanol becomes more and more branched; as observed in the behavior of acetonitrile + propan-2-ol, +2-methylpropan-1-ol, and +2-methylpropan-2-ol.

V^E values increase with increasing temperature suggesting more declustering of alkanols at higher temperatures. Figure 2 shows that the deviatons in viscosity are negative in all systems and become more negative with an increase in chain length and branching of alkanols, suggesting decrease in heteroassociation of molecules with increase in molar mass of alkanols. $\Delta\eta$ values at equimolar concentrations of acetonitrile and alkanols follow the order methanol > ethanol > propan-1-ol > propan-2-ol > butan-1-ol > 2-methylpropan-1-ol > 2-methylpropan-2-ol.

At equimolar concentrations, our $\Delta\eta$ values at 298.15 K for acetonitrile + methanol (−0.0845 mPa·s) agress well with the value (−0.0893 mPa·s) reported by Saha et al. (1995), and similarly our $\Delta\eta$ values at 303.15K for acetomitrile + propan-1-ol and acetonitrile + propan-2-ol (−0.447 and −0.5579 mPa·s) agree well with the value (−0.4511 and −0.5343 mPa·s) as reported by Paez and Contreras (1989).

Viscosities of all acetonitrile−alkanol binary mixtures decrease with increase of temperature.

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