ORIGINAL ARTICLE

Excess molar volumes and deviation in viscosities of binary liquid mixtures of acrylic esters with hexane-1-ol at 303.15 and 313.15 K

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Abstract   Densities and viscosities for the four binary liquid mixtures of methyl acrylate, ethyl acrylate, butyl acrylate and methyl methacrylate with hexane-1-ol at temperatures 303.15 and 313.15 K and at atmospheric pressure were measured over the entire composition range. These values were used to calculate excess molar volumes and deviation in viscosities which were fitted to Redlich–Kister polynomial equation. Recently proposed Jouyban Acree model was also used to correlate the experimental values of density and viscosity. The mixture viscosities were correlated by several semi-empirical approaches like Hind, Choudhary–Katti, Grunberg–Nissan, Tamura and Kurata, McAllister three and four body model equations. A graphical representation of excess molar volumes and deviation in isentropic compressibility shows positive nature whereas deviation in viscosity shows negative nature at both temperatures for all four binary liquid mixtures. Positive values of excess molar volumes show that volume expansion is taking place causing rupture of H-bonds in self associated alcohols. The results were discussed in terms of molecular interactions prevailing in the mixtures.

1. Introduction

Under real use conditions involving various processes such as separation of chemicals, fluid flow, heat flow, or chemical reactions, the common practice is that several liquid components that differ in chemical nature and polarity are mixed together. This situation results in a very complex fluid state, the understanding of which becomes very difficult. Due to this, thermodynamic information, especially literature data on various thermo physical properties of binary liquid mixtures containing acrylic esters and higher alkane-1-ols at wide temperature

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range, has been found to be scarce (Sastry and Valand, 2000; Sastry and Patel, 2000; Peralta et al., 2002, 2004a,b, 2005a,b). The study of binary mixtures containing acrylic ester and alkane-1-ol is of considerable interest and importance not only because of the wide use of the former as monomers in the production of polymer and emulsion formulations and the latter as industrial solvents, but also from a theoretical point of view. The study and knowledge of thermodynamic, volumetric, transport, acoustic and dielectric properties of the binary mixtures of acrylic esters with different types of polar associating and nonpolar solvents are expected to provide useful and vital process parameters for efficient design of transesterification processes of industrial interest. The qualitative and quantitative analysis of excess functions also provides information on the nature of molecular interactions in the binary mixtures. Thermodynamic parameters have been used to understand different kinds of association, molecular packing, molecular motion and various types of intermolecular interactions and their strength influenced by size in pure components and in mixtures. These properties are generally convenient parameters for interpreting solute–solvent and solute–solute interactions in solution phase, also in designing industrial equipments with better precision. Structure making and breaking properties of liquids are assumed as a measure of solute–solvent interactions.

Alcohols serve as simple example of biologically and industrially important amphiphilic materials. Whereas, acrylic esters, apart from their practical applications, are also interesting theoretically as they have an unsaturated structure along the side of a carbonyl group in the same molecule. Thus keeping both industrial and scientific interests in mind, here we report the measured densities, ρ and viscosities, η of binary liquid mixtures of acrylic esters with hexne-1-ol at 303.15 and 313.15 K temperatures. The derived parameters' excess molar volume, V^E, and deviation in viscosity, $\Delta\eta$, have been used to gain a better understanding of the intermolecular interactions between the component molecules of the liquid mixtures.

2. Methods

Chemicals used in the present study were of analytical grade and supplied by S.D. Fine Chemicals Pvt., Mumbai, with quoted mass fraction purities: methyl acrylate, MA (>0.997), ethyl acrylate, EA (>0.998), butyl acrylate, BA (>0.995), methyl methacrylate, MMA (>0.997) and hexane-1-ol (>0.99) Prior to use all liquids were stored over 0.4 nm molecular sieves to reduce the water content and were degassed. In addition, all the four acrylates were distilled before use. The binary mixtures of varying composition were prepared by mass in special air-tight bottles. The solutions of each composition were prepared fresh and all properties were measured the same day. The masses were recorded on a Mettlar one pan balance, which can read up to fifth place of decimal, with an accuracy of ± 0.01 mg. Care was taken to avoid evaporation and contamination during mixing. The estimated uncertainty in mole fraction was $<1 \times 10^{-4}$.

The densities of the solutions were measured using a single capillary pycnometer made up of borosil glass with a bulb of 8 cm³ and capillary with internal diameter of 0.1 cm was chosen for present work. The detailed pertaining to calibration,

experimental set up and operational procedure has been previously described. An average of triplicate measurement was taken into account. The reproducibility of density measurement was $\pm 5 \times 10^{-5}$ g/cm³. The dynamic viscosities were measured using an Ubbelohde suspended level viscometer, calibrated with conductivity water. An electronic digital stop watch with readability of ± 0.01 s was used for the flow time measurements. At least three repetitions of each data reproducible to ± 0.05 s were obtained, and the results were averaged. Since all flow times were greater than 300 s and capillary radius (0.1 mm) was far less than its length (50–60 mm), the kinetic energy and end corrections, respectively, were found to be negligible. The uncertainties in dynamic viscosities are of the order of ± 0.003 mPa s (Mahajan et al., 2007). A comparison of measured values of pure components with the literature values as presented in Table 1 shows a good agreement.

Twenty-one density and viscosity measurements were performed with repetitions for each binary liquid system namely, methyl acrylate (1) + hexane-1-ol (2), ethyl acrylate (1) + hexane-1-ol (2), butyl acrylate (1) + hexane-1-ol (2) and methyl methacrylate(1) + hexane-1-ol (2) over the entire mole fraction range (0 < x < 1), at temperatures 303.15 and 313.15 K and at atmospheric pressure. Experimental values of densities, ρ, and viscosities, η, excess molar volumes, V^E, and viscosity deviations, $\Delta\eta$, of these mixtures at T = 303.15 and 313.15 K as a function of acrylic esters mole fraction are listed in Table 2.

The excess molar volumes, V^E, of the solutions of molar compositions x were calculated from the densities of the pure liquids and their mixtures according to the following equation:

$$V^E (\text{cm}^3 \text{ mol}^{-1}) = [x_1 M_1 + x_2 M_2]/\rho_{12} - [(x_1 M_1/\rho_1) + (x_2 M_2/\rho_2)] \qquad (1)$$

where ρ_{12} is the density of the mixture and x_1, M_1, ρ_1 and x_2, M_2, ρ_2 are the mole fraction, the molecular weight, and the density of pure components 1and 2, respectively. The first term on the right-hand side of Eq. (1) represents the actual molar

Table 1 Densities, ρ, viscosities, η, for pure components at T = 303.15 and 313.15 K.

	T = 303.15 K		T = 313.15 K	
	Expt.	Lit.	Expt.	Lit.
Hexane-1-ol				
ρ (g m⁻³)	0.81181	0.81168(20)	0.80426	0.80423(20)
η (mPa s)	3.790	3.795(20)	2.939	2.933(20)
Methyl acrylate				
ρ (g m⁻³)	0.94130	–	0.9292	–
η (mPa s)	0.420	–	0.361	–
Ethyl acrylate				
ρ (g m⁻³)	0.90950	–	0.89720	–
η (mPa s)	0.487	–	0.425	–
Butyl acrylate				
ρ (g m⁻³)	0.89000	–	0.88170	–
η (mPa s)	0.737	–	0.636	–
Methyl methacrylate				
ρ (g m⁻³)	0.93172	0.93174(21)	0.92024	0.92026(21)
η (mPa s)	0.549	–	0.479	–

Table 2 Densities, ρ, viscosities, η, excess molar volumes, V^E, and viscosity deviation, $\Delta\eta$, for acrylic esters (1) + hexane-1-ol (2) at $T = 303.15$ and 313.15 K.

x_1	$T = 303.15$ K				$T = 313.15$ K			
	ρ (g cm^{-3})	V^E (cm^3 mol^{-1})	η (mPa s)	$\Delta\eta$ (mPa s)	ρ (g cm^{-3})	V^E (cm^3 mol^{-1})	η (mPa s)	$\Delta\eta$ (mPa s)
MA (1) + Hexane-1-ol (2)								
0	0.81181	0.000	3.790	0.000	0.80426	0.000	2.939	0.000
0.0552	0.81635	0.109	3.358	−0.247	0.80881	0.084	2.618	−0.179
0.0997	0.82041	0.160	3.041	−0.412	0.81280	0.125	2.383	−0.298
0.1553	0.82552	0.228	2.693	−0.574	0.81784	0.179	2.122	−0.417
0.1997	0.82977	0.276	2.442	−0.675	0.82203	0.216	1.933	−0.491
0.2554	0.83532	0.326	2.161	−0.769	0.82747	0.256	1.720	−0.560
0.2991	0.83995	0.358	1.959	−0.820	0.83200	0.281	1.567	−0.599
0.3550	0.84595	0.390	1.734	−0.858	0.83786	0.306	1.395	−0.628
0.3999	0.85097	0.407	1.572	−0.870	0.84274	0.320	1.270	−0.638
0.4554	0.85749	0.420	1.391	−0.864	0.84908	0.330	1.131	−0.634
0.4998	0.86295	0.421	1.262	−0.844	0.85437	0.331	1.030	−0.620
0.5555	0.87003	0.417	1.117	−0.802	0.86121	0.327	0.917	−0.590
0.5999	0.87596	0.405	1.012	−0.756	0.86693	0.318	0.835	−0.557
0.6554	0.88364	0.380	0.897	−0.686	0.87432	0.298	0.744	−0.506
0.6999	0.89017	0.353	0.812	−0.619	0.88058	0.277	0.677	−0.457
0.7556	0.89854	0.310	0.720	−0.526	0.88860	0.243	0.603	−0.389
0.7998	0.90567	0.267	0.652	−0.442	0.89539	0.210	0.549	−0.328
0.8554	0.91492	0.206	0.577	−0.330	0.90442	0.161	0.489	−0.245
0.8999	0.92267	0.148	0.523	−0.234	0.91157	0.116	0.445	−0.174
0.9555	0.93285	0.064	0.463	−0.107	0.92123	0.048	0.396	−0.080
1	0.94130	0.000	0.420	0.000	0.92920	0.000	0.361	0.000
EA (1) + hexane-1-ol (2)								
0	0.81181	0.000	3.790	0.000	0.80426	0.000	2.939	0.000
0.0555	0.81619	0.055	3.385	−0.223	0.80856	0.035	2.642	−0.158
0.0999	0.81977	0.103	3.088	−0.372	0.81205	0.071	2.423	−0.265
0.1555	0.82434	0.152	2.755	−0.522	0.81651	0.105	2.176	−0.372
0.1998	0.82807	0.186	2.515	−0.615	0.82013	0.128	1.997	−0.440
0.2556	0.83285	0.221	2.244	−0.703	0.82476	0.153	1.793	−0.504
0.2997	0.83675	0.244	2.048	−0.751	0.82852	0.169	1.646	−0.540
0.3551	0.84173	0.267	1.827	−0.789	0.83332	0.185	1.478	−0.568
0.3999	0.84581	0.279	1.668	−0.801	0.83724	0.193	1.356	−0.578
0.4551	0.85102	0.288	1.488	−0.797	0.84222	0.200	1.218	−0.576
0.4998	0.85525	0.293	1.359	−0.780	0.84626	0.204	1.118	−0.565
0.5555	0.86074	0.286	1.212	−0.743	0.85148	0.198	1.003	−0.539
0.5998	0.86517	0.278	1.106	−0.702	0.85569	0.192	0.921	−0.510
0.6550	0.87085	0.261	0.987	−0.638	0.86107	0.180	0.827	−0.464
0.6999	0.87548	0.242	0.902	−0.578	0.86544	0.166	0.760	−0.421
0.7555	0.88146	0.212	0.804	−0.491	0.87107	0.145	0.682	−0.358
0.7998	0.88635	0.182	0.734	−0.414	0.87565	0.124	0.626	−0.302
0.8554	0.89259	0.139	0.655	−0.309	0.88149	0.094	0.562	−0.226
0.8999	0.89768	0.098	0.598	−0.220	0.88624	0.065	0.516	−0.161
0.9550	0.90430	0.031	0.533	−0.101	0.89241	0.013	0.463	−0.074
1	0.90950	0.000	0.487	0.000	0.89720	0.000	0.425	0.000
BA (1) + hexane-1-ol (2)								
0	0.81181	0.000	3.790	0.000	0.80426	0.000	2.939	0.000
0.0552	0.81654	0.030	3.461	−0.160	0.80904	0.015	2.700	−0.112
0.0998	0.82032	0.047	3.218	−0.267	0.81280	0.030	2.522	−0.187
0.1555	0.82498	0.068	2.938	−0.377	0.81746	0.044	2.316	−0.264
0.1999	0.82867	0.082	2.732	−0.448	0.82114	0.054	2.164	−0.314
0.2554	0.83323	0.097	2.494	−0.516	0.82568	0.065	1.988	−0.363
0.2999	0.83685	0.107	2.319	−0.555	0.82929	0.072	1.857	−0.391
0.3554	0.84132	0.117	2.117	−0.587	0.83374	0.078	1.705	−0.415
0.3998	0.84486	0.123	1.968	−0.600	0.83726	0.082	1.593	−0.425
0.4556	0.84923	0.127	1.798	−0.602	0.84159	0.085	1.464	−0.427
0.5000	0.85273	0.127	1.671	−0.593	0.84505	0.086	1.367	−0.421
0.5551	0.85703	0.126	1.526	−0.568	0.84931	0.085	1.255	−0.404
0.5998	0.86043	0.123	1.419	−0.540	0.85266	0.083	1.173	−0.384
0.6554	0.86465	0.116	1.296	−0.494	0.85683	0.078	1.078	−0.352

Table 2 (*continued*)

x_1	$T = 303.15$ K				$T = 313.15$ K			
	ρ (g cm^{-3})	V^E (cm^3 mol^{-1})	η (mPa s)	$\Delta\eta$ (mPa s)	ρ (g cm^{-3})	V^E (cm^3 mol^{-1})	η (mPa s)	$\Delta\eta$ (mPa s)
0.7000	0.86800	0.108	1.205	−0.449	0.86014	0.073	1.007	−0.321
0.7554	0.87215	0.096	1.100	−0.384	0.86422	0.064	0.925	−0.275
0.8000	0.87546	0.083	1.022	−0.325	0.86748	0.055	0.864	−0.233
0.8554	0.87953	0.065	0.934	−0.245	0.87147	0.043	0.793	−0.176
0.8999	0.88278	0.048	0.868	−0.175	0.87465	0.032	0.741	−0.125
0.9555	0.88676	0.029	0.792	−0.080	0.87857	0.016	0.681	−0.058
1	0.89000	0.000	0.737	0.000	0.88170	0.000	0.636	0.000
MMA (1) + hexane-1-ol (2)								
0	0.81181	0.000	3.790	0.000	0.80426	0.000	2.939	0.000
0.0555	0.81709	0.062	3.408	−0.204	0.80946	0.049	2.660	−0.144
0.0999	0.82140	0.118	3.125	−0.341	0.81375	0.088	2.452	−0.241
0.1555	0.82693	0.174	2.807	−0.480	0.81920	0.130	2.217	−0.340
0.1998	0.83143	0.213	2.576	−0.566	0.82364	0.158	2.045	−0.402
0.2556	0.83722	0.254	2.313	−0.649	0.82932	0.189	1.849	−0.462
0.2997	0.84195	0.281	2.123	−0.695	0.83396	0.208	1.706	−0.496
0.3551	0.84801	0.307	1.907	−0.731	0.83987	0.228	1.542	−0.523
0.3999	0.85297	0.322	1.750	−0.744	0.84471	0.239	1.423	−0.533
0.4551	0.85952	0.334	1.572	−0.742	0.85089	0.247	1.286	−0.532
0.4998	0.86452	0.337	1.443	−0.727	0.85594	0.249	1.187	−0.523
0.5555	0.87121	0.333	1.295	−0.694	0.86242	0.246	1.072	−0.500
0.5998	0.87666	0.324	1.189	−0.657	0.86767	0.240	0.990	−0.474
0.6550	0.88365	0.305	1.068	−0.598	0.87440	0.226	0.895	−0.432
0.6999	0.88934	0.284	0.981	−0.542	0.87988	0.210	0.826	−0.392
0.7555	0.89673	0.251	0.880	−0.461	0.88696	0.186	0.746	−0.334
0.7998	0.90278	0.217	0.808	−0.390	0.89274	0.161	0.688	−0.283
0.8554	0.91052	0.169	0.726	−0.292	0.90013	0.125	0.622	−0.212
0.8999	0.91685	0.124	0.666	−0.208	0.90615	0.092	0.574	−0.151
0.9550	0.92497	0.063	0.598	−0.095	0.91385	0.049	0.519	−0.069
1	0.93172	0.000	0.549	0.000	0.92024	0.000	0.479	0.000

Table 3 Adjustable parameters of Eqs. (3) and (4) for the mathematical representation of excess functions for binary liquid mixture of acrylic esters (1) + hexane-1-ol (2) at $T = 303.15$ and 313.15 K.

	T (K)	a_0	a_1	a_2	a_3	a_4	σ
MA (1) + hexane-1-ol (2)							
V^E (cm^3 mol^{-1})	303.15	1.6967	0.1053	−0.1209	−0.4452	0.3051	0.00572
	313.15	1.3286	0.0905	−0.0313	−0.3729	0.0999	0.00473
$\Delta\eta$ (mPa s)	303.15	−3.3739	1.1907	−0.3251	0.0631	−0.0069	0.00036
	313.15	−2.4812	0.8344	−0.2023	0.0482	−0.0323	0.00030
EA (1) + hexane-1-ol (2)							
V^E (cm^3 mol^{-1})	303.15	1.1443	0.0507	0.3039	−0.2092	−0.6953	0.00465
	313.15	0.7859	0.0575	0.3430	−0.2434	−0.7965	0.00547
$\Delta\eta$ (mPa s)	303.15	−3.1220	1.0317	−0.2463	0.0478	−0.0331	0.00032
	313.15	−2.2589	0.7052	−0.1566	0.0337	−0.0228	0.00026
BA (1) + hexane-1-ol (2)							
V^E (cm^3 mol^{-1})	303.15	0.5202	−0.0283	−0.1534	0.0901	0.3375	0.00270
	313.15	0.3457	−0.0182	−0.0349	0.0817	0.0405	0.00144
$\Delta\eta$ (mPa s)	303.15	−2.3703	0.6381	−0.1191	0.0063	−0.0206	0.00029
	313.15	−1.6814	0.4222	−0.0921	0.0108	0.0175	0.00039
MMA (1) + hexane-1-ol (2)							
V^E (cm^3 mol^{-1})	303.15	1.3504	−0.0391	0.0028	0.2108	−0.0281	0.00360
	313.15	1.0038	−0.0234	−0.0663	0.1318	0.1132	0.00289
$\Delta\eta$ (mPa s)	303.15	−2.9088	0.9136	−0.2166	0.0281	−0.0051	0.00040
	313.15	−2.0896	0.6167	−0.1469	0.0154	0.0054	0.00035

volume, V, of the solution and the second represents the molar volume it would occupy if the mixture behaved ideally. In general, while these two molar volumes are similar in size (usually larger than $100\ cm^3\ mol^{-1}$) their difference is usually smaller by two to three orders of magnitude and thus may carry a significantly larger error.

The viscosity deviations ($\Delta\eta$) were calculated using equation:

$$\Delta\eta\,(mPa\,s) = \eta_{12} - x_1\eta_1 - x_2\eta_2 \qquad (2)$$

where $\eta 12$ is the viscosity of the mixture and x1, x2 and η1, η2 are the mole fraction and the viscosity of pure components 1 and 2, respectively (Pal and Kumar, 2001).

The excess molar volumes and deviations in viscosity were fitted to Redlich–Kister equation of the type:

$$Y = x_1 x_2 \sum_i^n a_i(x_1 - x_2)^i \qquad (3)$$

where Y is either V^E or $\Delta\eta$ and n is the degree of polynomial. Coefficient a_i was obtained by fitting Eq. (3) to experimental results using a least-squares regression method. In each case, the optimum number of coefficients is ascertained from an examination of the variation in standard deviation (σ).

σ was calculated using the relation:

$$\sigma(Y) = \left[\frac{\sum (Y_{expt} - Y_{calc})^2}{N - n} \right]^{1/2} \qquad (4)$$

where N is the number of data points and n is the number of coefficients (Redlich and Kister, 1948). The calculated values of the coefficients a_i along with the standard deviations (σ) are given in Table 3.

Several semi-empirical relations have been proposed to evaluate the dynamic viscosity η and to check the suitability of the equation for experimental data fits by taking into account the number of empirical adjustable coefficients. The equations of Hind, Choudhary–Katti, Grunberg–Nissan and Tamura–Kurata have one adjustable parameter.

The expression for Hind et al. (1960) equation is

$$\eta_{12} = x_1^2\eta_1 + x_2^2\eta_2 + 2x_1 x_2 H_{12} \qquad (5)$$

where H_{12} is the interaction parameter.

The expression for Choudhary–Katti (Katti and Choudhary, 1964) equation is

$$\ln(\eta_n V_m) = x_1 \ln(\eta_1 V_1) + x_2 \ln(\eta_2 V_2) + x_1 x_2[Wvis/(RT)] \qquad (6)$$

where $Wvis$ is the interaction energy for activation of viscous flow.

The expression for Grunberg and Nissan (1949) equation is

$$\ln \eta_{12} = x_1 \ln \eta_1 + x_2 \ln \eta_2 + x_1 x_2 G_{12} \qquad (7)$$

where G_{12} is a parameter proportional to the interchange energy.

Tamura and Kurata (1952) developed expression for viscosity of binary mixtures as

$$\eta = x_1\phi_1\eta_1 + x_2\phi_2\eta_2 + 2(x_1 x_2\phi_1\phi_2)^{1/2}T_{12} \qquad (8)$$

where T_{12} is the interaction parameter, ϕ_1 and ϕ_2 are the volume fractions. The calculated values of adjustable parameters H_{12}, $Wvis$, G_{12} and T_{12} with their standard deviations (σ) calculated using Eq. (11) are given in Table 4.

McAllister's (1960) multibody interaction model was widely used to correlate kinematic viscosity, v, and data. The two parameter McAllister equation based on Eyring's theory of absolute reaction rates, taken into account interactions of both

Table 5 Adjustable parameters of Eqs. (9)–(11) for binary liquid mixture of acrylic esters (1) + hexane-1-ol (2) at $T = 303.15$ and 313.15 K.

T (K)	Z_{12}	Z_{21}	σ	Z_{1112}	Z_{1122}	Z_{2221}	σ
MA (1) + hexane-1-ol (2)							
303.15	0.995	2.172	0.035	0.813	1.346	2.628	0.999
313.15	0.835	1.759	0.041	0.688	1.111	2.108	2.720
EA (1) + hexane-1-ol (2)							
303.15	1.106	2.284	0.049	0.921	1.581	2.725	0.983
313.15	0.940	1.859	0.032	0.791	1.311	2.199	1.564
BA (1) + hexane-1-ol (2)							
303.15	1.469	2.621	0.035	1.271	2.188	3.023	1.526
313.15	1.237	2.123	0.027	1.081	1.800	2.431	1.065
MMA (1) + hexane-1-ol (2)							
303.15	1.184	2.360	0.037	0.994	1.675	2.797	1.198
313.15	1.002	1.923	0.048	0.849	1.378	2.254	1.468

Table 4 Adjustable parameters of Eqs. (5)–(8) and (11) for binary liquid mixture of acrylic esters (1) + hexane-1-ol (2) at $T = 303.15$ and 313.15 K.

T (K)	H_{12}	σ	$Wvis$	σ	G_{12}	σ	T_{12}	σ
MA (1) + hexane-1-ol (2)								
303.15	0.386	8.986	0.065	0.048	−0.001	0.033	0.129	13.421
313.15	0.388	7.557	0.061	0.047	−0.001	0.033	0.195	11.390
EA (1) + hexane-1-ol (2)								
303.15	0.552	6.990	0.017	0.034	−0.002	0.033	0.444	8.497
313.15	0.536	5.672	0.014	0.028	−0.001	0.027	0.457	6.914
BA (1) + hexane-1-ol (2)								
303.15	1.066	3.194	0.012	0.025	−0.001	0.025	1.172	2.373
313.15	0.938	2.550	0.011	0.027	−0.001	0.027	1.019	1.853
MMA (1) + hexane-1-ol (2)								
303.15	0.694	5.654	0.023	0.035	−0.001	0.033	0.569	7.169
313.15	0.650	4.518	0.019	0.042	−0.001	0.045	0.558	5.777

like and unlike molecules by a two dimensional three body model. The three body model was defined by the relation

$$\ln v = x_1^3 \ln v_1 + x_2^3 \ln v_2 + 3x_1^2 x_2 \ln Z_{12} + 3x_1 x_2^2 \ln Z_{21}$$
$$- \ln[x_1 + (x_2 M_2/M_1)] + 3x_1^2 x_2 \ln[(2/3) + (M_2/3M_1)] + 3x_1 x_2^2 \ln[(1/3) + (2M_2/3M_1)] + x_2^3 \times \ln(M_2/M_1) \quad (9)$$

Similarly, the four body model was defined by the relation

$$\ln v = x_1^4 \ln v_1 + 4x_1^3 x_2 \ln Z_{1112} + 6x_1^2 x_2^2 \ln Z_{1122} + 4x_1 x_2^3 \times \ln Z_{2221} + x_2^4 \ln v_2 - \ln[x_1 + x_2(M_2/M_1)]$$
$$+ 4x_1^3 x_2 \ln[(3 + M_2/M_1)/4] + 6x_1^2 2x_2^2 \ln[1 + M_2/M_1)/2] + 4x_1 x_2^3 \ln[(1 + 3M_2/M_1)/4] + x_2^4 \times \ln(M_2/M_1) \quad (10)$$

Table 6 Adjustable parameters of Eqs. (12) and (13) for binary liquid mixture of acrylic esters (1) + hexane-1-ol (2) at $T = 303.15$ and 313.15 K.

	a_0	a_1	a_2	a_3	a_4	σ	APD
MA (1) + hexane-1-ol (2)							
ρ (g m^{-3})	−15.4568	-2.3410	−0.2255	1.0479	−0.2582	3.8573	0.0278
η (mPa s)	−0.1376	−0.3615	−0.9520	−0.5340	0.1687	1.7863	0.0208
EA (1) + hexane-1-ol (2)							
ρ (g m^{-3})	−5.3782	−0.4643	−0.8716	0.6475	1.9585	1.8993	0.0270
η (mPa s)	−0.2974	−0.0551	0.4016	−1.1276	−1.8522	1.8644	0.0208
BA (1) + hexane-1-ol (2)							
ρ (g m^{-3})	3.9850	−0.3402	0.2665	−0.2079	−0.4868	0.3231	0.0152
η (mPa s)	−0.2892	−0.2887	−0.4166	−0.4525	−0.1715	2.0848	0.0213
MMA (1) + hexane-1-ol (2)							
ρ (g m^{-3})	−7.0447	−0.3759	−0.0117	−0.4662	0.0041	2.2248	0.0254
η (mPa s)	−0.0165	0.7512	1.0246	−3.1582	−3.5082	1.9043	0.0244

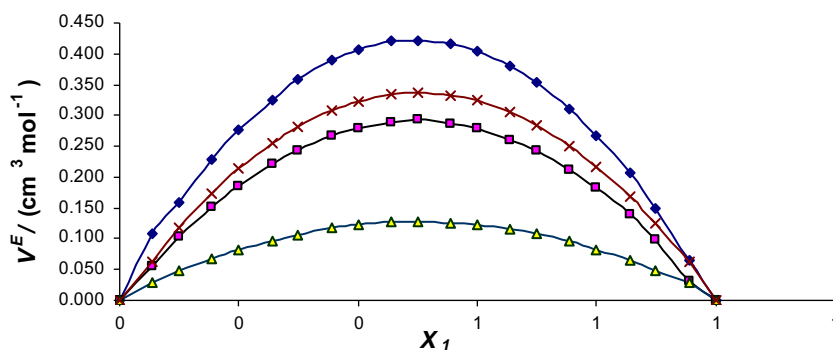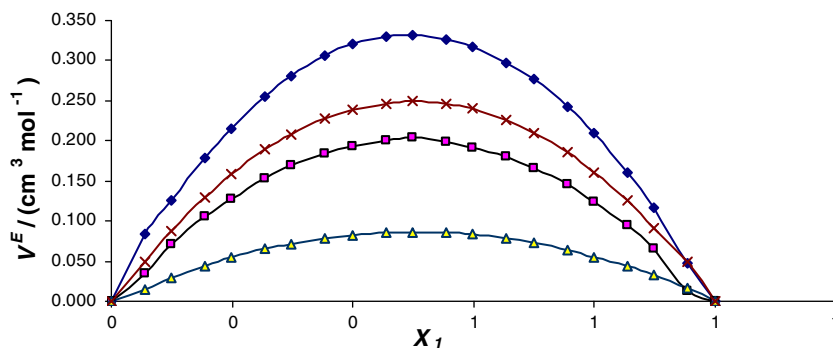**Figure 1** Variation of excess molar volumes for binary mixtures of acrylic esters (1) + hexane-1-ol (2) at 303.15 K: ♦, methyl acrylate; ■, ethyl acrylate; ▲, butyl acrylate; ×, methyl methacrylate.

Figure 2 Variation of excess molar volumes for binary mixtures of acrylic esters (2) + hexane-1-ol (2) at 313.15 K: ♦, methyl acrylate; ■, ethyl acrylate; ▲, butyl acrylate; ×, methyl methacrylate.

where Z_{12}, Z_{21}, Z_{1112}, Z_{1122} and Z_{2221} are model parameters and M_i and v_i are the molecular mass and kinematic viscosity of pure component i.

To perform a numerical comparison of the correlating capability of Eqs. (10)–(13) we have calculated the standard percentage deviation (σ %) using the relation

$$\sigma\% = \left[1/(\eta_{expt} - k) \times \sum (100(\eta_{expt} - \eta_{cal})/\eta_{expt})^2\right]^{1/2} \quad (11)$$

where k represents the number of numerical coefficients in the respective equations. The interaction parameters H_{12}, $Wvis$, G_{12}, T_{12}, Z_{12}, Z_{21}, Z_{1112}, Z_{1122} and Z_{2221} in Eqs. (5)–(10) have been considered as adjustable parameters, estimated by a non-linear regression analysis based on a least-squares method (Pal and Bhardwaj, 2002). The parameters Z_{12}, Z_{21}, Z_{1112}, Z_{1122} and Z_{2221} are presented with their standard percentage deviation (σ %) in Table 5.

Recently Jouyban and Acree (Jouyban et al., 2005a,b) proposed a model for correlating the density and viscosity of liquid mixtures at wide range of temperatures. This model could be used in data modeling. The proposed equation is

$$\ln y_{mT} = f_1 \ln y_{1T} + f_2 \ln y_{2T} + f_1 f_2 \sum [A_j (f_1 - f_2)^j / T] \quad (12)$$

where y_{mT}, y_{1T} and y_{2T} are densities or viscosities of the mixture and solvents 1 and 2 at temperature T, respectively, f_1 and f_2 are the volume fractions of solvents in case of density, and mole fraction in case of viscosity, and A_j is the model constant. The correlating ability of the Jouyban–Acree model was tested by calculating the average percentage deviation (APD) between the experimental and calculated density and viscosity as

$$APD = (100/N) \sum [(|y_{expt} - y_{cal}|)/y_{expt})] \quad (13)$$

where N is the number of data points in each set. The optimum numbers of constant A_j, in each case, were determined from the examination of the average percentage deviation value. The constant A_j calculated from the least square analysis along with the average percentage deviation (APD) is presented in Table 6. The proposed model provides reasonably accurate calculations for the density and viscosity of binary liquid mixtures at various temperatures.

3. Results and discussion

A graphical comparison of the dependence of excess molar volume, V^E, on acrylic esters at 303.15 and 313.15 K for the binary mixtures of each acrylic ester with hexane-1-ol is given in Figs. 1 and 2. A systematic decrease in V^E is noted with the rise in the carbon chain length of acrylic esters from methyl acrylate to butyl acrylate at both temperatures in all the binary mixtures. The observed positive excess molar volumes in the present investigation may be discussed in terms of several effects. Excess molar volumes can be considered as arising from three types of interactions between the component molecules; namely physical, chemical and geometrical types of molecular interactions. Positive values of excess molar volumes can be visualized as being due to a closer approach of unlike molecules having significantly different molecular size. Due to the presence of nonpolar molecule like acrylic esters, existing H-bonding in alcohol molecule breaks and system shows weak intermolecular interactions. Longer the chain length of acrylic esters, weaker will be the interaction between liquid components. Positive values of excess molar volumes show that volume expansion is taking place causing rupture of hydrogen bonds in self associated alcohols.

A graphical comparison of the dependence of deviation in viscosity, $\Delta\eta$, on acrylic esters at 303.15 and 313.15 K for the binary mixtures of each acrylic ester with hexane-1-ol is given in Figs. 3 and 4. Negative values of $\Delta\eta$ over whole composition range suggest that viscosities of associates formed between unlike molecules are relatively less than those of pure components, which are exhibited by decreased values of viscosity with mole fraction. This decrease in viscosity attributed to breaking of dipolar association of alcohol into small dipoles. Weak types of dipole-induced dipole type of interactions are not sufficient to produce bulky or less mobile entities in system and hence decreased trend of viscosity is observed in the present binary liquid mixture of acrylics esters with the hexane-1-ol. Negative values of deviation in viscosity may be due to mutual loss of dipolar association and the difference in size and shape of unlike molecules. Negative values of deviation in viscosities due to breaking of hydrogen bonding of hexane-1-ol that makes mixture flow more easily.

Grunberg–Nissan models used to correlate mixture viscosity that shows least negative values of G_{12} parameters supporting weak molecular interactions. Hind, Choudhary–Katti and Tamura and Kurata model shows slightly positive values of
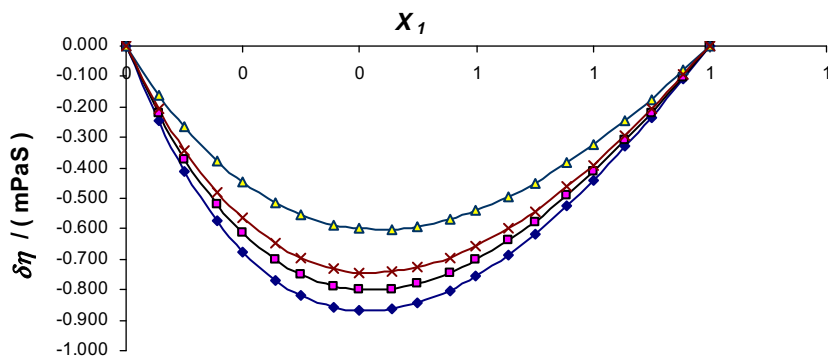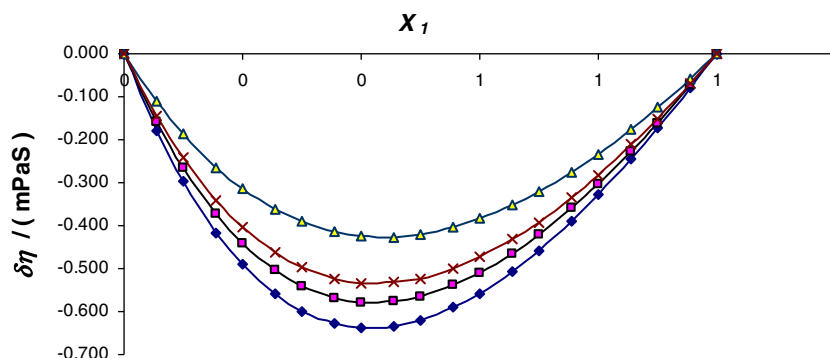

Figure 3 Variation of deviation in viscosity for binary mixtures of acrylic esters (1) + hexane-1-ol (2) at 303.15 K: ♦, methyl acrylate; ■, ethyl acrylate; ▲, butyl acrylate; ×, methyl methacrylate.

Figure 4 Variation of deviation in viscosity for binary mixtures of acrylic esters (2) + hexane-1-ol (2) at 313.15 K: ♦, methyl acrylate; ■, ethyl acrylate;▲, butyl acrylate; ×, methyl methacrylate.

their H_{12}, $Wvis$ and T_{12} adjustable parameters, respectively, supporting existing of weak interactions for all binary liquid mixtures at both temperatures. In the similar way, among McAllister three and four body models show the values of Z_{12}, Z_{21}, Z_{1112}, Z_{1122} and Z_{2221} adjustable parameters positive, supporting weak type of molecular interactions for all the four binary liquid mixtures. Lowest values of the standard deviations for the McAllister there body model suggest that it is most suitable than the other one.

4. Conclusions

The overall positive magnitude of excess molar volumes for the systems acrylates with the hexane-1-ol is the result of the breaking and dislocation of the ester's dipole–dipole association. The free volume difference and interstitial accommodation of smaller molecules are the chief factors for negative excess molar volumes. In higher alcohols, geometrical fitting of one into other is negligibly small; therefore association decreases with increase in chain length of alcohols.

Declaration of interest

The authors report no declaration of interest.

Acknowledgements

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