DENSITIES, VISCOSITIES AND SPEEDS OF SOUND FOR BINARY LIQUID MIXTURES OF HEXYL ACETATE AND PhX (X=F, Cl, Br, NO_2) COMPOUNDS AT DIFFERENT TEMPERATURES.

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Densities and viscosities of binary mixtures of hexyl acetate with chlorobenzene, bromobenzene, fluorobenzene and nitrobenzene have been measured at (298.15, 303.15, 308.15 and 313.15) K over the entire composition range. Speeds of sound of these binary liquid mixtures have also been measured at 303.15 K. From the experimental density and viscosity data, the values of excess molar volume V^E , free energy of activation for viscous flow ΔG^E, while from the speed of sound data the isentropic compressibility K_S, intermolecular free length L_f, internal pressure π_i, free volume V_f, and specific acoustic impedance Z have been calculated. The excess molar volumes for these binary mixtures were negative over the whole composition range at all temperatures. The viscosity values were correlated using Frenkel and McAllister (four-body) models.

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Introduction

Hexyl acetate a short-chain ester with fruity odor, is a significant green note flavour compound and widely used in the food industry. It has been found that hexyl acetate has a potential use[1] for both the extension of shelf life and an improvement of hygienic safety of minimally processed foods. An aryl halide (also known as haloarene or halogenoarene) is an aromatic compound in which one or more hydrogen atoms directly bonded to an aromatic ring are replaced by a halide. Aryl halides are mainly used as an intermediate in pharmaceuticals and find applications in many chemical and technological processes. Nitrobenzene is used in shoe and floor polishes, leather dressings, paint solvents and other materials to mask unpleasant odors. Nitrobenzene has also been used as an inexpensive perfume for soaps. In view of these importance it is of interest to study the thermophysical properties of these chemicals, in order to understand the intermolecular interactions in their binary mixtures.

Comelli et al[2] investigated the excess enthalpies and excess molar volumes of diethyl carbonate with alkyl acetates at 298.15K. El-Banna[3] has studied densities and viscosities of pentyl acetate and hexyl acetate each with normal alkanols. Ismadji et al[4-5] determined densities and viscosities for binary mixtures of ethyl valerate and hexyl acetate with 1-pentanol and 1-hexanol. Arce et al[6] determined VLE of hexyl acetate with methanol and ethanol. Likewise, there have been some reports on physical properties for binary mixtures of aryl halides with organic solvents.[7-12] In continuation of our earlier work,[13] we report in this paper densities and viscosities for the binary mixtures of hexyl acetate with chlorobenzene, bromobenzene, fluorobenzene and nitrobenzene at (298.15, 303.15, 308.15 and 313.15) K. Also the speeds of sound for these mixtures were determined at 303.15 K over the entire composition range. From the experimental values of density, viscosity and speed of sound, the excess molar volume V^E, the free energy of activation for viscous flow ΔG^E, isentropic compressibility K_S, intermolecular free length L_f, internal pressure π_i, free volume V_f and specific acoustic impedance have been calculated. The results of calculated excess or deviation properties viz: V^E, ΔK_S, L_f^E, π_i^E, V_f^E, Z^E were fitted to the Redlich- Kister equation.[14] The viscosity data were correlated using singal-parameter equation of Frenkel,[15] and three-parameter equation of Mc Allister's (four-body)[16] models.

Experimental

Materials : High purity and AR grade samples of hexyl acetate (Fluka AG), chlorobenzene, bromobenzene, fluorobenzene and nitrobenzene all Sigma Aldrich obtained from S.D.fine- Chem Limited, Mumbai, India were used. The claimed mass fraction purity for these chemicals range from 0.990 to 0.997. All the liquids were degassed ultrasonically and dried over 0.4 mm molecular sieves. The mass fraction purities tested by gas chromatography (HP 8610) using FID were as follows hexyl acetate (>0.994), chlorobenzene (>0.995), bromobenzene (>0.995), fluorobenzene (>0.995), and nitrobenzene (>0.997).

Methods : The compositions (mole fraction) of binary mixtures were prepared by mass in airtight glass stoppered bottles. Mass measurements accurate to ± 0.01 mg were made on a digital electronic balance (Mettler, AE, 240 Switzerland). To prevent the samples from

undergoing preferential evaporation, the mixtures were prepared by transferring aliquots via syringe into the stoppered bottles. The resulting mole fraction uncertainty was estimated to be less than ± 0.0001.

Densities of the pure and their binary mixtures were determined using a density meter a (DMA-4500 Anton Paar). The instrument was calibrated frequently before the start of the actual experiments using deionized doubly distilled water and dry air according to the established standard procedures. The instrument has a temperature sensor which measures the sample temperature right at the measuring cell. The density of the sample was measured after achieving thermal equilibrium with successive increments of 5K for a temperature range from 298.15 to 313.15 K. All measurements for each sample were made in triplicate and the results presented are the average. The average uncertainty in the density measurements was found to be less than ± 0.0002 g.cm^{-3}.

The kinematic viscosities ν were measured with an Ubbelohde viscometer. The viscometer is kept in a transparent walled water bath with a thermal stability of ± 0.01K for about 20 min to obtain thermal equilibrium. An electronic digital stopwatch with an uncertainty of ± 0.01s was used for flow time measurements. The kinematic viscosities of liquids were calculated with the measured flow time and the calibration constants using the relation ν = A*t*-B/*t* ,where *t* is the flow time in the viscometer. A and B are the viscometer constants, determined by calibrating viscometer with double distilled water and pure benzene. Dynamic viscosities η (mPa.s) were then determined by using the relation η = ν.ρ. The experimental viscosities were obtained by averaging five to six measures of flow times. The average uncertainty of dynamic viscosity values was found to be less than ± 0.007 mPa.s.

The speed of sound of pure liquids and liquid mixtures was measured with a singal-crystal variable path interferometer (model F-81) supplied by Mittal Enterprises, New Delhi, India. A crystal controlled high frequency generator was used to excite the transducer at a frequency of 2 MHz. The accuracy of the velocity measurements is 0.02%. The measuring cell of interferometer has a specially designed double walled vessel with provision for temperature constancy. An electronically operated digital temperature bath (model SSI-0.3 spl) supplied by Mittal Enterprises New Delhi, operating in the temperature range -10°c to 85°c with an accuracy of ±0.1 K has been used to circulate water through the outer jacket of the double walled measuring cell containing the sample liquid. The instrument was calibrated by measuring the velocity in standard liquids viz AR grade benzene and carbon tetrachloride. The uncertainty in the measured speeds of sound was found to be ± 1 m.s^{-1}.

Results and Discussion

The results of density ρ, excess volume V^E, and viscosity η of the studied binary mixtures at (298.15, 303.15, 308.15 and 313.15) K are given in Table 1. From the density data, excess volumes V^E (cm^3 mol^{-1}) have been calculated as

$$V^E = \frac{(x_1M_1 + x_2M_2)}{\rho_{12}} - \left(\frac{x_1M_1}{\rho_1} + \frac{x_2M_2}{\rho_2}\right) \quad (1)$$

where

x, M, and ρ are the mole fraction, molar mass, and density, respectively of pure components 1 and 2 and ρ_{12} is the density of the liquid mixture.

The excess free energy of activation (ΔG^{*E}, J.mol^{-1}) for viscous flow were obtained with the expression

$$\Delta G^{*E} = RT\left[\ln(\eta v) - \left\{\left[x_1 \ln(\eta_1 v_1) + x_2 \ln(\eta_2 v_2)\right]\right\}\right] \quad (2)$$

where η_1, η and v denote the viscosity, and molar volume of the pure components and their mixtures respectively.

Table 2 lists the experimental values of speed of sound u, isentropic compressibility K_S, intermolecular free length L_f, internal pressure π_i , free volume V_f , and specific acoustic impedance Z, These properties have been calculated using the following equations

$$K_S = \frac{1}{u^2\rho} \quad (3)$$

$$L_f = K\left(K_S\right)^{1/2} \quad (4)$$

$$\pi_i = bRT\left(\frac{K\eta}{u}\right)^{1/2}\left(\frac{\rho^{2/3}}{M_{eff}^{7/6}}\right) \quad (5)$$

$$V_f = \left(\frac{M_{eff}u}{\eta k}\right)^{3/2} \quad (6)$$

$$Z = u\rho \quad (7)$$

where K is the temperature dependent Jacobson constant, b is the cubical packing fraction taken as 2 for all the liquids, R is the universal gas constant, T is the experimental temperature, $M_{eff} = \Sigma x_i m_i$ where, x is the mole fraction and m is the molecular weight of ith component. The excess parameters such as isentropic compressibility ΔK_S, excess intermolecular free length L_f^E, excess internal pressure π_i^E, excess free volume V_f^E and excess acoustic impedance Z^E have been obtained using the general equation

$$Y^E = Y_m - x_1Y_1 - x_2Y_2 \quad (8)$$

where Y^E refers to deviation or excess property in question, Y_m refers to the property of mixture x_1Y_1 and x_2Y_2 refer to the mole fraction and specific property of the pure components of 1 and 2 respectively.

Table 1. Values of Density ρ, Excess Volume V^E, Viscosity η for the Binary Liquid Mixtures.

x_1	ρ, g.cm^{-3}	V^E, cm^3.mol^{-1}	η, mPa.s	ρ, g.cm^{-3}	V^E, cm^3.mol^{-1}	η, mPa.s
	Hexyl acetate (1) + Chlorobenzene (2)					
	***T*/K = 298.15**			***T*/K = 303.15**		
0.0000	1.0999		0.758	1.0951		0.700
0.0635	1.0776	-0.074	0.805	1.0733	-0.118	0.740
0.1334	1.0559	-0.260	0.843	1.0518	-0.323	0.774
0.2071	1.0350	-0.481	0.880	1.0309	-0.542	0.803
0.2872	1.0146	-0.785	0.917	1.0103	-0.821	0.834
0.3797	0.9925	-1.075	0.954	0.9882	-1.107	0.866
0.4770	0.9710	-1.340	0.991	0.9669	-1.393	0.894
0.5875	0.9471	-1.388	1.026	0.9433	-1.479	0.924
0.7081	0.9223	-1.230	1.057	0.9189	-1.378	0.953
0.8407	0.8961	-0.738	1.077	0.8928	-0.898	0.971
1.0000	0.8676		1.071	0.8635		0.960
x_1	***T*/K = 308.15**			***T*/K = 313.15**		
0.0000	1.0900		0.665	1.0849		0.620
0.0635	1.0687	-0.161	0.700	1.0642	-0.214	0.650
0.1334	1.0473	-0.371	0.733	1.0430	-0.439	0.676
0.2071	1.0273	-0.688	0.758	1.0230	-0.752	0.701
0.2872	1.0069	-0.992	0.783	1.0034	-1.148	0.723
0.3797	0.9855	-1.369	0.809	0.9817	-1.487	0.747
0.4770	0.9638	-1.609	0.836	0.9600	-1.723	0.772
0.5875	0.9403	-1.713	0.865	0.9368	-1.865	0.796
0.7081	0.9153	-1.518	0.892	0.9122	-1.728	0.821
0.8407	0.8893	-1.048	0.910	0.8860	-1.218	0.835
1.0000	0.8593		0.898	0.8552		0.824
	Hexyl acetate (1) + Bromobenzene (2)					
x_1	***T*/K = 298.15**			***T*/K = 303.15**		
0.0000	1.4880		1.114	1.4816		1.008
0.0667	1.4255	-0.021	1.136	1.4220	-0.230	1.021
0.1375	1.3685	-0.418	1.148	1.3656	-0.679	1.029
0.2147	1.3130	-1.062	1.158	1.3092	-1.248	1.039
0.2981	1.2586	-1.894	1.165	1.2550	-2.099	1.047
0.3873	1.2030	-2.631	1.169	1.2000	-2.900	1.051
0.4842	1.1440	-3.078	1.171	1.1421	-3.476	1.054
0.5941	1.0789	-3.099	1.168	1.0770	-3.508	1.050
0.7152	1.0098	-2.509	1.157	1.0072	-2.825	1.036
0.8477	0.9391	-1.334	1.132	0.9361	-1.574	1.011
1.0000	0.8676		1.071	0.8635		0.960
x_1	***T*/K = 308.15**			***T*/K = 313.15**		
0.0000	1.4752		0.947	1.4689		0.892
0.0667	1.4161	-0.256	0.956	1.4120	-0.415	0.897
0.1375	1.3609	-0.795	0.965	1.3575	-1.014	0.903
0.2147	1.3053	-1.432	0.972	1.3026	-1.718	0.909
0.2981	1.2518	-2.353	0.978	1.2489	-2.629	0.913
0.3873	1.1973	-3.212	0.982	1.1934	-3.388	0.915
0.4842	1.1393	-3.784	0.984	1.1355	-3.966	0.913
0.5941	1.0743	-3.831	0.980	1.0729	-4.312	0.908
0.7152	1.0043	-3.115	0.969	1.0061	-4.083	0.896
0.8477	0.9330	-1.817	0.945	0.9355	-2.986	0.872
1.0000	0.8593		0.898	0.8552		0.824

Table 1. (cont.)

Hexyl acetate (1) + Fluorobenzene (2)						
x_1	***T*/K = 298.15**			***T*/K = 303.15**		
0.0000	1.0180		0.564	1.0128		0.514
0.0602	1.0032	-0.043	0.616	0.9986	-0.091	0.559
0.1243	0.9890	-0.110	0.664	0.9845	-0.161	0.603
0.1959	0.9746	-0.192	0.713	0.9703	-0.257	0.648
0.2740	0.9601	-0.252	0.763	0.9557	-0.296	0.691
0.3627	0.9455	-0.351	0.813	0.9412	-0.397	0.735
0.4592	0.9312	-0.451	0.864	0.9272	-0.528	0.779
0.5693	0.9163	-0.513	0.918	0.9121	-0.551	0.823
0.6926	0.9010	-0.497	0.972	0.8968	-0.519	0.869
0.8358	0.8850	-0.400	1.030	0.8810	-0.440	0.917
1.0000	0.8676		1.071	0.8635		0.960
x_1	***T*/K = 308.15**			***T*/K = 313.15**		
0.0000	1.0069		0.494	1.0014		0.460
0.0602	0.9934	-0.144	0.533	0.9884	-0.181	0.495
0.1243	0.9794	-0.210	0.569	0.9748	-0.277	0.526
0.1959	0.9656	-0.334	0.606	0.9610	-0.390	0.559
0.2740	0.9514	-0.406	0.645	0.9469	-0.462	0.595
0.3627	0.9368	-0.481	0.684	0.9324	-0.535	0.630
0.4592	0.9228	-0.596	0.726	0.9185	-0.649	0.668
0.5693	0.9077	-0.599	0.766	0.9035	-0.650	0.706
0.6926	0.8926	-0.577	0.813	0.8886	-0.642	0.748
0.8358	0.8770	-0.508	0.858	0.8730	-0.554	0.787
1.0000	0.8593		0.898	0.8552		0.824
Hexyl acetate (1) + Nitrobenzene (2)						
x_1	***T*/K = 298.15**			***T*/K = 303.15**		
0.0000	1.1981		1.838	1.1934		1.625
0.0643	1.1684	-0.308	1.816	1.1654	-0.463	1.602
0.1334	1.1412	-0.877	1.776	1.1385	-1.071	1.573
0.2078	1.1144	-1.536	1.728	1.1110	-1.670	1.531
0.2905	1.0856	-2.142	1.667	1.0819	-2.251	1.480
0.3804	1.0545	-2.537	1.594	1.0506	-2.626	1.418
0.4778	1.0217	-2.714	1.513	1.0177	-2.790	1.344
0.5889	0.9854	-2.584	1.421	0.9815	-2.669	1.261
0.7099	0.9477	-2.097	1.321	0.9440	-2.204	1.176
0.8468	0.9082	-1.268	1.209	0.9049	-1.432	1.075
1.0000	0.8676		1.071	0.8635		0.960
x_1	***T*/K = 308.15**			***T*/K = 313.15**		
0.0000	1.1883		1.517	1.1838		1.395
0.0643	1.1617	-0.589	1.486	1.1590	-0.760	1.364
0.1334	1.1353	-1.251	1.450	1.1324	-1.416	1.330
0.2078	1.1083	-1.911	1.408	1.1050	-2.046	1.294
0.2905	1.0790	-2.481	1.359	1.0754	-2.593	1.250
0.3804	1.0470	-2.782	1.304	1.0432	-2.876	1.198
0.4778	1.0140	-2.934	1.241	1.0110	-3.134	1.139
0.5889	0.9786	-2.922	1.166	0.9758	-3.160	1.070
0.7099	0.9417	-2.554	1.084	0.9388	-2.787	0.995
0.8468	0.9025	-1.776	0.994	0.8999	-2.066	0.910
1.0000	0.8593		0.898	0.8552		

The results of V^E, ΔG^{*E}, ΔK_S, L_f^E, π_i^E, V_f^E, and Z^E versus the mole fraction x_1 are graphically represented in Figures (1-7). The calculated values of these excess or deviation functions of the mixtures were fitted to Redlich- Kister[14] polynomials of the form

$$Y^E = x_1 x_2 \sum_{k=0} A_k (x_1 - x_2)^k \qquad (9)$$

where A_k are the adjustable parameters obtained by a least squares fit method and k is the degree of the polynomial equation. Table 3 lists the parameters with the standard deviations σ. The coefficients A_k's were used to calculate the solid curves of Figures 1-8. The standard deviations σ are defined as

$$\sigma = \left[\frac{\sum \left(Y^E_{expt} - Y^E_{calc} \right)^2}{(D - N)} \right]^{0.5} \qquad (10)$$

where

D and N are the number of experimental data and equation parameters respectively.

The V^E against x_1 plots of the studied binary systems at (298.15, 303.15, 308.15 and 313.15) K are shown in Figure 1. The V^E values are negative over the whole composition range. Excess molar volumes reflect the type of interactions involving in the mixtures. For hexyl acetate + bromobenzene and hexyl acetate + nitrobenzene the negative values of V^E are large in magnitude as compared to those for hexyl acetate + fluorobenzene for which the V^E values are less in magnitude and follow the order

$$BrPh > O_2NPh > ClPh > FPh$$

The V^E values at other higher temperatures follow the same trends but with different values. It is observed that there is an effect of temperature on V^E as these values increase systematically with increase in temperature. These negative values indicate the strong attractive forces involving between the liquid components. The large negative V^E for the systems of bromobenzene and nitrobenzene may be attributed to the differences in dipole moments of the liquid components leading to dipole-induced dipole interactions resulting in the formation of electron donor-acceptor complexes.[17,18] No published data was found for the present systems with which to compare our results. However comparing the present results with our earlier published data of V^E for binary mixtures of aryl halides with several esters,[13] it was found that the same trends were followed by the systems of bromobenzene and nitrobenzene. This further confirms that the large negative V^E values for bromobenzene and nitrobenzene may be due to the differences in the dipole moments of the pure components.

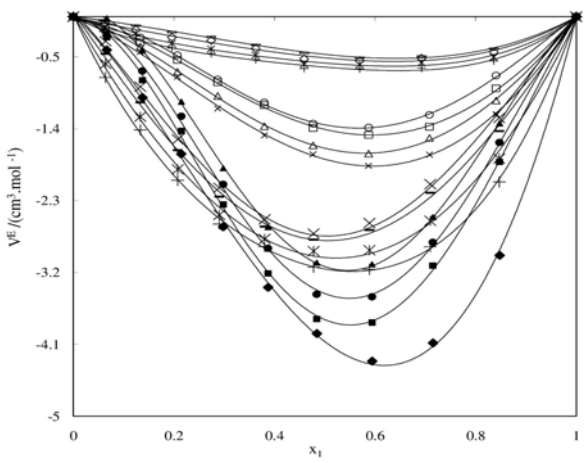

Figure 1. Curves of excess volumes V^E versus mole fraction x_1 for the binary mixtures of hexyl acetate + chlorobenzene at (o, 298.15 ; □ , 303.15; Δ, 308.15; x, 313.15) K, hexyl acetate + bromobenzene at (▲, 298.15; ●, 303.15; ■, 308.15; ◆, 313.15) K, hexyl acetate + fluorobenzene at (▭, 298.15; ◇, 303.15; ✳, 308.15; + , 313.15) and hexyl acetate nitrobenzene at (X**,** 298.1; -, 303.15; ✳, 308.15; +,313.15) K

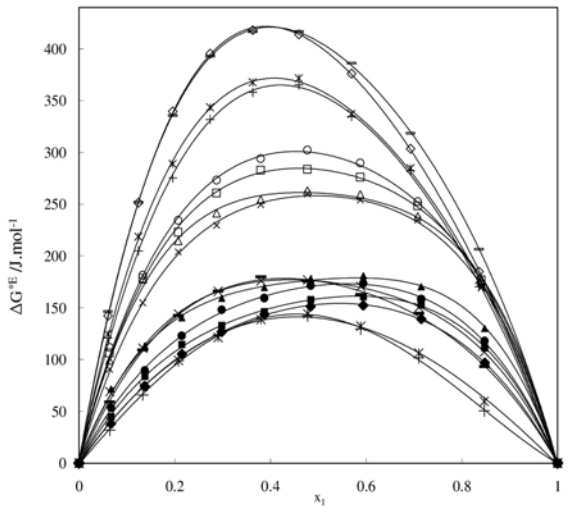

Figure 2. Curves of excess free energy of activation of viscous flow ΔG^{*E} versus mole fraction x_1 for the binary mixtures of hexyl acetate + chlorobenzene at (o, 298.15;□, 303.15; Δ, 308.15; x, 313.15) K, hexyl acetate + bromobenzene at (▲, 298.15; ●, 303.15; ■, 308.15; ◆, 313.15) K, hexyl acetate + fluorobenzene at (▭, 298.15; ◇ , 303.15; ✳ , 308.15; + , 313.15) K and hexyl acetate + nitrobenzene at (X , 298.15; -,303.15; ✳, 308.15; + , 313.15) K.

The plots of ΔG^E versus x_1 at (298.15, 303.15, 308.15 and 313.15) K are displayed in Figure 2, It is observed that the variation of ΔG^E is completely positive over the entire composition range of the mixtures. This indicates the existence of specific interactions in the liquid mixtures. The magnitude of ΔG^E is an excellent indicator of the strength of specific interactions in liquid mixtures.[19,20] Figure 3 shows the variation of ΔK_S with mole fraction x_1 of hexyl acetate. The ΔK_S values of chlorobenzene exhibit positive deviations. For bromobenzene the ΔK_S values are slightly positive in lower mole fraction of ester (x_1=0.2).

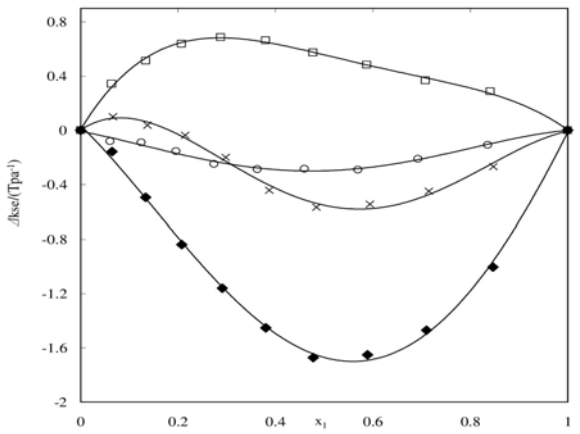

Figure 3. Deviations in isentropic compressibility ΔKs versus mole fraction x_1 for the binary mixtures of hexyl acetate + chlorobenzene at (□, 303.15) K, hexyl acetate + bromobenzene at (X, 303.15) K, hexyl acetate + fluorobenzene at (o, 303.15) K and hexyl acetate + nitrobenzene at (◆, 303.15) K.

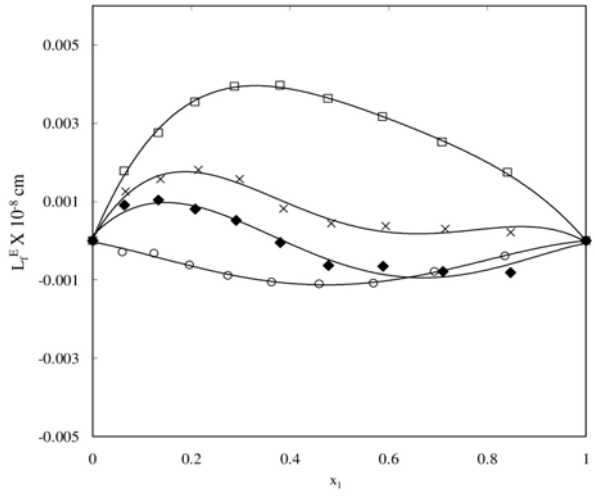

Figure 4. Plots of excess intermolecular free length L_f^E versus mole fraction x_1 for the binary mixtures of hexyl acetate + chlorobenzene at (□, 303.15) K, hexyl acetate + bromobenzene at (X, 303.15) K, hexyl acetate + fluorobenzene at (o, 303.15) K and hexyl acetate + nitrobenzene at (◆, 303.15) K.

However, ΔK_S becames negative as the composition of ester increases (x_1>0.2). While for fluorobenzene and nitrobenzene the ΔK_S values are completely negative over the entire composition range. The variation of the excess intermolecular free length, L_f^E versus x_1 displayed in Figure 4, shows a positive deviation in L_f^E for mixtures of chlorobenzene and bromobenzene. While for the mixtures of fluorobenzene the L_f^E values are completely negative. Where as for nitrobenzene the L_f^E values exhibit positive deviation upto x_1=0.38, but as the composition of ester increases (x_1>0.38) these values become negative. The intermolecular free length, L_f in binary liquid mixtures can be used to assess the attraction between the component molecules. These values in a binary mixture depend on concentration. For a given binary system the intermolecular free length increases with increase in concentration of ester.

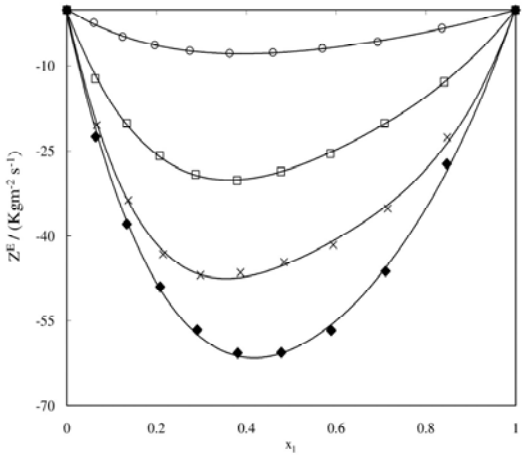

Figure 5. Plots of excess specific acoustic impedance Z^E versus mole fraction x_1 for the binary mixtures of hexyl acetate + chlorobenzene at (□, 303.15) K, hexyl acetate + bromobenzene at (X, 303.15) K, hexyl acetate + fluorobenzene at (o, 303.15) K and hexyl acetate + nitrobenzene at (◆, 303.15) K.

The dependence of excess acoustic impedance with mole fraction x_1 is shown in Figure 5, wherein it is observed that Z^E values for all the studied systems exhibit negative deviation over the entire range of composition. The Z^E values of nitrobenzene are large negative, while these values are small negative for fluorobenzene and follow the order

$$O_2NPh > BrPh > ClPh > FPh$$

The results of the excess internal pressure, π_i^E versus mole fraction x_1 at 303.15 K are displayed in Figure 6. For the systems of chlorobenzene, bromobenzene and fluorobenzene positive π_i^E is observed, while for nitrobenzene the π_i^E values exhibit negative deviations.

The results of excess free volume, V_f^E as a function of mole fraction x_1 at 303.15 K are presented in Figure 7. Like Z^E the V_f^E values are completely negative over the entire range of composition. The V_f^E values are small negative for bromobenzene, while for fluorobenzene they are large negative and follow the order

$$FPh > ClPh > O_2NPh > BrPh$$

Viscosity Models and Interaction Parameters

The experimental viscosities of mixtures have been correlated with the one-parameter model proposed by Frenkel and three-parameter model proposed by McAllister four–body interaction. The equations of these models are

Frenkel model:

$$\log \eta = x_1^2 \log \eta_1 + x_2^2 \log \eta_2 + 2x_1x_2 \log \eta_{12} \qquad (11)$$

where η is the viscosity coefficient, x_1 and x_2 are the mole fractions and η_{12} is the interaction parameter.

Table 2. Values of Speed of sound u, isentropic compressibility K_S, intermolecular free length L_f and internal pressure π_i, free volume V_f and specific acoustic impedance Z of binary liquid mixtures.

x_1	u, m.s^{-1}	K_S, Tpa^{-1}	L_f x 10^{-8}cm	π_i x10^6 Nm^{-2}	V_f x10^{-6} m^{3}mol^{-1}	Z, Kgm^{-2}s^{-1}
Hexyl acetate (1) + Chlorobenzene (2)						
x_1	T/K = 303.15					
0.0000	1246	588	0.5034	3.36	0.320	1365.4
0.0635	1242	604	0.5101	3.34	0.301	1333.0
0.1334	1239	619	0.5165	3.31	0.288	1303.2
0.2071	1236	635	0.5230	3.25	0.280	1274.2
0.2872	1233	651	0.5296	3.19	0.272	1245.7
0.3797	1230	669	0.5368	3.12	0.266	1215.5
0.4770	1227	687	0.5440	3.04	0.262	1186.4
0.5875	1224	708	0.5521	2.95	0.258	1154.6
0.7081	1221	730	0.5608	2.85	0.256	1122.0
0.8407	1218	755	0.5703	2.73	0.260	1087.4
1.0000	1216	783	0.5809	2.55	0.279	1050.0
Hexyl acetate (1) + Bromobenzene (2)						
x_1	T/K = 303.15					
0.0000	1138	521	0.4738	3.50	0.266	1686.1
0.0667	1142	540	0.4822	3.44	0.260	1623.2
0.1375	1146	558	0.4901	3.39	0.256	1565.0
0.2147	1151	577	0.4986	3.32	0.252	1506.2
0.2981	1155	597	0.5073	3.27	0.248	1449.5
0.3873	1161	618	0.5161	3.19	0.246	1393.2
0.4842	1168	642	0.5261	3.11	0.244	1333.4
0.5941	1176	671	0.5378	3.01	0.244	1266.6
0.7152	1188	704	0.5507	2.88	0.249	1196.1
0.8477	1201	741	0.5648	2.73	0.258	1124.3
1.0000	1216	783	0.5809	2.55	0.279	1050.0
Hexyl acetate (1) + Fluorobenzene (2)						
x_1	T/K = 303.15					
0.0000	1142	757	0.5711	3.43	0.352	1156.6
0.0602	1150	758	0.5714	3.41	0.328	1147.9
0.1243	1157	759	0.5720	3.38	0.310	1138.6
0.1959	1164	761	0.5724	3.33	0.295	1129.4
0.2740	1172	762	0.5729	3.26	0.285	1120.1
0.3627	1180	764	0.5736	3.17	0.278	1110.1
0.4592	1186	766	0.5745	3.07	0.273	1100.0
0.5693	1194	769	0.5756	2.96	0.270	1089.0
0.6926	1201	773	0.5771	2.84	0.270	1077.1
0.8358	1208	778	0.5789	2.70	0.272	1064.2
1.0000	1216	783	0.5809	2.55	0.279	1050.0

Table 2 (cont).

Hexyl acetate (1) + Nitrobenzene (2)						
x_1	T/K = 303.15					
0.0000	1438	405	0.4178	4.55	0.128	1716.1
0.0643	1416	428	0.4292	4.42	0.130	1650.8
0.1334	1396	451	0.4406	4.28	0.133	1589.3
0.2078	1376	475	0.4525	4.12	0.138	1528.7
0.2905	1355	503	0.4657	3.95	0.145	1466.0
0.3804	1335	534	0.4798	3.76	0.155	1402.0
0.4778	1314	569	0.4951	3.55	0.168	1337.3
0.5889	1291	611	0.5132	3.32	0.184	1267.1
0.7099	1268	659	0.5328	3.08	0.205	1197.0
0.8468	1243	715	0.5551	2.83	0.235	1124.8
1.0000	1216	783	0.5809	2.55	0.279	1050.0

Table 3. Coefficients of the Redlich-Kister Equation and Standard deviations for the Excess functions of Binary mixtures.

Function	T/K	A_0	A_1	A_2	σ
Hexyl acetate + Chlorobenzene					
V^E	298.15	-5.4063	-2.3712	2.9680	0.019
	303.15	-5.6285	-2.9548	1.6338	0.023
	308.15	-6.5757	-2.9874	1.9844	0.019
	313.15	-7.1378	-3.4807	1.0957	0.023
ΔG^{*E}	298.15	1194.65	-152.00	485.49	5.4
	303.15	1133.56	-99.70	589.25	4.3
	308.15	1042.33	-54.36	728.30	4.7
	313.15	1032.54	-11.44	559.50	2.8
ΔK_S	303.15	2.2277	-1.7165	2.1076	0.019
L_f^E	303.15	0.0142	-0.0080	0.0086	0.000
Z^E	303.15	-112.081	53.531	-45.071	0.384
π_i^E	303.15	0.2606	-0.0187	0.3137	0.004
V_f^E	303.15	-0.1520	-0.1520	-0.1200	0.001
Hexyl acetate + Bromobenzene					
V^E	298.15	-12.5120	-4.3492	11.0443	0.021
	303.15	-13.8476	-4.7303	10.0017	0.070
	308.15	-15.1538	-5.1778	9.9205	0.058
	313.15	-16.2728	-9.6783	0.9153	0.061
ΔG^{*E}	298.15	707.88	68.35	549.43	3.0
	303.15	686.60	99.88	307.11	2.0
	308.15	635.10	121.81	305.87	1.7
	313.15	613.67	86.94	155.53	1.6
ΔK_S	303.15	-2.2176	-1.5717	3.0225	0.033
L_f^E	303.15	0.0019	-0.0076	0.0128	0.000
Z^E	303.15	-178.462	69.181	-108.780	0.785
π_i^E	303.15	0.2866	0.0902	-0.1640	0.005
V_f^E	303.15	-0.1135	-0.0319	0.0219	0.001

Table 3 (cont).

Hexyl acetate + Fluorobenzene					
V^E	298.15	-1.8815	-1.3112	-0.1815	0.012
	303.15	-2.0599	-1.1687	-0.5188	0.027
	308.15	-2.3204	-1.0362	-1.0608	0.028
	313.15	-2.5212	-1.0091	-1.5458	0.025
ΔG^{*E}	298.15	1627.78	-528.16	525.25	2.8
	303.15	1611.65	-645.80	393.60	1.5
	308.15	1422.81	-456.27	370.08	3.4
	313.15	1425.13	-411.46	264.52	4.7
ΔK_S	303.15	-1.1909	0.2125	0.6402	0.019
L_f^E	303.15	-0.0045	0.0008	0.0025	0.000
Z^E	303.15	-29.953	12.301	-6.173	0.153
π_i^E	303.15	0.1601	-0.3151	0.2497	0.003
V_f^E	303.15	-0.1728	0.1066	-0.0904	0.001
Hexyl acetate + Nitrobenzen					
V^E	298.15	-10.9000	-0.5168	4.2507	0.085
	303.15	-10.9000	-0.5030	1.1008	0.089
	308.15	-10.9000	-1.2163	-4.4278	0.203
	313.15	-10.9000	-1.6922	-7.2208	0.302
ΔG^{*E}	298.15	703.09	-85.21	384.46	2.2
	303.15	702.78	-140.79	250.19	2.4
	308.15	565.87	-107.18	-43.00	2.3
	313.15	569.60	-133.71	-166.81	1.6
ΔK_S	303.15	-6.6933	-2.0456	1.5726	0.043
L_f^E	303.15	-0.0023	-0.0086	0.0081	0.000
Z^E	303.15	-239.977	69.002	-59.020	1.183
π_i^E	303.15	-0.1815	-0.1449	0.0945	0.004
V_f^E	303.15	-0.1310	-0.0220	-0.0313	0.000

Table 4. Adjustable Parameters and Standard Percentage Deviations of Viscosity Models for Binary Liquid Mixtures

***T*/K**	**Frenkel**		**McAllister (Four - body)**			
	η_{12}	100σ	υ_{1112}	υ_{1122}	υ_{2221}	100σ
Hexyl acetate (1) + Chlorobenzene (2)						
298.15	0.1122	0.07	0.2134	0.0071	-0.0479	0.02
303.15	0.0048	0.07	0.1230	-0.1061	-0.1346	0.02
308.15	-0.0693	0.09	0.0712	-0.1915	-0.1877	0.02
313.15	-0.1559	0.07	-0.0217	-0.2451	-0.2811	0.01
Hexyl acetate (1) + Bromobenzene (2)						
298.15	0.2340	0.06	0.2187	0.1406	-0.0450	0.01
303.15	0.1203	0.06	0.0910	0.0694	-0.1743	0.01
308.15	0.0476	0.06	0.0250	0.0025	-0.2424	0.01
313.15	-0.0279	0.07	-0.0712	-0.0502	-0.3187	0.01
Hexyl acetate (1)+ Fluorobenzene (2)						
298.15	0.0272	0.17	0.1599	-0.0621	-0.1362	0.01
303.15	-0.0839	0.19	0.0304	-0.1455	-0.2355	0.01
308.15	-0.1776	0.13	-0.0272	-0.2146	-0.3180	0.01
313.15	-0.2669	0.11	-0.1141	-0.2791	-0.4074	0.02
Hexyl acetate (1)+ Nitrobenzene (2)						
298.15	0.4742	0.05	0.3635	0.3591	0.4894	0.01
303.15	0.3540	0.05	0.2351	0.2639	0.3641	0.01
308.15	0.2523	0.03	0.1321	0.2205	0.2531	0.01
313.15	0.1661	0.03	0.0367	0.1546	0.1629	0.01

McAllister four-body interaction model:

$$\ln \upsilon = x_1^4 \ln \upsilon_1 - 4x_1^3 x_2 \ln \upsilon_{1112} + 6x_1^2 x_2^2 \ln \upsilon_{1122} +$$

$$4x_1 x_2^3 \ln \upsilon_{2221} + x_2^4 \ln \upsilon_2 - \ln\left(x_1 + \frac{x_2 M_2}{M_1} \right) +$$

$$4x_1^3 x_2 \ln\left[\frac{\left\{ 3 + \frac{M_2}{M_1} \right\}}{4} \right] + 6x_1^2 x_2^2 \ln\left[1 + \frac{2M_2}{M_1} \right] +$$

$$+ 4x_1 x_2^3 \ln\left[\frac{\left\{ 1 + \frac{3M_2}{M_1} \right\}}{4} \right] + x_2^4 \ln\left[\frac{M_2}{M_1} \right] \qquad (12)$$

where υ, υ_1, υ_2 are the kinematic viscosities of binary mixtures and those of the pure components 1 and 2 respectively. υ_{1112}, υ_{1122} and υ_{2221} are the model parameters which are obtained by non-linear regression.

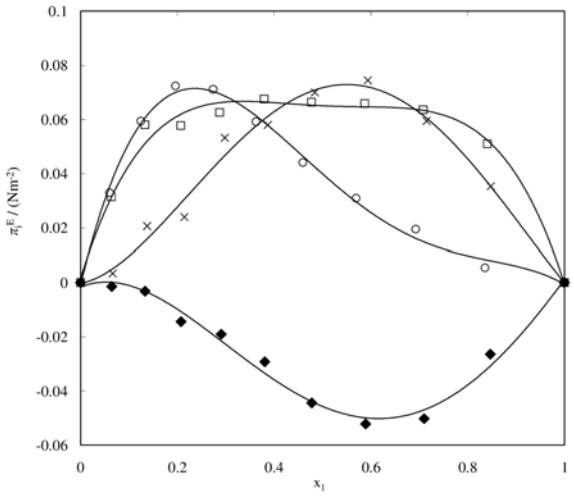

Figure 6. Plots of excess internal pressure π_i^E versus mole fraction x_1 for the binary mixtures of hexyl acetate + chlorobenzene at (□, 303.15) K, hexyl acetate + bromobenzene at (X, 303.15) K, hexyl acetate + fluorobenzene at (o, 303.15) K and hexyl acetate + nitrobenzene at (◆ , 303.15) K.

The interaction parameters and standard percentage deviations σ(%) of the Frenkel and McAllister models at (298.15, 303.15, 308.15 and 313.15) K for the studied mixtures are presented in Table 4. It is clear that both the models are suitable for correlating the viscosities of the binary mixtures. However, as compared to one-parameter model of Frenkel, the McAllister's 3-parameter model gave very low σ(%) values. Thus it can be concluded that the McAllister model predicts the mixture viscosities of the studied binary mixtures more satisfactorily.

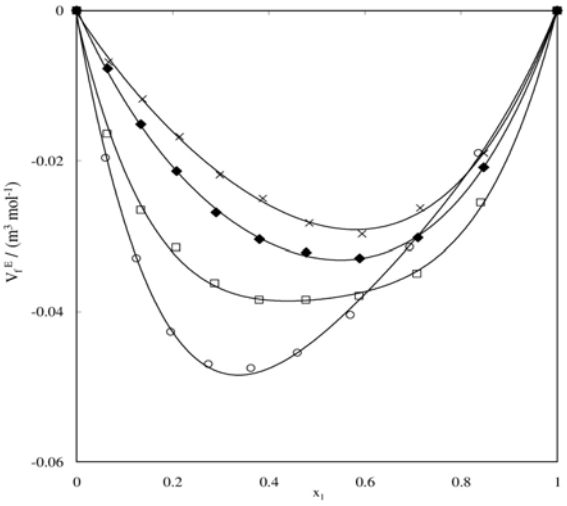

Figure 7. Plots of excess free volume V_f^E versus mole fraction x_1 for the binary mixtures of hexyl acetate + chlorobenzene at (□, 303.15) K, hexyl acetate + bromobenzene at (X, 303.15) K, hexyl acetate + fluorobenzene at (o, 303.15) K and hexyl acetate + nitrobenzene at (◆ , 303.15) K.

Conclusion

Densities, viscosities for the binary mixtures of hexyl acetate with chlorobenzene, bromobenzene, fluorobenzene and nitrobenzene have been measured at (298.15, 303.15, 308.15 and 313.15) K. While the speed of sound for these mixtures have been measured at 303.15 K. From the measured density and viscosity values, excess volume and excess free energy of activation were calculated at the respective temperatures.

From the speed of sound data isentropic compressibility K_S, intermolecular free length L_f, specific acoustic impedance Z, internal pressure π_i, free volume V_f and their corresponding excess properties (ΔK_S, L_f^E, Z^E, π_i^E, V_f^E) have been calculated at 303.15 K. The excess or deviation values were correlated using the Redlich-Kister Polynomial equation to obtain their coefficients and standard deviations. It has been observed that negative deviations were observed for excess volumes and positive deviations were observed for the excess free energy of activation of viscous flow. While the acoustic properties exhibit both positive and negative deviations for the studied mixtures. It was observed that the studied viscosity models exhibit the standard deviation values within the range of experimental errors. Better results for McAllister equation are due to number of experimental parameters.

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