Role of substituent on benzene ring and their importance on thermodynamic properties

L.Venkatramana[1], K.Sreenivasulu[2], K.Sivakumar,[2] K. Dayananda Reddy[*1]

[1] Department of Chemistry, P.V.K.N.Govt. Degree & P.G. College, Chittoor-517001, A.P., India.
[2] Department of Chemistry, S.V.Arts Degree & P.G.College (T.T.D'S), Tirupati-517502, A.P., India.

Abstract

Densities (ρ) of pure liquids and their mixtures have been measured at 298.15 K to 313.15 K and atmospheric pressure over the entire composition range for the binary mixtures of benzyl alcohol with benzene, toluene, chlorobenzene, bromobenzene and nitrobenzene by using Rudolph Research Analytical Digital densitometer (DDM-2911 model). Further, the ultrasonic sound velocities for the above said mixtures were also measured at 303.15 K and 313.15 K. The measured density data were used to compute excess molar volumes (V^E) and these were compared with Hwang equations. Isentropic compressibility (k_s) and excess isentropic compressibilities (k_s^E) were evaluated from experimental sound velocity and density data. Moreover, the experimental sound velocities were analyzed in terms of theoretical models namely collision factor theory (CFT) and free length theory (FLT). The experimental results were discussed in terms of intermolecular interactions between component molecules.

Keywords: Density, excess volume, sound velocity, Theoretical analysis, molecular interaction.

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*Corresponding Author

K. Dayananda Reddy, Department of Chemistry, P.V.K.N.Govt. Degree & P.G. College, Chittoor-517001, A.P., India. E-mail: ramanapvkn@gmail.com

1 Introduction

For many years the chemical industry has recognized the importance of thermodynamic and physical properties in design calculations involving chemical separations, fluid flow, and heat transfer. The study of molecular interaction in the liquid mixtures is of considerable in the elucidation of the structural properties of the molecules. The intermolecular interactions influence the structural arrangement along with the shape of the molecules. The sign and magnitude of these properties guide us to understand possible interactions between the component molecules [1-4]. Fundamental thermodynamic and thermo physical properties are the essential sources of information that necessary for a better understanding of the non-ideal behavior of complex systems because of physical and chemical effects, which are caused by molecular interactions ,intermolecular forces etc., of unlike molecules. The knowledge of the structure and molecular interactions of liquid mixtures are very important from fundamental and engineering point of view. From a practical point of consideration, these properties are necessary for the development of thermodynamic models required in adequate and optimized processes of the chemical, petro chemical, pharmaceutical, and other industries. In addition, extensive information about structural phenomena of mixtures is of essential importance in development of theories of the liquid state and predictive method. The experimental data on macroscopic properties such as excess molar volumes, excess viscosities, surface tension and refractive index are often useful to understand the nature of homo and hetero molecular interactions, between component molecules. A survey of the literature as shown that excess volume and ultrasonic sound velocity data for the binary mixtures of benzylalcohol with benzene, chlorobenzene, nitrobenzene and benzonitrile were reported at 303.15 K [5]**.** In the present study, densities (ρ) of pure liquids and their mixtures namely benzylalcohol with benzene, toluene, chlorobenzene bromobenzene, and nitrobenzene were measured over the entire composition range at 298.15 K, 303.15 K, 308.15

K and 313.15 K and ultrasonic sound velocity data at 303.15 K and 313.15 K. From these data excess volumes (V^E) and excess isentropic compressibility (k_s^E) were calculated. Further, the experimental the sound velocity data were compared with various theories namely collision factor theory (CFT) and free length theory (FLT). The organic liquids that were chosen in the present investigation are having many industrial applications. Benzyl alcohol is a versatile compound used as a solvent for gelatin, cellulose acetate, shellac and for pharmaceutical aid as an antimicrobial agent [6]. Further, benzyl alcohol is also used in perfumery, in microscopy as an embedding material, and in veterinary applications [7]. Commercial use of benzene and toluene includes synthesis of different intermediate compounds during the process of manufacture of plastics, dyestuffs, detergents and insecticides [8, 9]. The major use of chlorobenzene is an intermediate in the production of commodities such as herbicides, dye stuffs and rubber. Bromobenzene is an important compound in the preparation of Grignard reagent and also an ingredient in the manufacture of phenylcyclidine [10, 11].The largest end use for nitrobenzene is in the production of aniline, p-aminophenol, nigrosine dyes, dyestuffs and resins. The present work was under taken to know the influence of various substituents on benzene ring that may influence both the sign magnitude of excess volume and isentropic compressibility.

2 Experimental

2.1 Materials

All the chemicals used in the present work were of analytical reagent grade procured from (S.D.Fine chemicals Ltd.,India and Merck and their purities were as follows: benzyl alcohol 99.7%, benzene 99.5%, toluene 99.5%,chlorobenzene 99.8%, bromobenzene 99.5% and nitrobenzene 99.7% . Prior to experimental measurements, all the liquids were purified as described in the literature [12, 13]. The purity samples were attained by fractional distillation and the purity of chemicals were checked by comparing the measured densities and ultrasonic

sound velocity, which were in good agreement with literature values [5, 14-17] and these are given in Table 1. The purity of the sample was further confirmed by GLC single sharp peak. Before use, the chemicals were stored over 0.4nm molecular sieves for about 72hrs to remove water and were later degassed.

2.2 Apparatus and procedure

All the binary liquid mixtures are prepared by weighing an appropriate amount of pure liquids an electronic balance (Afoset, ER –120A, India) with a precision of ±0.1 mg by syringing each component into airtight stopper bottles to minimize evaporation losses.

Table 1 Densities (ρ) and sound velocity (u) of pure components at 303.15 K.

Component	ρ (g cm^{-3})		u (ms^{-1})	
	Present work	Literature	Present work	Literature
Benzyl alcohol	1.03760	1.03700[5]	1514	1511[5]
Benzene	0.86855	0.86850[14]	1274	1276[14]
Toluene	0.85264	0.85260[15]	1277	1278[15]
Bromobenzene	1.48156	1.48150[14]	1140	1138[14]
Chlorobenzene	1.09553	1.09550[16]	1250	1252[14]
Nitrobenzene	1.19345	1.19341[17]	1446	1444[17]

Ref:[5], Ref:[14], Ref:[15], Ref:[16], Ref:[17]

The uncertainty of the mole fraction was ± 1 × 10^{-4}. After mixing the sample, the bubble free homogenous sample was transferred into the U-tube of the densimeter through a syringe. The density measurements were performed with a Rudolph Research Analytical digital densimeter (DDM-2911 Model), equipped with a built-in solid-state thermostat and a resident program with accuracy of temperature of 303.15 K ±0.03 K. The uncertainty density measurement liquid mixtures are ±2×10^{-5} gm.cm^{-3}. Proper calibrations at each temperature were achieved with doubly distilled, deionized water and with air as standards. A multi frequency ultrasonic interferometer (M-82 Model, Mittal Enterprise, New Delhi, India)

operated at 2 MHz, was used to measure the ultrasonic velocities of the binary liquid mixtures at temperatures, at 303.15K and 313.15 K by using a digital constant temperature water bath. The uncertainty in the measurement of ultrasonic sound velocity is ±0.3%. The temperature stability is maintained within ± 0.01 K by circulating thermostatic water bath around the cell with a circulating pump. In order to minimize the uncertainty of the measurement, several maxima are allowed to pass and their number (50) in the present study is counted. All maxima are recorded with the highest swing of the needle on the micrometer scale. The total distance d (cm) moved by the reflector is given by $d= n\lambda/2$, where λ is the wave length. The frequency, ν, of the crystal being accurately known (2.0 MHz), the speed of sound, u in ms^{-1} is calculated by using the relation $u= \nu\lambda$. The working of the interferometer was tested by making measurements for pure samples of benzyl alcohol, benzene, toluene, chlorobenzene, bromobenzene and nitrobenzene and the measured sound velocities of these liquids are in good agreement which was reported in the literature [18].

3 Results and discussion

The measured densities of pure liquids and their mixtures were given in Table 2 for all the binary mixtures of benzylalcohol with benzene, toluene, chlorobenzene, bromobenzene and nitrobenzene at temperature range from 298.15 to 313.15 K. The excess molar volume (V^E) of all the binary mixtures were calculated from the measured densities using the following equation.

$$V^E/cm^3.mol^{-1} = [x_1M_1 + x_2M_2]/\rho_m - [x_1M_1/\rho_1 + x_2M_2/\rho_2] \quad (1)$$

where, x_i is the mole fraction of component i(i=1,2) in the mixture; M_i is the molar mass ρ and ρ_i are the measured density of the mixture and the pure component i, respectively. The computed V^E data was also given in Table 2 along with predicted in terms of Hwang equation

[19].The methods and calculation of V^E in terms of Hwang equation were described earlier [20-22].

Table 2

Mole fraction of benzylalcohol (x_1), densities (ρ), excess volumes (V^E) and predicted excess molar volumes (Hwang) at T= 298.15 K to 313.15 K for the binary mixtures of benzylalcohol with benzene and substituted benzenes

x_1	P ($gm.cm^{-3}$)	V^E(Experimental) $cm^3\ mol^{-1}$	V^E(Hwang)
Benzyl alcohol (1)+Benzene (2)			
		T=298.15 K	
0.0743	0.88816	-0.003	-0.006
0.1198	0.89688	-0.016	-0.013
0.1624	0.90490	-0.025	-0.021
0.2323	0.91781	-0.038	-0.035
0.2837	0.92712	-0.047	-0.046
0.3566	0.94005	-0.057	-0.059
0.4828	0.96171	-0.068	-0.073
0.5904	0.97946	-0.069	-0.074
0.6784	0.99351	-0.064	-0.066
0.7390	1.00295	-0.058	-0.057
0.7997	1.01218	-0.047	-0.046
0.8574	1.02080	-0.035	-0.033
0.8936	1.02613	-0.027	-0.024
0.9362	1.03232	-0.017	-0.015
0.9587	1.03551	-0.006	-0.009
		T=303.15 K	
0.0743	0.88290	-0.006	-0.009
0.1198	0.89170	-0.021	-0.018
0.1624	0.89977	-0.030	-0.026
0.2323	0.91280	-0.045	-0.041
0.2837	0.92220	-0.055	-0.052
0.3566	0.93524	-0.065	-0.065
0.4828	0.95710	-0.076	-0.079
0.5904	0.97502	-0.077	-0.082
0.6784	0.98922	-0.073	-0.075
0.7390	0.99873	-0.065	-0.067
0.7997	1.00808	-0.055	-0.055
0.8574	1.01682	-0.045	-0.042
0.8936	1.02219	-0.035	-0.032
0.9362	1.02842	-0.022	-0.020
0.9587	1.03165	-0.011	-0.013
		T=308.15 K	
0.0743	0.87768	-0.015	-0.018
0.1198	0.88652	-0.029	-0.028
0.1624	0.89468	-0.040	-0.037

0.2323	0.90779	-0.053	-0.049
0.2837	0.91725	-0.062	-0.058
0.3566	0.93041	-0.073	-0.068
0.4828	0.95246	-0.084	-0.080
0.5904	0.97057	-0.087	-0.085
0.6784	0.98491	-0.082	-0.085
0.7390	0.99454	-0.076	-0.080
0.7997	1.00399	-0.065	-0.072
0.8574	1.01281	-0.054	-0.059
0.8936	1.01826	-0.046	-0.049
0.9362	1.02458	-0.034	-0.032
0.9587	1.02785	-0.024	-0.022
		T=313.15 K	
0.0743	0.87768	-0.015	-0.024
0.1198	0.87242	-0.022	-0.025
0.1624	0.88137	-0.040	-0.035
0.2323	0.88957	-0.050	-0.048
0.2837	0.90280	-0.065	-0.063
0.3566	0.91234	-0.074	-0.071
0.4828	0.92561	-0.085	-0.082
0.5904	0.94788	-0.098	-0.093
0.6784	0.96614	-0.098	-0.097
0.7390	0.98061	-0.093	-0.094
0.7997	0.99035	-0.086	-0.089
0.8574	0.99988	-0.074	-0.079
0.8936	1.00880	-0.062	-0.065
0.9362	1.01424	-0.047	-0.053
0.9587	1.02064	-0.035	-0.035
		Benzylalcohol (1)+Toluene (2)	
		T=298.15 K	
0.1066	0.88221	-0.016	-0.020
0.1585	0.89138	-0.030	-0.030
0.2116	0.90077	-0.043	-0.041
0.2651	0.91026	-0.055	-0.050
0.3151	0.91913	-0.063	-0.058
0.3593	0.92698	-0.069	-0.064
0.4171	0.93725	-0.075	-0.071
0.5177	0.95517	-0.080	-0.079
0.6169	0.97288	-0.078	-0.079
0.7147	0.99036	-0.069	-0.073
0.7675	0.99980	-0.061	-0.066
0.8111	1.00762	-0.054	-0.059
0.8644	1.01717	-0.043	-0.046
0.9062	1.02467	-0.033	-0.035
0.9556	1.03354	-0.021	-0.018
		T=303.15 K	
0.1066	0.87666	-0.020	-0.024
0.1585	0.88591	-0.035	-0.036
0.2116	0.89540	-0.050	-0.047
0.2651	0.90496	-0.061	-0.056

0.3151	0.91392	-0.070	-0.065
0.3593	0.92185	-0.077	-0.075
0.4171	0.93223	-0.083	-0.079
0.5177	0.95034	-0.088	-0.087
0.6169	0.96825	-0.087	-0.088
0.7147	0.98593	-0.078	-0.083
0.7675	0.99550	-0.071	-0.076
0.8111	1.00340	-0.062	-0.068
0.8644	1.01308	-0.051	-0.055
0.9062	1.02066	-0.040	-0.042
0.9556	1.02963	-0.025	-0.022
		T=308.15 K	
0.1066	0.87294	-0.026	-0.030
0.1585	0.88219	-0.042	-0.043
0.2116	0.89167	-0.056	-0.054
0.2651	0.90123	-0.068	-0.064
0.3151	0.91018	-0.077	-0.073
0.3593	0.91809	-0.083	-0.077
0.4171	0.92847	-0.089	-0.084
0.5177	0.94658	-0.096	-0.092
0.6169	0.96448	-0.095	-0.095
0.7147	0.98216	-0.086	-0.091
0.7675	0.99172	-0.078	-0.085
0.8111	0.99962	-0.070	-0.077
0.8644	1.00930	-0.059	-0.063
0.9062	1.01687	-0.046	-0.048
0.9556	1.02583	-0.030	-0.026
		T=313.15 K	
0.1066	0.86833	-0.035	-0.034
0.1585	0.87761	-0.050	-0.051
0.2116	0.88713	-0.065	-0.063
0.2651	0.89671	-0.075	-0.073
0.3151	0.90570	-0.084	-0.082
0.3593	0.91368	-0.094	-0.088
0.4171	0.92412	-0.102	-0.095
0.5177	0.94231	-0.108	-0.103
0.6169	0.96030	-0.106	-0.107
0.7147	0.97809	-0.098	-0.102
0.7675	0.98770	-0.089	-0.096
0.8111	0.99568	-0.084	-0.088
0.8644	1.00539	-0.069	-0.073
0.9062	1.01300	-0.055	-0.056
0.9556	1.02196	-0.033	-0.030
		Benzylalcohol (1)+ Bromobenzene(2)	
		T=298.15 K	
0.1277	1.43250	-0.029	-0.032
0.1722	1.41302	-0.043	-0.043
0.2221	1.39109	-0.056	-0.055
0.2627	1.37321	-0.066	-0.064
0.3032	1.35534	-0.075	-0.072

0.4133	1.30651	-0.090	-0.089
0.5233	1.25745	-0.098	-0.098
0.6544	1.19859	-0.094	-0.095
0.7249	1.16678	-0.086	-0.087
0.7669	1.14776	-0.078	-0.080
0.8091	1.12862	-0.070	-0.071
0.8430	1.11321	-0.061	-0.062
0.8743	1.09896	-0.052	-0.053
0.9137	1.08099	-0.040	-0.038
0.9503	1.06423	-0.023	-0.023
		T=303.15 K	
0.1277	1.42605	-0.033	-0.036
0.1722	1.40671	-0.047	-0.047
0.2221	1.38496	-0.061	-0.060
0.2627	1.36723	-0.072	-0.069
0.3032	1.34949	-0.081	-0.077
0.4133	1.30103	-0.098	-0.095
0.5233	1.25232	-0.106	-0.105
0.6544	1.19385	-0.102	-0.103
0.7249	1.16226	-0.095	-0.096
0.7669	1.14334	-0.086	-0.088
0.8091	1.12431	-0.076	-0.078
0.8430	1.10900	-0.068	-0.069
0.8743	1.09482	-0.057	-0.059
0.9137	1.07695	-0.044	-0.044
0.9503	1.06030	-0.028	-0.027
		T=308.15 K	
0.1277	1.41974	-0.038	-0.043
0.1722	1.40058	-0.055	-0.055
0.2221	1.37901	-0.071	-0.068
0.2627	1.36139	-0.081	-0.078
0.3032	1.34376	-0.089	-0.085
0.4133	1.29564	-0.107	-0.102
0.5233	1.24725	-0.115	-0.112
0.6544	1.18915	-0.110	-0.112
0.7249	1.15774	-0.102	-0.105
0.7669	1.13895	-0.094	-0.098
0.8091	1.12003	-0.084	-0.088
0.8430	1.10482	-0.076	-0.078
0.8743	1.09071	-0.065	-0.067
0.9137	1.07294	-0.051	-0.051
0.9503	1.05638	-0.034	-0.032
		T=313.15 K	
0.1277	1.41354	-0.049	-0.050
0.1722	1.39446	-0.062	-0.064
0.2221	1.37303	-0.077	-0.078
0.2627	1.35556	-0.089	-0.087
0.3032	1.33807	-0.099	-0.096
0.4133	1.29031	-0.119	-0.113
0.5233	1.24222	-0.126	-0.124

0.6544	1.18451	-0.123	-0.122
0.7249	1.15328	-0.114	-0.115
0.7669	1.13459	-0.104	-0.107
0.8091	1.11577	-0.093	-0.097
0.8430	1.10064	-0.084	-0.087
0.8743	1.08661	-0.072	-0.075
0.9137	1.06894	-0.057	-0.056
0.9503	1.05244	-0.037	-0.035
	Benzylalcohol (1)+ Chlorobenzene (2)		
	T=298.15 K		
0.1016	1.09491	-0.035	-0.037
0.1512	1.09212	-0.052	-0.052
0.2028	1.08918	-0.066	-0.065
0.2274	1.08779	-0.073	-0.071
0.3037	1.08340	-0.089	-0.086
0.3526	1.08057	-0.097	-0.094
0.4042	1.07757	-0.103	-0.100
0.5044	1.07171	-0.112	-0.108
0.6042	1.06580	-0.111	-0.109
0.7037	1.05984	-0.102	-0.103
0.7446	1.05734	-0.093	-0.097
0.8028	1.05382	-0.083	-0.085
0.8474	1.05106	-0.069	-0.073
0.9016	1.04769	-0.050	-0.053
0.9529	1.04450	-0.031	-0.028
	T=303.15 K		
0.1016	1.08961	-0.039	-0.041
0.1512	1.08691	-0.057	-0.057
0.2028	1.08405	-0.071	-0.071
0.2274	1.08270	-0.079	-0.077
0.3037	1.07844	-0.095	-0.093
0.3526	1.07570	-0.105	-0.102
0.4042	1.07279	-0.112	-0.109
0.5044	1.06710	-0.122	-0.118
0.6042	1.06134	-0.122	-0.121
0.7037	1.05553	-0.113	-0.114
0.7446	1.05311	-0.106	-0.109
0.8028	1.04963	-0.092	-0.096
0.8474	1.04695	-0.079	-0.082
0.9016	1.04364	-0.058	-0.060
0.9529	1.04049	-0.035	-0.032
	T=308.15 K		
0.1016	1.08442	-0.049	-0.048
0.1512	1.08179	-0.065	-0.065
0.2028	1.07901	-0.078	-0.081
0.2274	1.07770	-0.085	-0.087
0.3037	1.07361	-0.105	-0.103
0.3526	1.07094	-0.113	-0.111
0.4042	1.06815	-0.123	-0.118
0.5044	1.06264	-0.133	-0.127

0.6042	1.05707	-0.134	-0.131
0.7037	1.05143	-0.125	-0.125
0.7446	1.04907	-0.117	-0.120
0.8028	1.04569	-0.103	-0.107
0.8474	1.04307	-0.088	-0.092
0.9016	1.03986	-0.067	-0.068
0.9529	1.03674	-0.039	-0.037
	T=313.15 K		
0.1016	1.07920	-0.056	-0.054
0.1512	1.07668	-0.075	-0.074
0.2028	1.07398	-0.087	-0.091
0.2274	1.07274	-0.097	-0.098
0.3037	1.06875	-0.115	-0.115
0.3526	1.06620	-0.126	-0.123
0.4042	1.06348	-0.135	-0.130
0.5044	1.05815	-0.147	-0.140
0.6042	1.05274	-0.148	-0.143
0.7037	1.04725	-0.138	-0.138
0.7446	1.04494	-0.129	-0.132
0.8028	1.04165	-0.114	-0.118
0.8474	1.03909	-0.098	-0.103
0.9016	1.03594	-0.075	-0.076
0.9529	1.03287	-0.044	-0.042
	Benzyl alcohol(1)+ Nitrobenzene(2)		
	T=298.15 K		
0.0409	1.19191	-0.031	-0.030
0.0996	1.18304	-0.066	-0.065
0.1481	1.17558	-0.084	-0.086
0.1988	1.16774	-0.098	-0.103
0.2561	1.15219	-0.113	-0.116
0.3509	1.13667	-0.129	-0.129
0.4356	1.12110	-0.136	-0.132
0.5275	1.11289	-0.135	-0.129
0.6459	1.10522	-0.121	-0.118
0.7207	1.09737	-0.104	-0.105
0.7613	1.08926	-0.095	-0.097
0.8257	1.08205	-0.081	-0.079
0.8562	1.07335	-0.069	-0.069
0.8934	1.06522	-0.053	-0.054
0.9409	1.05200	-0.034	-0.033
	T=303.15 K		
0.0409	1.18705	-0.036	-0.032
0.0996	1.17815	-0.063	-0.069
0.1481	1.17081	-0.086	-0.091
0.1988	1.16307	-0.104	-0.109
0.2561	1.14767	-0.123	-0.123
0.3509	1.13226	-0.138	-0.136
0.4356	1.11685	-0.15	-0.141
0.5275	1.10869	-0.148	-0.140
0.6459	1.10110	-0.136	-0.131

0.7207	1.09331	-0.120	-0.119
0.7613	1.08520	-0.106	-0.111
0.8257	1.07804	-0.092	-0.092
0.8562	1.06937	-0.077	-0.081
0.8934	1.06133	-0.064	-0.065
0.9409	1.04818	-0.043	-0.040
		T=308.15 K	
0.0409	1.18218	-0.039	-0.035
0.0996	1.17335	-0.066	-0.074
0.1481	1.16613	-0.095	-0.099
0.1988	1.15848	-0.116	-0.119
0.2561	1.14316	-0.132	-0.135
0.3509	1.12793	-0.154	-0.151
0.4356	1.11261	-0.164	-0.156
0.5275	1.10454	-0.165	-0.155
0.6459	1.09696	-0.149	-0.145
0.7207	1.08921	-0.132	-0.132
0.7613	1.08116	-0.118	-0.122
0.8257	1.07398	-0.098	-0.101
0.8562	1.06541	-0.087	-0.089
0.8934	1.05740	-0.072	-0.071
0.9409	1.04428	-0.045	-0.043
		T=313.15 K	
0.0409	1.17735	-0.045	-0.040
0.0996	1.16867	-0.080	-0.086
0.1481	1.16148	-0.107	-0.115
0.1988	1.15393	-0.132	-0.137
0.2561	1.13876	-0.151	-0.155
0.3509	1.12364	-0.174	-0.172
0.4356	1.10842	-0.183	-0.177
0.5275	1.10038	-0.182	-0.173
0.6459	1.09282	-0.163	-0.157
0.7207	1.08509	-0.142	-0.141
0.7613	1.07710	-0.129	-0.129
0.8257	1.06994	-0.105	-0.105
0.8562	1.06137	-0.088	-0.091
0.8934	1.05341	-0.073	-0.072
0.9409	1.04036	-0.044	-0.043

The V^E data for all the binary systems of benzylalcohol with benzene, toluene, chlorobenzene, bromobenzene and nitrobenzene were graphically represented in Figures 1-5. An examination of curves in figures 1-5 shows that, excess volume (V^E) data for the binary mixtures benzylalcohol with benzene, toluene, chlorobenzene, bromobenzene and nitrobenzene are negative over the entire composition range at all temperatures.

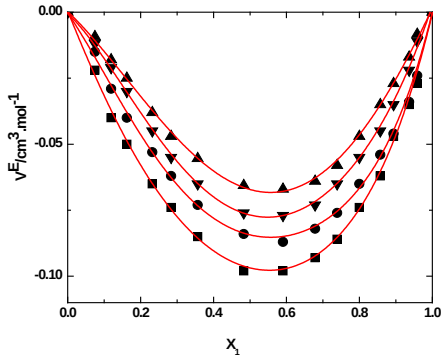

Figure.1 Variation of excess volume (V^E) of The binary liquid mixture of benzylalcohol(1) with benzene (2) at 298.15 K (▲), 303.15 K (▼), 308.15 K (●) and 313.15 K (■).

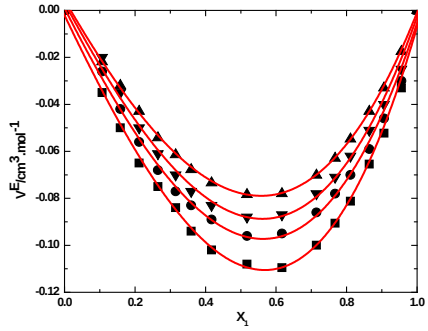

Figure.2 Variation of excess volume (V^E) of The binary liquid mixture of benzylalcohol(1) with toluene (2) at 298.15 K (▲), 303.15 K (▼), 308.15 K (●) and 313.15 K (■).

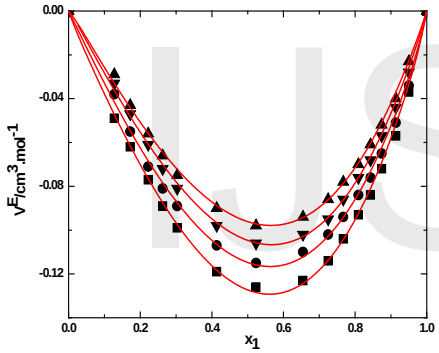

Figure.3 Variation of excess volume (V^E) of The binary liquid mixture of benzylalcohol(1) with bromobenzene (2) at 298.15 K (▲), 303.15 K (▼), 308.15 K (●) and 313.15 K (■).

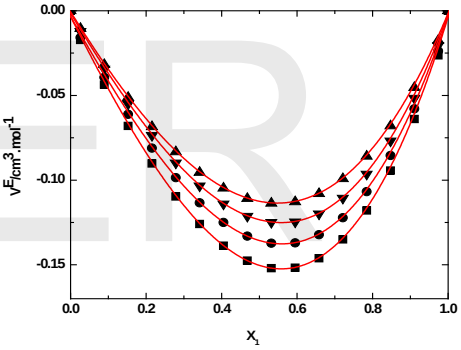

Figure.4 Variation of excess volume (V^E) of The binary liquid mixture of benzylalcohol(1) with chlorobenzene (2) at 298.15 K (▲), 303.15 K (▼), 308.15 K (●) and 313.15 K (■).

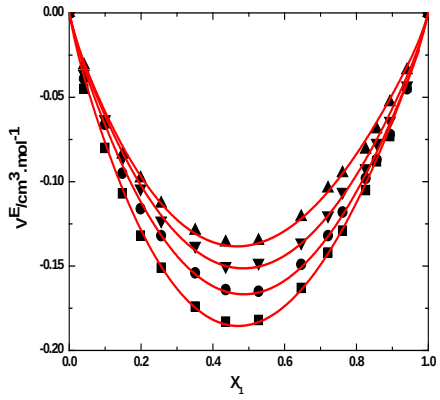

Figure.4 Variation of excess volume (V^E) of The binary liquid mixture of benzylalcohol(1) with chlorobenzene (2) at 298.15 K (▲), 303.15 K (▼), 308.15 K (●) and 313.15 K (■).

In general, the sign of excess volume (V^E) depends on the relative magnitude of contractive and expansive effects that arise on mixing of the component liquids. The factor that causes contraction in volume on mixing are:

"Strong specific interactions, generally a kind of chemical interactions, strong physical interactions such as dipole-dipole or dipole-induced dipole interactions and accommodation of molecules of one component in to the interstitial of the structural network of molecules of the other component".

On the other hand, dissociation of one component or both of one components and when the molecular size of the component molecules are very large, which does not favor for fitting of the molecules with each other hand formation of weaker solute-solvent bond than solute-solute and solvent-solvent bonds and these forces are contributing expansion of volume on mixing the components.

An examination of curves in figures from 1-5 indicate that the factors which are responsible for contraction in volume are dominant over the entire composition range for all the binary mixtures. The algebraic excess volume data of all the binary mixtures will fall in the order:

benzene < toluene < chlorobenzene < bromobenzene < nitrobenzene

The above order indicates that extent of negative magnitude of negative excess volume increases due to nature of different substituents that are present on benzene ring.

An examination of V^E data in Table 2 for the binary systems benzene and toluene shows that, more negative V^E values is observed in latter case. This is due to introduction of methyl group on benzene ring [23]. So, the electron density on benzene ring increases there by these interactions becomes stronger and this should lead to more negative values of V^E benzyl alcohol with

toluene. Further, the more negative excess volume data of chlorobenzene when compared to bromobenzene may explained as follows: Chlorobenzene is more reactive than bromobenzene because of the chlorine atom is bonded with sp^3 hybridized carbon atom and thereby it can be removed easily. Hence, the rate of reaction of chlorobenzene becomes faster [24-26] when compared to bromobenzene.

The experimental results in the present investigations support this contention. Chlorine atom in chlorobenzene is an electron withdrawing atom, which tries to attract the π-electrons of the benzene ring, there by the electron density of the aromatic ring decreases. As result, the benzene ring in chlorobenzene becomes relatively poor electron donor towards electron seeking proton of any group [27].Hence chlorobenzene interacts strongly with benzylalcohol leading to more v^E values.

Further bromobenzene is less reactive when compared to chlorobenzene because of its double bond character between carbon and bromine atom and also it may be attributed its heavier

size. Further, the less negative V^E of bromobenzene when compared to chlorobenzene may be postulated in terms of the presence of vacant 3d-orbital in bromine atom of bromobenzene.So that it act as an electron acceptor towards π-electrons of aromatic compounds [28,29]. The more negative V^E data for the binary system benzyl alcohol with nitrobenzene when compared to benzene, toluene, chlorobenzene and bromobenzene may be due to its high dipole moment and dielectric constant. Nitrobenzene is supposed to be a relatively complex molecule and its non-ideality arises due to rotation of nitro group freely along the C-N axis where it gives more flexibility to the interaction arising due to the two highly polar N→O bonds [24]. Further, the more negative V^E data for the mixture benzylalcohol with nitrobenzene when compared to other mixtures of present investigation may also due to the following reasons: i) Nitro group withdraw the electron cloud from the benzene ring while chloro and bromo groups release the electron cloud to the benzene ring and ii) viscous nature of nitrobenzene[14].

Data for mole fraction (x_1) of benzylalcohol density of pure liquids and their liquid mixtures and experimental sound velocities (u), are included in columns 1-3 of Table 3.

Table 3

Molefraction(x_1) of benzylalcohol, densities (ρ), sound velocities(u), isentropic compressibilities (κ_s), excess isentropic compressibilities (k_s^E) and theoretical sound velocity values of benzylalcohol (1) with benzene and substituted benzenes(2) at 303.15K and 313.15 K.

x_1	P (g. cm^{-3})	u ($m.s^{-1}$) (Exp)	κ_S (Tpa^{-1})	u_{FLT} ($m.s^{-1}$)	u_{CFT} ($m.s^{-1}$)	(k_s^E) (Tpa^{-1})
			Benzylalcohol (1)+Benzene (2)			
			T=303.15 K			
0.0743	0.88290	1299	671	1297	1301	-13.8
0.1198	0.89170	1313	651	1305	1311	-24.8
0.1624	0.89977	1327	631	1324	1327	-34.5
0.2323	0.91280	1348	603	1327	1338	-45.7
0.2837	0.92220	1366	581	1338	1351	-54.3

0.3566	0.93524	1388	555	1353	1369	-60.9
0.4828	0.95710	1423	516	1381	1397	-64.1
0.5904	0.97502	1452	486	1406	1422	-61.6
0.6784	0.98922	1471	467	1428	1442	-54.1
0.739	0.99873	1483	455	1443	1456	-47.3
0.7997	1.00808	1494	444	1459	1469	-39.2
0.8574	1.01682	1501	437	1474	1482	-29.0
0.8936	1.02219	1508	430	1484	1491	-23.9
0.9362	1.02842	1514	424	1496	1500	-16.4
0.9587	1.03165	1518	421	1502	1505	-12.9
			T=313.15 K			
0.0743	0.87242	1305	673	1294	1316	-16.6
0.1198	0.88137	1321	650	1302	1326	-29.7
0.1624	0.88957	1336	630	1320	1342	-40.4
0.2323	0.90280	1357	602	1328	1355	-51.7
0.2837	0.91234	1374	580	1346	1372	-59.3
0.3566	0.92561	1396	554	1381	1401	-65.9
0.4828	0.94788	1435	512	1403	1426	-71.6
0.5904	0.96614	1465	482	1421	1446	-69.1
0.6784	0.98061	1484	463	1432	1460	-61.0
0.739	0.99035	1495	451	1447	1474	-53.1
0.7997	0.99988	1503	442	1461	1487	-42.9
0.8574	1.00880	1511	434	1468	1495	-32.9
0.8936	1.01424	1512	431	1480	1504	-24.1
0.9362	1.02064	1515	427	1484	1509	-14.7
0.9587	1.02397	1515	425	1472	1514	-8.8
			Benzylalcohol (1)+Toluene (2)			
			T=303.15 K			
0.1066	0.87666	1307	668	1306	1309	-21.6
0.1585	0.88591	1325	643	1315	1320	-32.1
0.2116	0.89540	1345	617	1325	1332	-42.2
0.2651	0.90496	1364	594	1335	1343	-49.0
0.3151	0.91392	1383	572	1345	1354	-56.2

0.3593	0.92185	1400	553	1353	1364	-59.9
0.4171	0.93223	1418	553	1365	1377	-66.1
0.5177	0.95034	1451	500	1387	1399	-68.4
0.6169	0.96825	1477	473	1410	1422	-67.3
0.7147	0.98593	1495	454	1434	1445	-58.7
0.7675	0.99550	1500	446	1448	1457	-51.7
0.8111	1.00340	1504	441	1460	1468	-42.8
0.8644	1.01308	1508	434	1474	1481	-32.2
0.9062	1.02066	1506	432	1486	1491	-21.8
0.9556	1.02963	1505	429	1500	1503	-8.6
			T=313.15 K			
0.1066	0.86833	1317	663	1290	1316	-22.9
0.1585	0.87761	1336	638	1299	1327	-36.0
0.2116	0.88713	1356	613	1309	1339	-47.1
0.2651	0.89671	1374	591	1320	1351	-57.0
0.3151	0.90570	1393	569	1329	1362	-65.3
0.3593	0.91368	1409	551	1338	1371	-70.6
0.4171	0.92412	1428	531	1350	1384	-76.4
0.5177	0.94231	1459	499	1372	1407	-81.0
0.6169	0.96030	1485	477	1394.	1429	-79.7
0.7147	0.97809	1503	453	1417	1452	-69.0
0.7675	0.98770	1511	443	1430	1464	-61.2
0.8111	0.99568	1512	439	1441	1474	-51.1
0.8644	1.00539	1514	434	1455	1486	-38.7
0.9062	1.01300	1513	431	1466	1496	-27.2
0.9556	1.02196	1509	429	1480	1508	-11.6
			Benzylalcohol (1)+ Bromobenzene(2)			
			T=303.15 K			
0.1277	1.42605	1187	497	1048	1187	-30.5
0.1722	1.40671	1213	483	1064	1204	-39.3
0.2221	1.38496	1242	468	1084	1223	-49.7
0.2627	1.36723	1267	456	1100	1238	-56.6

0.3032	1.34949	1291	445	1117	1253	-63.6
0.4133	1.30103	1359	416	1165	1294	-73.9
0.5233	1.25232	1414	399	1217	1335	-75.8
0.6544	1.19385	1466	390	1286	1384	-68.9
0.7249	1.16226	1486	391	1327	1411	-61.2
0.7669	1.14334	1493	392	1352	1426	-54.1
0.8091	1.12431	1498	396	1379	1442	-44.3
0.8430	1.10900	1502	400	1401	1455	-36.7
0.8743	1.09482	1503	404	1422	1467	-27.9
0.9137	1.07695	1505	410	1450	1481	-16.3
0.9503	1.06030	1506	416	1476	1495	-7.0
			T=313.15 K			
0.1277	1.41354	1193	493	1039	1194	-34.2
0.1722	1.39446	1217	480	1055	1211	-48.0
0.2221	1.37303	1246	465	1075	1231	-60.5
0.2627	1.35556	1271	453	1091	1246	-67.3
0.3032	1.33807	1296	441	1107	1262	-73.9
0.4133	1.29031	1364	413	1155	1303	-84.5
0.5233	1.24222	1421	395	1206	1345	-87.5
0.6544	1.18451	1476	384	1274	1394	-80.2
0.7249	1.15328	1498	383	1313	1420	-70.0
0.7669	1.13459	1504	387	1338	1435	-63.5
0.8091	1.11577	1509	391	1364	1450	-55.2
0.843	1.10064	1510	395	1385	1462	-46.2
0.8743	1.08661	1511	400	1405	1474	-37.8
0.9137	1.06894	1512	406	1431	1488	-26.8
0.9503	1.05244	1512	413	1457	1501	-15.8
			Benzyl alcohol (1)+ Chlorobenzene(2)			
			T=303.15 K			
0.1016	1.08961	1292	550	1273	1275	-21.1
0.1512	1.08691	1313	534	1285	1287	-32.1
0.2028	1.08405	1338	515	1298	1301	-43.5
0.2274	1.08270	1351	506	1304	1307	-50.1

0.3037	1.07844	1386	483	1323	1326	-62.2
0.3526	1.07570	1409	468	1335	1339	-69.6
0.4042	1.07279	1433	454	1348	1352	-76.9
0.5044	1.06710	1474	431	1374	1379	-83.9
0.6042	1.06134	1506	415	1401	1405	-82.4
0.7037	1.05553	1528	406	1428	1432	-75.1
0.7446	1.05311	1532	405	1439	1443	-67.0
0.8028	1.04963	1540	401	1456	1459	-56.3
0.8474	1.04695	1537	404	1468	1471	-45.4
0.9016	1.04364	1533	407	1484	1486	-28.2
0.9529	1.04049	1470	445	1499	1500	-14.6
			T=313.15 K			
0.1016	1.07920	1306	543	1224	1258	-26.7
0.1512	1.07668	1328	527	1220	1260	-40.8
0.2028	1.07398	1355	507	1216	1262	-52.1
0.2274	1.07274	1366	500	1214	1262	-61.1
0.3037	1.06875	1402	476	1207	1265	-72.7
0.3526	1.06620	1424	463	1204	1267	-81.1
0.4042	1.06348	1448	448	1199	1269	-85.6
0.5044	1.05815	1490	426	1192	1272	-92.2
0.6042	1.05274	1523	410	1184	1275	-91.6
0.7037	1.04725	1549	398	1176	1279	-82.7
0.7446	1.04494	1555	396	1173	1280	-77.1
0.8028	1.04165	1559	395	1168	1281	-64.1
0.8474	1.03909	1557	396	1165	1283	-52.3
0.9016	1.03594	1550	402	1161	1284	-36.2
0.9529	1.03287	1541	408	1157	1285	-18.9
			Benzyl alcohol (1) + Nitrobenzene(2)			
			T=303.15 K			
0.0409	1.18705	1480	385	1448	1448	-20.6
0.0996	1.17815	1512	371	1451	1452	-36.6
0.1481	1.17081	1539	361	1454	1455	-50.5
0.1988	1.16307	1561	353	1457	1459	-61.0

0.2561	1.14767	1590	345	1464	1463	-72.2
0.3509	1.13226	1618	337	1471	1469	-81.8
0.4356	1.11685	1633	336	1478	1475	-88.2
0.5275	1.10869	1639	336	1480	1481	-88.8
0.6459	1.10110	1628	343	1481	1489	-81.8
0.7207	1.09331	1613	352	1484	1494	-72.7
0.7613	1.08520	1603	359	1488	1497	-66.6
0.8257	1.07804	1583	370	1491	1501	-53.7
0.8562	1.06937	1578	376	1496	1504	-46.4
0.8934	1.06133	1565	385	1500	1506	-36.4
0.9409	1.04818	1551	396	1508	1509	-22.5
			T=313.15 K			
0.0409	1.17735	1490	383	1410	1443	-26.9
0.0996	1.16867	1535	363	1391	1435	-45.1
0.1481	1.16148	1561	353	1376	1427	-59.6
0.1988	1.15393	1585	345	1360	1419	-71.1
0.2561	1.13876	1615	337	1346	1410	-82.6
0.3509	1.12364	1644	329	1319	1396	-97.8
0.4356	1.10842	1663	326	1297	1382	-103.4
0.5275	1.10038	1664	328	1268	1367	-104.8
0.6459	1.09282	1643	339	1232	1348	-97.9
0.7207	1.08509	1630	347	1211	1335	-88.8
0.7613	1.07710	1624	352	1202	1328	-78.8
0.8257	1.06994	1601	365	1186	1317	-63.7
0.8562	1.06137	1593	371	1181	1312	-57.8
0.8934	1.05341	1581	380	1173	1305	-47.4
0.9409	1.04036	1562	394	1166	1297	-30.4

Isentropic compressibilities (κ_s) and excess isentropic compressibilities (k_s^E) , were also included in columns 4 and 7 of Table 3. The excess isentropic compressibility data were

also represented graphically in Figures 6-10.The isentropic compresibilities (k_s^E) and excess isentropic compresibilities (k_s^E) were calculated by using the following equations

$$\kappa_S = u^{-2}\rho^{-1} \quad (2)$$

The corresponding excess isentropic compressibilities (k_s^E) were obtained from the relation [30]

$$\kappa_s^E = \kappa_S - \kappa_s^{id} \quad (3)$$

where κ_s^{id} is the ideal value of the isentropic compressibility and was calculated from the following equation [30].

$$\kappa_s^{id} = \sum_{i=1}^{2} \phi_i \left[\kappa_{s.i} + TV_i\left(\alpha_i^2\right)/C_{p.i}\right] - \left\{T\left(\sum_{i=1}^{2} x_i V_i\right)\left(\sum_{i=1}^{2} \phi_i \alpha_i\right)^2 / \sum_{i=1}^{2} x_i C_{p.i}\right\} \quad (4)$$

Here, C_{pi} and α_i are the molar heat capacity and the thermal expansion coefficient of the i^{th} component respectively. The value of C_{pi} and α_i obtained and evaluated from literature [17,31] and given in Table 4.

Table 4 Thermal coefficient (α) and heat capacity (c_p) for pure component liquids at temperatures 303.15K and 313.15 K.

Component	303.15	313.15
Benzyl alcohol		
α (kK^{-1})	0.7402	0.7456
C_p ($J.mol^{-1}.k^{-1}$)	224.35[17]	227.62[32]
Benzene		
α (kK^{-1})	1.1915	1.2048
C_p ($J.mol^{-1}.k^{-1}$)	137.4[17]	140.6[32]
Toluene		
α (kK^{-1})	1.2666	1.0612
C_p ($J.mol^{-1}.k^{-1}$)	153.4[17]	160.2[32]
Bromobenzene		
α (kK^{-1})	0.9048	0.8785
C_p ($J.mol^{-1}.k^{-1}$)	156.9[17]	157.3[32]
Chlorobenzene		

α (kK^{-1})	0.9725	0.9673
C_p ($J.mol^{-1}.k^{-1}$)	150.6[17]	152.2[32]
Nitrobenzene		
α (kK^{-1})	0.8198	0.8217
C_p ($J.mol^{-1}.k^{-1}$)	177.3[17]	173.8[32]

An examination of curves in Figures 6-10 suggest that excess isentropic compressibility data (k_s^E) for the binary mixtures of benzylalcohol with benzene, toluene, chlorobenzene, bromobenzene and nitrobenzene are negative over the entire composition range at 303.15 K and 313.15 K. This may be interpreted in terms of two opposing effects: i) loss of dipolar association and difference in size and shape of the component molecules; and ii) dipole-dipole, dipole-induced dipole, electron-donor-acceptor interactions and interstitial accommodation of benzylalcohol lattice. The former effect contributes to an increase in free length, described by Jacobson [32]. This leads to negative deviation in sound speed and positive deviation in excess compressibility.

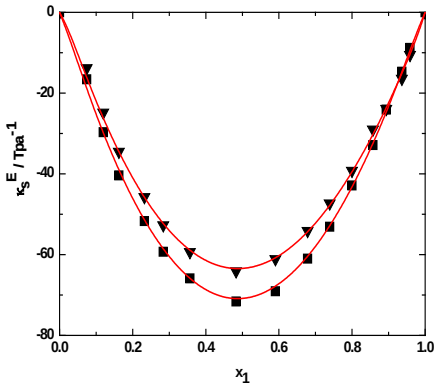

Figure.6 Variation of excess isentropic compressibility (k_s^E) of the binary liquid mixture of benzylalcohol (1) with benzene (2) at 303.15 K (▼) and 313.15 K (■).

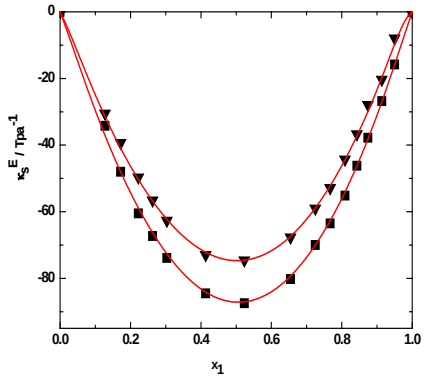

Figure.7 Variation of excess isentropic compressibility (k_s^E) of the binary liquid mixture of benzylalcohol (1) with toluene (2) at 303.15 K (▼) and 313.15 K (■).

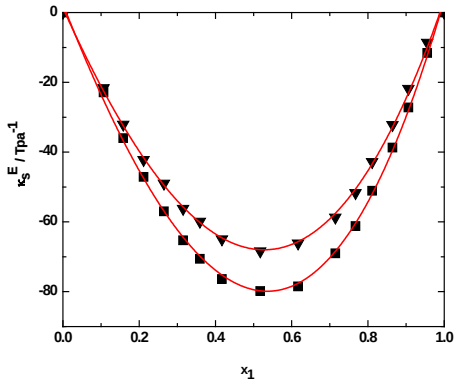

Figure.8 Variation of excess isentropic compressibility (k_s^E) of the binary liquid mixture of benzylalcohol (1) with bromobenzene (2) at 303.15 K (▼) and 313.15 K (■).

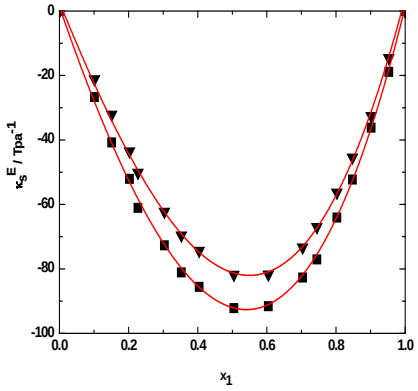

Figure.9 Variation of excess isentropic compressibility (k_s^E) of the binary liquid mixture of benzylalcohol (1) with chlorobenzene (2) at 303.15 K (▼) and 313.15 K (■).

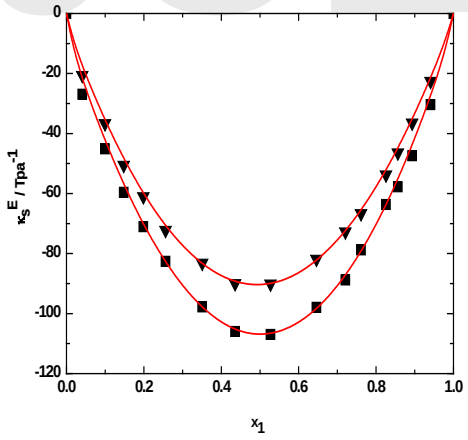

Figure.10 Variation of excess isentropic compressibility (k_s^E) of the binary liquid mixture of benzylalcohol (1) with nitrobenzene (2) at 303.15 K (▼) and 313.15 K (■).

The latter effect, on the other hand, leads to positive deviation in sound speed and negative deviation in excess compressibility. The sign and magnitude of the actual deviation depends on the relative strengths of the two opposing effects. As already reported by Benson and Kiyohara [30] the sign and magnitude of the excess isentropic compressibility, that arises through charge transfer, dipole induced dipole and dipole-dipole interactions interstitial accommodation and orientation ordering lead to a more compact structure which contributes to negative excess isentropic compressibility. Our experimental results were also supports this contention. The algebraic values of κ_S^E values for all the binary systems fall in the order

Benzene < Toluene < Chlorobenzene < Bromobenzene < Nitrobenzene

The above order indicates that the extent of stronger interactions increases as the free spaces between benzene and substituted benzenes. Experimental ultrasonic sound velocities were analyzed in terms of collision factor theory (CFT) [33], free length theory (FLT) [34,35] and these were also included in Table 3 along with experimental ultrasonic sound velocities. The pure component data namely, the molar volume (V_m), molar volume at absolute zero (V_0), molar available volume (V_a), free length (L_f), surface area (Y), collision factor(S), average molecular radius (r_m), actual volume of molecules per mole (B) and molecular sound velocity(R) that were used to calculate the above said theories were collected from the literature [36]. The methods and details of calculation of theories were discussed earlier [37, 38].

The details of various theories and relevant equations are given as follows:

A comparison between experimental sound velocities and theoretical values suggest that the model proposed by Schaaff's CFT gives better estimation of sound velocity data. The methods of calculation of these theories were described in earlier. The merits of these

theories were compared in terms of relative root mean deviation by using the following formula [39].

$$\text{RMSD} = \left[\frac{1}{n}\sum_{i=1}^{n}\left[\frac{y_{exp}-y_{pred}}{y_{exp}}\right]^2\right]^{1/2} \quad (5)$$

The RMSD for all the binary systems values given in Table 5 shows that Schaaff's CFT model gives better estimation in sound velocity for the binary mixtures under the investigation.

Table 5

RMSD of speed of sound (u) of benzylalcohol with benzene and substituted benzene at T= 303.15K and 313.15 K from different relations

RMSD	303.15 K	313.15 K
Benzyl alcohol (1) + benzene (2)		
CFT	0.013	0.008
FLT	0.020	0.023
Benzyl alcohol (1) + toluene(2)		
CFT	0.023	0.024
FLT	0.029	0.045
Benzyl alcohol (1) + bromobenzene(2)		
CFT	0.035	0.034
FLT	0.107	0.119
Benzyl alcohol(1) + chlorobenzene(2)		
CFT	0.046	0.137
FLT	0.048	0.194
Benzyl alcohol (1) + nitrobenzene(2)		
CFT	0.066	0.151
FLT	0.068	0.209

Table 6

Coefficients $\mathbf{A_i}$ of Redlich-Kister equation 6 and the corresponding standard deviations (σ) of all the systems

Temperature	Function	A_0	A_1	A_2	$\sigma(V^E)$
		Benzyl alcohol (1)+benzene (2)			
289.15 K	V^E	-0.295	-0.088	0.178	0.003
303.15 K	V^E	-0.323	-0.111	0.114	0.003
308.15 K	V^E	-0.325	-0.146	-0.102	0.004
313.15 K	V^E	-0.376	-0.118	-0.131	0.003
303.15 K	κ_s^E	-252.1	-252.1	-1.55	2.9
313.15 K	κ_s^E	-294.3	12.6	55.82	1.3
		Benzyl alcohol (1)+Toulene(2)			
289.15 K	V^E	-0.311	-0.115	0.002	0.004
303.15 K	V^E	-0.342	-0.135	-0.044	0.004
308.15 K	V^E	-0.364	-0.144	-0.124	0.005
313.15 K	V^E	-0.408	-0.153	-0.181	0.004
303.15 K	κ_s^E	-284.6	-20.77	-20.77	1.9
313.15 K	κ_s^E	-332.6	-44.61	88.15	1.4
		Benzyl alcohol (1)+bromobenzene (2)			
289.15 K	V^E	-0.388	-0.123	0.014	0.002
303.15 K	V^E	-0.414	-0.138	-0.025	0.002
308.15 K	V^E	-0.440	-0.147	-0.107	0.004
313.15 K	V^E	-0.484	-0.147	-0.145	0.003
303.15 K	κ_s^E	-327.6	11.13	147.19	3.2
313.15 K	κ_s^E	-357.5	-13.60	41.63	1.2
		Benzyl alcohol (1)+chlorobenzene (2)			
289.15 K	V^E	-0.434	-0.111	-0.105	0.003
303.15 K	V^E	-0.472	-0.138	-0.142	0.003
308.15 K	V^E	-0.510	-0.144	-0.214	0.003
313.15 K	V^E	-0.560	0.152	-0.269	0.003
303.15 K	κ_s^E	-338.6	-65.97	87.86	1.2
313.15 K	κ_s^E	-373.47	-67.21	24.1	1.2

		Benzyl alcohol (1)+nitrobenzene (2)			
289.15 K	V^E	-0.523	0.086	-0.196	0.003
303.15 K	V^E	-0.563	0.044	-0.261	0.005
308.15 K	V^E	-0.626	0.045	-0.258	0.005
313.15 K	V^E	-0.700	0.118	-0.254	0.005
303.15 K	κ_s^E	-344.3	29.06	-114.5	2.2
313.15 K	κ_s^E	-394.07	24.08	-209.9	2.5

The experimental V^E values and κ_S^E data in have been fitted to Redlich-Kister type polynomial equation[40].

$$y^E = x_1 x_2 \sum_{i=0}^{n} a_i (x_1 - x_2)^i \quad (6)$$

Where $Y^E = V^E$ or κ_S^E the subscription 'i' in the equation takes value from 0 to 2 ; A_i is the adjustable parameter of the function and are determined using the least-squares method. The corresponding standard deviations $\sigma(Y^E)$ have been computed using the relation.

$$\sigma(Y^E) = [\ \Sigma(Y^E_{exp} - Y^E_{cal})^2/(m-n)]^{1/2} \quad (7)$$

where 'm' is the total number of experimental points and 'n' is the number of coefficients in equation 6, and the standard deviations of all the binary mixtures have been presented in Table 6.

5.Conclusion

In the present work excess volume data of binary mixture of bezylalcohol with benzene, toluene, bromobenzene, chlorobenzene and nitrobenzene were observed the entire composition range from at 298.15 K to 313.15 K and the property is negative in all the binary mixtures.This shows that strong intermolecular interactions are prevailing in liquid mixtures. Since the nitro group of nitrobenzene is more powerful electron withdrawing group when

compared to bromobenzene, chlorobenzene, more negative V^E data were observed in the binary system benzylalcohol with nitrobenzene. Further κ_S^E data in all the binary mixtures shows that the property is negative at 303.15 K and 313.15 K, which arises due to changes of free volume in the real mixtures and presence of π-electrons in benzylalcohol resulting in the formation of weak intermolecular complexes leading to positive deviation in sound velocity and negative excess isentropic compressibility.

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