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Density and Ultrasonic Study of Benzene Sulphonyl Chloride with Hydrocarbon at 303.15 K.

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ABSTRACT: Experimental values of Ultrasonic velocity and density for the binary mixture of Benzene Sulphonyl Chloride with Hydrocarbons have been measured at 303.15 K over the entire mole fraction range, using these data the excess Adiabatic compressibility (β_s^E) and excess Free length (L_f^E) have been calculated. These parameter were used to study the nature and extent of intermolecular interaction between component molecules, present in binary mixture. excess value of Adiabatic compressibility (β_s^E), sound velocity (U^E) and free length(L_f^E) were plotted against the mole fraction of Benzene Sulphonyl Chloride over the whole composition range the value of β_s^E, U^E, L_f^E for these three binary mixture have been found to be negative, the non linear variation of these parameter show the presence of interaction and their excess value is indicative of interaction between the components molecule in all system.

KEYWORDS: Adiabatic compressibility, Benzene Sulphonyl Chloride, Density, Free length, Molecular interaction, Sound Velocity.

INTRODUCTION

Properties of liquid-liquid mixtures are thermodynamically very important in part of thermodynamic, acoustic and transport aspects. The intermolecular forces of liquid mixture r show a considerable effect on the physical and chemical properties. There is continuing need for reliable thermodynamic data of binary systems for chemical industries as the data is essential in the design of process involving chemical separation, heat transfer and fluid flow Fundamental thermodynamic and thermo physical properties are essential sources of information necessary for a better understanding of the non-ideal behavior of complex systems because of physical and chemical effects which are used by molecular interaction, molecular forces, etc., of unlike molecules. Measurement of ultrasonic velocity has been adequately employed in understanding the nature of molecular interaction in pure liquid and liquid mixtures. Ultrasonic studies of aqueous mixed solvent systems are of importance because of their extensive use in textile, leather and pharmaceutical industries Organic solvents whose miscibility with water is unlimited usually form H-bonds in aqueous some solvents also present auto-association by hydrogen bonds in pure state but others do not. The fictional group of organic solvent can form H-bonds with water due to hydrophilic effects, while the hydrocarbon part of the organic solvents is responsible for hydrophobic part. The practical application of mixed solvents rather than single solvent in industrial and biological process has been recognized all over the world as they provide a wide choice of solutions with appropriate properties (A. Ali et al 2001).The evaluated excess quantities from experimental acoustical data have been interpreted in terms of the differences in the size of the molecule as well as the strength of specific and non specific interactions between components of the mixture. Further, measurements of excess thermodynamic properties are found to be greatly significant studying the structural changes associated with the liquids. They also provide important information about molecular packing, molecular motion and various types of intermolecular interactions and the strength influenced by the size, shape and the chemical nature of component molecules (Aminabhavi et al,1996).This in turn helps in bringing out the facts which have positive implementation for both industry as well as the building process A thorough knowledge of thermodynamic and transport properties of ternary liquid systems is essential in many industrial applications such as design, calculations, heat transfer, mass transfer, fluid flow and so forth (Nikam, S.P et al 1998-2003).

EXPERIMENTAL

Material

The chemicals used in the present work were high purity laboratory reagent grade samples of Benzene Sulphonyl chloride, n-pentane, n-hexane and n-heptane were purchased from Merck Chem. Ltd India. All chemicals was stored over sodium hydroxide

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pellets for several days and fractionally distilled twice (Perrin,et al,1988). All chemicals was purified by the method described by Zhao et al (2000) ethyl acetate was dried over K_2CO_3, filtered and distilled were discarded. All the chemicals were stored in dark bottles over freshly activated molecular sieve to minimize absorption of moisture. The purity of the solvent was ascertained by comparing the measured density, dynamic viscosities and sound velocity of the pure component at 303.15K. as shown in Table 1. The reported experimental values of density (ρ) and ultrasonic velocity (U) conform closely to their corresponding literature values,

Measurements

Three binary system viz. Benzene sulphonyl chloride + n-pentane, Benzene sulphonyl chloride + n-hexane and Benzene sulphonyl chloride + n-heptane were studied. Each sample mixture was prepared, on mass basis, by mixing the calculated volume of liquid components in specially designed glass stopper bottles. All binary mixture were prepared by weight covering the entire mole fraction range. The components of binary mixtures were injected by means of syringe in to the glass vials of sealed with rubber stopper in order to check evaporation losses during sample preparation. The mass measurements were carried out using an single pan analytical balance (Model K-15 Deluxe, K Roy Instruments Pvt. Ltd.) with an accuracy of $\pm 0.00001\times10^{-3}$ kg as described elsewhere (R.R. Yadava, et al 1994). The possible error in the mole fraction was estimated to be less than $1x10^{-4}$. Five samples were prepared for one system, and their density and sound velocity were measured on the same day.

Density

Densities of pure liquids and their binary mixtures were determined by using a double-arm pycnometer (Sathyanarayan, et al 2007) with a bulb of 25 cm^3 and a capillary of an internal diameter of about 1 mm is used to measure the densities (ρ) of pure liquids and binary mixtures. The pycnometer is calibrated by using conductivity water (having specific conductance less than 1×10^6 ohm^{-1}) with 0.9970 and 0.9940 gem as its densities at T = 303.15 K, respectively. The pycnometer filled with air bubbles free liquids is kept in a thermostate water both (MSI Goyal Scientific, Meerut, India) controlled with a thermal equilibrium. The precision of the density measurements was estimated to be ±0.0002 g cm^3. The observed values of densities of pure BenzeneSulphonyl chloride, n-pentane, n-hexane and n-heptane, at 303.15K were 1.3093, 0.6135, 0.6634 and 0.6629 g./cm^3 which compare well with corresponding literature values of respectively.

Sound velocity

The ultrasonic velocities were measured using a multifrequency ultrasonic interferometer (Model F-80D, Mittal Enterprise, New Delhi, India) working at 3 M.Hz. The meter was calibrated with water and benzene at 303.15K. The measured values of ultrasonic velocities of pure n-pentane, n-hexane and n-heptane 303.15K were 1233, 975, 1095 and 1131 $m.s^{-1}$ respectively, which compare well with the corresponding literature values.

Table1. Value of Sound velocity (U) and Density (ρ) of pure organic liquids At 303.15K

Liquids	Sound Velocity Experimental (U_{exp})ms^{-1}	Sound Velocity Literature (U_{exp})ms^{-1}	Density Experimental (ρ_{exp})gm/cm^3	Density Literature (ρ_{exp})gm/cm^3
n- pentane	960	975	0.6134	0.6135
n-hexane	1065	1095	0.6632	0.6634
n-heptane	1120	1131	0.6529	0.6629
Benzene Sulphonyl Chloride	1220	1233	1.3901	1.3903

THEORITICAL

The intermolecular free lengh (L_f), that is distance covered by a sound wave between the surface of the two molecules is given by the equation

$$L_f = K\,\beta_s^{1/2} \quad (1)$$

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Where K is temperature dependent constant and β, is the isentropic compressibility, which is given by the relation

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

Where ρ is the density of liquid.

The excess value of A^E of these thermodynamic parameters have been obtained by subtracting the ideal value from the experimental value

$$A^E = A_{exp.} - (X_1 A_1 + X_2 A_2) \quad (3)$$

RESULT AND DISCUSSION

The Experimental values of Ultrasound velocities and density are reported in table 2. For all the binary system studies at 303 K. A perusal of table 2 shows that the sound Velocities increases with mole fraction of hydrocarbon for all the binary mixtures in the presence investigation. Ultrasound waves are high frequency mechanical waves their velocities in a medium depends inversely and density of the medium. The Increase in velocities with decrease mole fraction of hydrocarbon for the binary mixtures Increase with decrease the mole fraction of the hydrocarbons.

The excess ultrasound Velocities (U^E) if valuated from the experimental value of Ultrasound Velocities for component liquid and their mixtures vials.

$$U^E = U_{Mix} - (U_1 X_1 + U_2 X_2) \quad (4)$$

Where U_{Mix} is ultrasound velocities in mixtures and U_1 U_2 and X_1 X_2 are the Ultrasound velocity and Mole fraction respectively of the Component, liquids (1) and (2).

The Plots of Excess sound velocity (U^E) with mole fraction X_1 for the binary mixture of benzene sulphonyl chloride with pentane hexane and heptanes at 303.15 K were depicted in fig.1.

Excess Ultrasound velocities evaluated on the basis of the above equation for all the binary mixtures of experimental temperature are given in table 3. It is evident from the table; the excess sound velocities values are negative for all the binary mixtures. The mole clues of Benzene sulphonyl Chloride are self associated when a hydro carbon added in to the Benzene sulphonyl chloride to from a binary mixture. Self association reduces Causing a negative deviations in velocities.

The negative excess sound velocities values over the entire range of mole fraction of the system also support the presence of interaction.

The case of adiabatic Compressibility's are reported in table 2 for the all of binary system studies at 303 K a perusal table 2 shows that the adiabatic Compressibility's decreases with mole fraction of hydro carbons for all the binary mixtures in the present investigation. The adiabatic compressibility's of the medium the decreases in adiabatic compressibility's increases with mole fraction of the hydrocarbons.

The excess adiabatic compressibility's (β_s) it evaluated from the experimental value of adiabatic compressibility's for component liquid and their mixture vials.

$$\beta_s = \beta_{s\,mix} - (\beta_{s\,1} X_1 + \beta_{s2} X_2) \quad (5)$$

Where β_{mix} is the adiabatic compressibility's in the mixtures and $\beta_{s\,1}$, $\beta_{s\,2}$ and X_1, X_2 are the adiabatic compressibility's and mole fraction respectively of the component liquid (1) and (2).

The Plots of Excess adiabatic compressibility(β_S^E) with mole fraction X_1 for the binary mixture of benzene sulphonyl chloride with pentane, hexane and heptanes at 303.15 K were depicted in fig.2

Excess adiabatic compressibility's evaluated on the basis of above equation for all the binary mixtures of experimental temperature are given in table 3. It is evident from the table of excess adiabatic compressibility's value are negative for all the binary mixture.

A perusal of table 2 suggested that adiabatic compressibility's decrease with the mole fraction of the hydrocarbons solvent for the binary mixtures with pentane, hexane and heptane.

The excess adiabatic compressibility's value (β_S^E) are negative for all three binary liquid mixtures. The negative value of excess adiabatic compressibility's suggested that the binary mixtures becomes high compressible. The molecules of benzene euphony chloride are self associated when a hydrocarbon added in to the Benzene euphony chloride to from a binary mixture. Self association

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reduces causing a negative deviation in compressibility's (Iloukhani, 2005), (Bhatia et al 2011) has explain positive and negative deviation in compressibility's in term of

1. Dispersion forces.

2. Charge transfer, dipole-dipole and dipole induced dipole interaction.

According to Rao (2004), Hari Babu, (1996) and Prakash, et al (1976) then the dispersion forces increase the inter molecules path length which causes negative deviation in second adiabatic compressibility. The negative deviation in adiabatic compressibility suggested that the binary mixture of Benzene sulphonyl chloride with hydrocarbons becomes more compressible.

Mehra *et.al* (2006) have suggested that the sign of excess compressibility plays a vital role in accessing the compactness due to molecules rearrangement and the extend of molecular interaction in liquid mixture negative value of excess adiabatic compressibility (β^{E}_{ad}) indicates strong interaction between component of the liquid mixtures which includes change transfer, dipole-induced dipole, dipole- dipole Interaction and initial accommodation.

The free length for the binary mixtures under investigation Benzene sulphonyl chloride + Pentane, Benzene sulphonyl chloride+ hexane, Benzene sulphonyl chloride heptanes and their pure components has been calculated using ultrasonic approaches vide equation.

The necessary data required for the calculation have been taken from table - 1. The calculated values of free length are reported in table 2. The excess free length L^{E} has been evaluated eq. (6) and the value of excess free length are also reported in table 3.

$$L_f^E = (L_f)_{mix} - (x_1L_{f1} + x_2L_{f2}) \quad (6)$$

The perusal of table 2 and 3 shows that the value of free length increase mole fraction of hydrocarbons. The excess free length for the all system are found to be negative. The ultrasonic method however have the limitation that the sound velocity 'U' should be less than U_∞ because in case $U \geq U_\infty$ the ratio U/ U_∞ will be either greater 1 or o and in either case, it will give negative value.

Therefore, the ultrasonic method fails when the values of sound velocities is more than 1600 m/s. It is to be noted that the value of free length decrease with increase of mole fractions of Hydrocarbon (Prasad et al 2016).

The Plots of Excess free length (L_f^E) with mole fraction X_1 for the binary mixture of benzene sulphonyl chloride with pentane, hexane and heptane at 303.15 K were depicted in fig.3

The sign of excess free length clearly indicates the presence of strong intermolecular interactions in the systems.

The free length of the binary mixtures under investigation Benzene sulphonyl chloride + pentane, Benzene sulphonyl chloride+ hexane, Benzene sulphonyl chloride+ heptanes and their pure component has been calculated using ultrasonic approaches vide equation.

CONCLUSION

In this paper, an attempt is made to measure densities (ρ) and ultrasonic velocity (U) at 303.15 K over the entire range of mixture composition of Benzene Sulphonyl Chloride with Pentane, Hexane and Heptane. From these data acoustical parameters such as adiabatic compressibility and free length, and their excess values are evaluated. The negative deviations are observed in the case of excess isentropic compressibility(β_S^E), excess free length (L_f^E), the negative deviations were observed. The results are analyzed in the sight of molecular interactions between the components. It may be concluded that the interaction resulting in the interstitial accommodation of Benzene Sulphonyl Chloride in to Pentane, Hexane and Heptane are the predominant factor over dipole-dipole interaction.

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Table2. Values of mole fraction (X_1), ultrasonic velocities (U), adiabatic compressibility (β_s), and free length (L_f) of binary liquid mixture of benzene sulphonyl chloride with hydrocarbons at 303.15 K.

Mole Fraction (x_1)	Density (ρ) gm.cm^{-3}	Ultrasonic Velocity (U) ms^{-1}	Adiabatic Compressibility (β_s)X10^6 (Pa)$^{-1}$	Free length (L_f)X10^6 (m)
Benzene suplhonyl chloride + pentane				
0.0000	0.6135	975	1.7146	0.8262
0.2012	0.6576	1020	1.4602	0.7456
0.3618	0.7056	1060	1.2613	0.6842
0.4928	0.8129	1090	1.0354	0.6297
0.6018	0.8746	1115	0.9196	0.5887
0.6939	0.9056	1140	0.8493	0.5486
0.7728	0.9789	1160	0.7584	0.5191
0.8411	1.0696	1175	0.6771	0.4986
0.9006	1.1783	1190	0.5993	0.4696
0.9892	1.3796	1210	0.4950	0.4439
1.0000	1.3901	1220	0.4833	0.4386
Benzene suplhonyl chloride + hexane				
0.0000	0.6632	1065	1.3294	0.7275
0.2012	0.6901	1070	1.2656	0.7098
0.3618	0.7801	1075	1.1092	0.6645
0.4928	0.9012	1085	0.9425	0.6125
0.6018	1.9881	1100	0.8363	0.5769
0.6939	1.1001	1110	0.7377	0.5419
0.7728	1.3094	1125	0.6034	0.4900
0.8411	1.3499	1140	0.5700	0.4763
0.9006	1.3601	1160	0.5464	0.4663
0.9892	1.3701	1190	0.5154	0.4529
1.0000	1.3901	1220	0.4833	0.4386
Benzene suplhonyl chloride + heptanes				
0.0000	0.6529	1120	1.2210	0.6971
0.2012	0.7289	1122	1.0897	0.6586
0.3618	0.7710	1125	1.0248	0.6387
0.4928	0.8712	1130	0.8989	0.5982
0.6018	0.9014	1140	0.8536	0.5829
0.6939	0.9901	1150	0.7637	0.5513
0.7728	1.0912	1160	0.6810	0.5207
0.8411	1.2610	1170	0.5793	0.4802
0.9006	1.3212	1180	0.5435	0.4651
0.9892	1.3701	1200	0.5068	0.4491
1.0000	1.3901	1220	0.4833	0.4386

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Table 3. Excess values of mole fraction (X_1) ultrasonic velocities (U^E), adiabatic compressibility (β_S^E) and free length (L_f^E) of binary liquid mixture of benzene sulphonyl chloride with hydrocarbons at 303.15 K.

Mole Fraction (x_1)	Density (ρ) gm.cm^{-3}	Excess Ultrasonic Velocity (U^E) ms^{-1}	Excess Adiabatic Compressibility (β_S^E)X10^6 (Pa)$^{-1}$	Excess Free length (L_f^E)X10^6 (m)
Benzene suplhonyl chloride + pentane				
0.0000	0.6135	0.0000	0	0
0.2012	0.6576	-4.2940	-0.0051	-0.00261
0.3618	0.7056	-4.6410	-0.0752	-0.0126
0.4928	0.8129	-5.7360	-0.0902	-0.1231
0.6018	0.8746	-6.3400	-0.1020	-0.2416
0.6939	0.9056	-5.0050	-0.1230	-0.3214
0.7728	0.9789	-4.3360	-0.1435	-0.2011
0.8411	1.0696	-5.0690	-0.1020	-0.1256
0.9006	1.1783	-4.6470	-0.0926	-0.0943
0.9892	1.3796	-3.6540	-0.0524	-0.0802
1.0000	1.3901	0.0000	0	0
Benzene suplhonyl chloride + hexane				
0.0000	0.6632	0.0000	0.0000	0.0000000
0.2012	0.6901	-2.8430	-0.0020	-0.0030817
0.3618	0.7801	-5.6000	-0.1295	-0.0320588
0.4928	0.9012	-6.4120	-0.2420	-0.0657714
0.6018	1.9881	-5.5410	-0.2880	-0.0806284
0.6939	1.1001	-5.2200	-0.3175	-0.0919964
0.7728	1.3094	-4.8520	-0.3719	-0.1166242
0.8411	1.3499	-5.8950	-0.3384	-0.1078767
0.9006	1.3601	-4.4170	-0.2512	-0.0796264
0.9892	1.3701	-3.3550	-0.1267	-0.0399554
1.0000	1.3901	0.0000	0.0000	0.000000
Benzene suplhonyl chloride + heptanes				
0.0000	0.6529	0.0000	0.0000	0.000000
0.2012	0.7289	-3.050	-0.0945	-0.0254458
0.3618	0.7710	-5.6900	-0.1173	-0.0307664
0.4928	0.8712	-7.0300	-0.1964	-0.0548775
0.6018	0.9014	-6.2000	-0.1888	-0.0616430
0.6939	0.9901	-5.3090	-0.2180	-0.0879219
0.7728	1.0912	-4.8000	-0.2360	-0.0683470
0.8411	1.2610	-3.7700	-0.2520	-0.0654896
0.9006	1.3212	-2.7200	-0.1990	-0.0621138
0.9892	1.3701	-1.1700	-0.1150	-0.0381756
1.0000	1.3901	0.0000	0.0000	0.0000000

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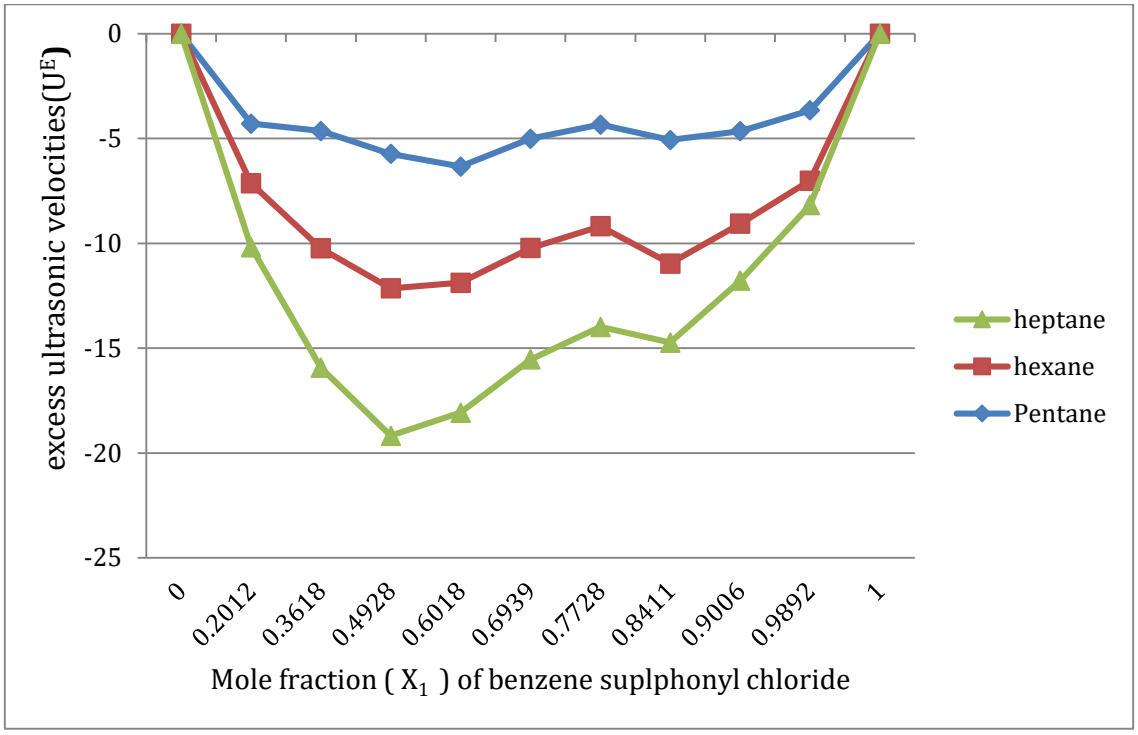

Fig .1 Plots of Excess sound velocity (U^E) with mole fraction X_1 for the binary mixture of benzene sulphonyl chloride with pentane, hexane and heptane at 303.15 K

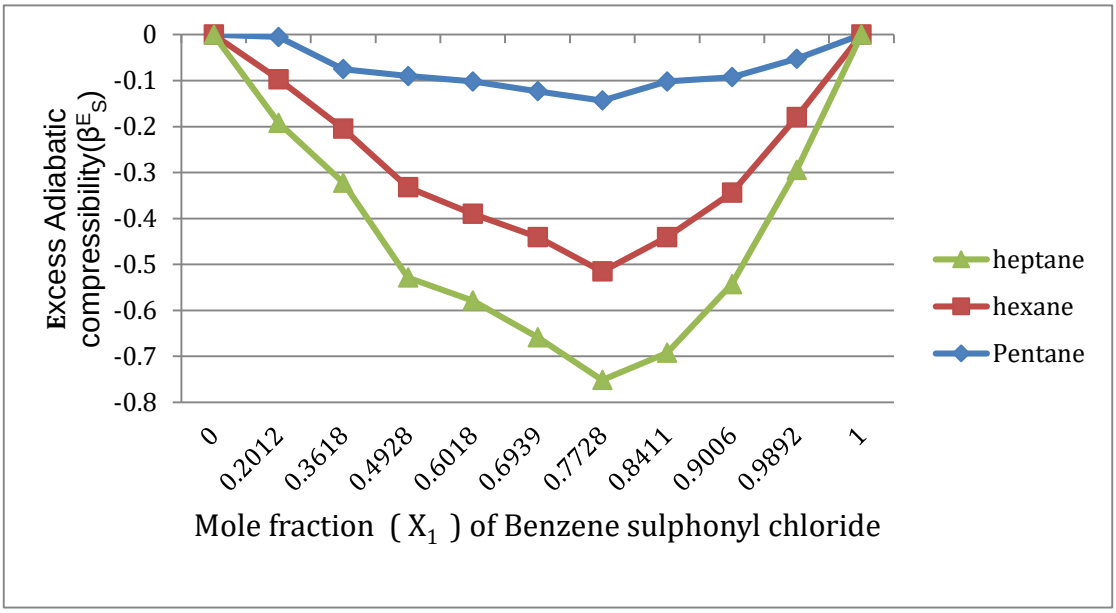

Fig. 2 Plots of Excess adiabatic compressibility (β_S^E) with mole fraction X_1 for the binary mixture of benzene sulphonyl chloride with pentane, hexane and heptane at 303.15 K

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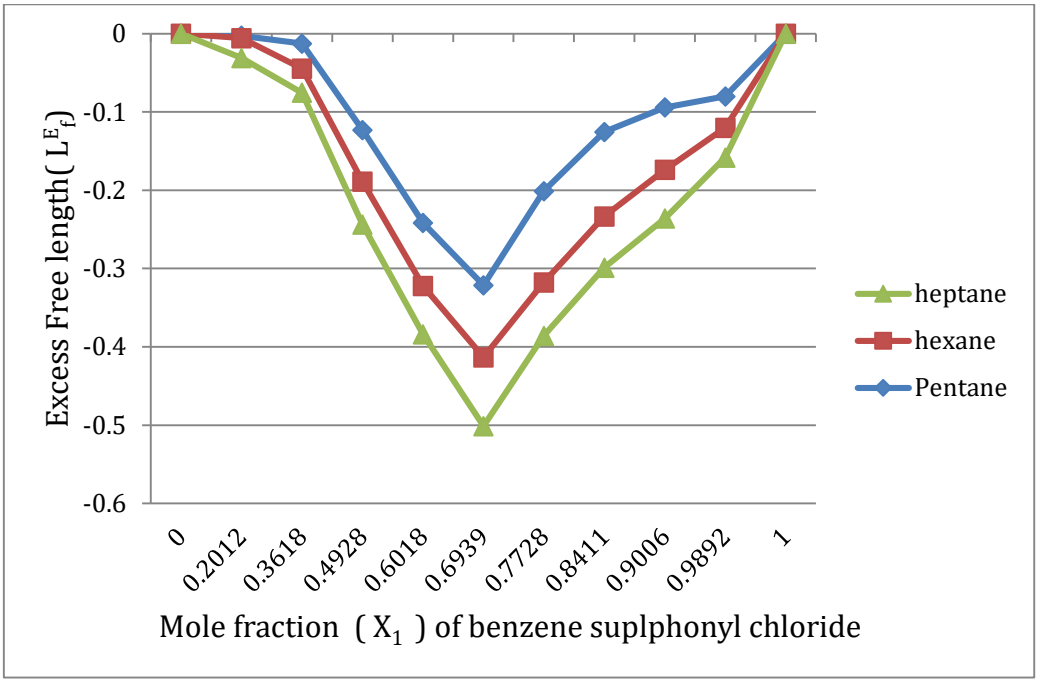

Fig.3. Plots of Excess free length (L_f^E) with mole fraction X_1 for the binary mixture of benzene sulphonyl chloride with pentane, hexane and heptane at 303.15 K

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