

Study of Intermolecular Interactions of Acetophenone and Benzene at 303.15, 313.15 and 323.15 K

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Abstract

The behaviour of mixture of acetophenone and benzene as a function of temperature and composition has been investigated by measuring sound velocity in conjunction with density at 303.15, 313.15 and 323.15 K. Derived parameters computed from density (ρ) and sound velocity (U) have been used to determine excess molar volumes (V_M^E), excess isentropic compressibilities (K_S^E) and excess inter molecular free length (L_f^E). The excess functions have been discussed in terms of intermolecular interactions between the components of binary mixture. The validity of various theoretical approaches of liquids has been tested for the system by comparing theoretical sound speeds with those experimentally determined over the entire composition range in the temperature range 303.15-323.15K. The computed results have been fitted to the Redlich-Kister polynomial equation to estimate the smoothing coefficients and standard deviations for this system. The validity of various theoretical approaches of liquids has been tested for the system by comparing theoretical sound speeds with those experimentally determined over the entire composition range in the temperature 303.15-323.15K.

Keywords: Sound velocity, Free length, Compressibility, Molar volume, Density, Binary mixture

1. Introduction

There has been an increasing interest in the study of systems comprising of unlike components with interactions of varying type. The sign and magnitude of excess parameters have been used to investigate the interactions between the components of a system "Venkatesu et al.(1996)". A commercial use of benzene includes synthesis of different intermediate compounds during the process of manufacture of plastic, dyestuffs, detergents and insecticides. An exhaustive survey of literature reveals that studies on the use of acoustic and volumetric properties and their excess functions in order to understand molecular interactions in binary liquid mixtures of acetophenone and benzene have not been studied so far. Hence excess molar volumes, excess isentropic compressibilities and excess intermolecular free length have been calculated at three temperatures at an interval of 10°C from 303.15 to 323.15 K. Experimental measurements of sound velocity and density are used to calculate various acoustical parameters viz. intermolecular free length, acoustical impedance, molar Volume and isentropic compressibility at three different temperatures. These acoustical parameters are further used to calculate excess parameters because excess parameters are a better measure of intermolecular interaction as compared to derived ones. The low magnitude values of V_M^E , K_S^E and L_f^E indicate interaction of less strength between the components. The theoretical approaches for liquids namely Free Length Theory (u^{FLT}), Impedance Dependence Relation (u^{IDR}) and Vandael Vangeal ideal mixing relation (u^{VAN}) applied to binary mixture under investigation at all three temperatures reflect the behavior of the system by measuring the deviation of theoretical values of sound speeds from experimental ones.

2. Experimental Procedure

All the chemicals used were of analytical grade. Acetophenone - (S.D. fine Chem. Pvt. Ltd.) with 98% purity and benzene - (Merck) with 99% purity were used after drying by standard procedures "Reddich et al. (1986),

Dean (1987)". The densities of pure liquids and mixtures were measured using a precalibrated bicapillary pycnometer, the accuracy of data being within $\pm 0.06\%$, sound velocity was measured by single crystal ultrasonic interferometer (Mittal Enterprises, New Delhi) at 2 MHz frequency and data were accurate upto $\pm 0.07\%$. All measurements were made in a thermostatically controlled water bath with temperature accuracy of $\pm 0.1^\circ\text{C}$. The purity of the components was ascertained by comparing their densities and velocities, with the corresponding literature values at 303.15K. (Table.1)

3. Theory

The experimentally measured density (ρ), and sound velocity are used to evaluate derived parameters like molar volume (V_M), intermolecular free length (L_f) and isentropic compressibility (K_s) using well established relations.

$$L_f = K / U \rho^{1/2} \quad (1)$$

$$V_{\text{mix}} = (X_1 M_1 + X_2 M_2) / \rho \quad (2)$$

$$K_s = 1 / (U^2 \rho) \quad (3)$$

$$Z = U \rho \quad (4)$$

Excess parameters have been calculated from following equation.

$$Y^E = Y_{\text{mix}} - (X_1 Y_1 + X_2 Y_2) \quad (5)$$

Where Y^E is V_M^E , K_s^E or L_f^E . All the excess parameters of binary liquid mixtures are fitted to Redlich –Kister "Redlich-Kister, (1948)" polynomial equation.

$$Y = X_1 X_2 \sum A_i (X_1 - X_2)^i \quad (6)$$

Where Y represents is V_M^E , K_s^E and L_f^E in corresponding equation. Coefficients A_i were obtained by fitting equation to experimental values using a least square regression method. Where X_1 and X_2 are mole fraction of acetophenone and benzene respectively. The standard deviation is calculated by using the following relation.

$$\sigma(Y^E) = [(Y_{\text{EXP}}^E - Y_{\text{cal}}^E)^2 / (n-p)]^{1/2} \quad (7)$$

Where n is the total number of observations and p is the degree of fitting. The theoretical values of sound speeds are evaluated using the following relationships:

Sound speed by Jacobson's free length theory "jacobson.(1952)" is calculated using the following formula.

$$u^{\text{FLT}} = K / L_{f(\text{mix})} \rho^{1/2}_{\text{exp}} \quad (8)$$

Where K is the Jacobson's constant ($K = (93.875 + 0.375T) 10^{-8}$) and depends only on temperature and $L_{f(\text{mix})}$ is intermolecular free length of mixture.

Vandael vangeal "Vandael vangeal .(1969)" ideal mixing relation is compared from the following formula.

$$u^{\text{VAN}} = [(x_1/m_1 U_1^2 + x_2/m_2 U_2^2) (x_1 m_1 + x_2 m_2)]^{-1/2} \quad (9)$$

Where x_1 and x_2 are mole fractions and u_1 and u_2 is speed of sound of acetophenone and benzene respectively. The sound speed in the mixture is given by impedance dependence relation "Shipra and Parsania.(1995)" as

$$u^{\text{IDR}} = [(\chi_1 Z_1 + \chi_2 Z_2) / (\chi_1 \rho_1 + \chi_2 \rho_2)] \quad (10)$$

Where χ_i , Z_i and ρ_i are the mole fractions, impedance and density of the i^{th} component respectively

4. Results and Discussion

The experimental values of density and sound velocity have been used to determine V_M^E , K_s^E , L_f^E , interaction parameters (ρ) relative association (R_A) for the system under study. The experimental data and derived parameters at 303.15, 313.15 and 323.15 K are reported in tables 2-4 respectively. The excess parameters V_M^E , K_s^E , L_f^E and Z^E have been plotted against mole fraction of acetophenone in figures 1-4. Table 5 presents the smoothening coefficients and standard deviations at 303.15, 313.15, and 323.15K for the system under investigated. Table 6 presents experimental and theoretical values of sound speed and deviations of these theories from experimental sound speeds at the temperatures take for study.

The deviation of V_m^E with the mole fraction x_i of acetophenone (1) + benzene (2) at 303.15, 313.15 and 323.15 k is represented in figure.1. This shows that the excess molar volumes are always negative for all the studied temperature and for any composition. Roux and Desnoyers "Roux and Desnoyers.(1987)" suggested that V_m^E is the resultant contribution from several opposing effects. These may be divided arbitrarily into three types, namely, physical, chemical and structural. Physical contributions, that are nonspecific interactions between the real species present in the mixture, contribute a positive term of V_m^E . The chemical or specific intermolecular

interactions result in a volume decrease, and these include charge transfer type forces and other complex forming interactions. This effect contributes negative values of V_m^E . The structural contribution are mostly negative and arise from several effects, especially from interstitial accommodation and changes of free volume. The negative values for acetophenone + benzene system indicate strong specific interactions through dipolar association between acetophenone and benzene molecules over the entire composition range.

The deviation of isentropic compressibility for acetophenone and benzene system with temperature is recorded in tables 2-4. The excess isentropic compressibility data over the entire composition range are shown in figure.2 at three temperatures taken for the study. K_S^E increases with rise in temperature but the magnitude of increase is very-very less. The intermolecular free length as shown in tables 2-4 decreases with increase in concentration of acetophenone which implies strong interactions between the components.

The excess intermolecular free length becomes increasingly negative with increase in concentration of acetophenone. Negative L_f^E values as shown in figure.3 exhibit strong interaction. The lessening of interactions at higher temperatures is expected in accordance with the decrease in the negative value of L_f^E with rise in temperatures. The values of L_f^E are supported by the variation of K_S^E which also exhibits insignificant interactions in the system of acetophenone and benzene.

The deviation of excess acoustic impedance Z^E are found to be positive as shown in fig.4. The effect of an increase in the temperature appears to increase the excess properties, suggesting the presence of specific molecular interactions. As the temperature increases the values of K_S^E and L_f^E become more negative and Z^E becomes more positive this may be due to thermal dissociation of hetero aggregates in liquid mixtures and more interstitial accommodation of one component into another. Relative association is found to increase with the molar concentration of acetophenone +benzene system. Relatively higher values of R_A for the acetophenone +benzene system signifies that unlike interactions are relatively strong compared to like interactions.

The experimental data are correlated with composition according to Redlich Kister polynomial equation and the smoothening coefficients obtained using least square method and the standard deviation are listed in table 5. The values of interaction parameter (α) are reported in tables 2-4 for the three temperatures taken for the study. The interaction parameter is positive over the entire range of composition at all the three temperatures. The less positive values of the interaction parameter suggest that dispersion forces are prevalent in the system but the magnitude of these forces is very less which is in support of the results as explained above.

The experimental values of sound speed for the system along with theoretical values and percentage deviations for Free Length Theory (FLT), Impedance Dependence Relation (IDR), Vandeal Vangael ideal mixing relation (VAN) are presented in table.6. data reveal that sound speed computed from FLT exhibit more satisfactory agreement with the experimental values in the temperature range 303.15-323.15K than other approaches in the binary system. A positive deviation is observed in various theories for acetophenone- benzene.

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Table 1. Acetophenone+ Benzene Mixture

	Liquid	Experimental		Literature	
		303.15K	313.15 K	303.15K	313.15K
Density (ρ) gm cm ⁻³	Acetophenone	1.0198	1.0116	1.0194	1.0106
	Benzene	0.8624	0.8453	0.8720	0.8450
Sound of velocity ms ⁻¹	Acetophenone	1401	1391	-	-
	Benzene	1280	1251	-	-

Experimental Density and Ultrasonic Velocity of pure liquids with literature values at 303.15K and 313.15K

Table 2. Acetophenone + Benzene Mixture at 303.15K.

Mole Fraction of acetophenone	$\rho \times 10^{-3}$ Kg m ⁻³	U ms ⁻¹	$K_s \times 10^{-10}$ m ² N ⁻¹	Molar Volume cm ³ /mol	$L_f \times 10^{-11}$ m	Acoustical Impedance Z x10 ⁶ kg/m ² s	α	Relative Association
0.00000	0.86740	1280	7.0365	89.9239	5.5043	1110.27200	0	1
0.07791	0.88264	1292	6.7872	92.0927	5.4058	1140.37088	0.0239	1.0144
0.15975	0.89788	1304	6.5497	94.3724	5.3105	1170.83552	0.0450	1.0288
0.24581	0.91312	1316	6.3235	96.7708	5.2179	1201.66592	0.0627	1.0431
0.33642	0.92836	1328	6.1078	99.2971	5.1282	1232.86208	0.0762	1.0573
0.43198	0.9436	1340	5.9020	101.9630	5.0410	1264.42400	0.0845	1.0715
0.53288	0.95884	1352	5.7055	104.7789	4.9564	1296.35168	0.0864	1.0856
0.63958	0.97408	1364	5.5179	107.7578	4.8742	1328.64512	0.0805	1.0996
0.75260	0.98932	1376	5.3385	110.9142	4.7944	1361.30432	0.0653	1.1132
0.87252	1.00456	1388	5.1670	114.2644	4.7167	1394.32928	0.0387	1.1275
1.00000	1.01980	1401	4.9958	117.8270	4.6379	1428.73980	0	1.1411

Mole fraction, Ultrasonic velocity, Isentropic Compressibility, Molar Volume, Free length, Acoustical impedance, Interaction parameters and Relative Association of Acetophenone + Benzene mixture at 303.15 K.

Table 3. Acetophenone + Benzene Mixture at 313.15 K

Mole Fraction of acetophenone	$\rho \times 10^{-3}$ Kg m^{-3}	U ms $^{-1}$	$K_s \times 10^{-10}$ m 2 N $^{-1}$	Molar Volume cm 3 /mol	$L_f \times 10^{-11}$ m	Acoustical Impedance Z $\times 10^6$ kg/m 2 s	α	Relative Association
0.00000	0.84531	1251	7.5590	92.2738	5.8094	1057.48281	0	1
0.07791	0.86193	1265	7.2501	94.3054	5.6895	1090.34145	0.02639	1.0159
0.15975	0.87856	1279	6.9580	96.4477	5.5737	1123.67824	0.04989	1.0317
0.24581	0.89519	1293	6.6817	98.7090	5.4619	1157.48067	0.06976	1.0475
0.33642	0.91182	1307	6.4200	101.0983	5.3539	1191.74874	0.08508	1.0632
0.43198	0.92845	1321	6.1721	103.6268	5.2495	1226.48245	0.09478	1.0787
0.53288	0.94508	1335	5.9370	106.3045	5.1485	1261.68180	0.09758	1.0943
0.63958	0.96171	1349	5.7138	109.1438	5.0509	1297.34679	0.09195	1.1097
0.75260	0.97834	1363	5.5019	112.1590	4.9563	1333.47742	0.07607	1.1250
0.87252	0.99497	1377	5.3005	115.3657	4.8648	1370.07369	0.04774	1.1403
1.00000	1.01162	1391	5.1089	118.7798	4.7760	1407.16342	0	1.1555

Mole fraction, Ultrasonic velocity, Isentropic Compressibility, Molar Volume, Frelength, Acoustical impedance, Interaction parameters and Relative Association of Acetophenone + Benzene mixture at 313.15 K.

Table 4. Acetophenone + Benzene Mixture at 323.15 K.

Mole Fraction of acetophenone	$\rho \times 10^{-3}$ Kg m^{-3}	U ms $^{-1}$	$K_s \times 10^{-10}$ m 2 N $^{-1}$	Molar Volume cm 3 /mol	$L \times 10^{-11}$ m	Acoustical Impedance Z $\times 10^6$ kg/m 2 s	α	Relative Association
0.00000	0.8198	1229	8.0753	95.1394	6.1111	1007.59565	0	1
0.07791	0.8377	1243.5	7.7196	97.0285	5.9750	1041.72969	0.0279	1.0178
0.15975	0.8556	1256	7.4085	99.0324	5.8534	1074.67128	0.0497	1.0361
0.24581	0.8735	1268.5	7.1145	101.1578	5.7360	1108.06012	0.0679	1.0543
0.33642	0.8914	1281.5	6.8310	103.4131	5.6206	1142.34192	0.0825	1.0723
0.43198	0.9093	1295	6.5577	105.8092	5.5070	1177.54350	0.0924	1.0901
0.53288	0.9271	1308	6.3039	108.3556	5.3994	1212.76452	0.0948	1.1079
0.63958	0.9450	1321	6.0635	111.0643	5.2954	1248.45068	0.0890	1.1256
0.75260	0.9629	1333	5.8442	113.9492	5.1988	1283.63901	0.0716	1.1435
0.87252	0.9808	1346	5.6273	117.0253	5.1014	1320.23756	0.0438	1.1610
1.00000	0.9987	1358	5.4293	120.3104	5.0108	1356.30250	0	1.1787

Mole fraction, Ultrasonic velocity, Isentropic Compressibility, Molar Volume, Free length, Acoustical impedance, Interaction parameters and Relative Association of Acetophenone + Benzene mixture at 323.15 K.

Table 5. Parameters of Redlich –Kister.

	303.15K							
	A_0	A_1	A_2	A_3	A_4	A_5	A_6	α
$K_S^E \times 10^{-10} \text{ m}^2 \text{ N}^{-1}$	-1.0327	0.0897	1.0634	1.0836	-4.5207	-1.1614	4.4819	1.1679
$L_f^E \times 10^{-11} \text{ m}$	-0.3644	0.0241	0.3679	0.3656	-1.538	-0.3856	1.5317	6.0390
$V_M^E \text{ cm}^3 \text{ mol}^{-1}$	-0.0595	0.0052	0.0626	0.0492	-0.2725	-0.0537	0.2688	0.0714
	313.15K							
$K_S^E \times 10^{-10} \text{ m}^2 \text{ N}^{-1}$	-1.3421	0.1266	1.3901	1.2777	-6.0877	-1.3891	6.0293	1.5013
$L_f^E \times 10^{-11} \text{ m}$	-0.4654	0.0335	0.4694	0.3933	-2.0384	-0.4218	2.031	6.6166
$V_M^E \text{ cm}^3 \text{ mol}^{-1}$	-0.3967	0.0341	0.3886	0.3575	-1.6552	-0.3873	1.6605	0.4122
	323.15K							
$K_S^E \times 10^{-10} \text{ m}^2 \text{ N}^{-1}$	-1.5528	0.0242	2.2533	2.074	-9.2242	-2.076	8.5083	2.2239
$L_f^E \times 10^{-11} \text{ m}$	-0.5372	-0.0096	0.7967	0.6795	-3.2098	-0.6625	2.9452	8.1022
$V_M^E \text{ cm}^3 \text{ mol}^{-1}$	-0.8337	0.068	0.8556	0.7417	-3.7314	-0.8005	3.7033	0.9140

Redlich kister Constants for Acetophenone+ Benzene Mixture at 303.15, 313.15 and 323.15 K.

Table 6. Ultrasonic Velocity

Mole fraction of (x1) acetophenone	u_{Exp}^{-1} m s	u^{IDR}_{-1} m s	u^{VAN}_{-1} m s	u^{FLT}_{-1} ms	% Deviation		
					u^{IDR}_{-1} m s	u^{VAN}_{-1} ms	u^{FLT}_{-1} m s
	303.15K						
0.00000	1280	1280	1280	1280	0	0	0.0
0.07791	1292	1290.9338	1286.694	1292	0.082526	0.410643	0.0
0.15975	1304	1302.1055	1294.142	1304	0.145285	0.756012	0.0
0.24581	1316	1313.5211	1302.453	1316	0.188369	1.029441	0.0
0.33642	1328	1325.1879	1311.762	1328	0.211752	1.222777	0.0
0.43198	1340	1337.1181	1322.235	1340	0.215069	1.325765	0.0
0.53288	1352	1349.3173	1334.069	1352	0.198424	1.326237	0.0
0.63958	1364	1361.7948	1347.511	1364	0.161674	1.208862	0.0
0.75260	1376	1374.5607	1362.868	1376	0.104602	0.954332	0.0
0.87252	1388	1387.6253	1380.531	1388	0.026998	0.538133	0.0
1.00000	1401	1401	1401	1401	0	0	0.0
	313.15K						
0.00000	1251	1251	1251	1251	0.00000	0.00000	0.0
0.07791	1265	1263.856	1258.688	1265	0.09041	0.49898	0.0
0.15975	1279	1276.95	1267.239	1279	0.16031	0.91952	0.0
0.24581	1293	1290.284	1276.785	1293	0.21004	1.25403	0.0
0.33642	1307	1303.866	1287.485	1307	0.23978	1.49308	0.0
0.43198	1321	1317.706	1299.538	1321	0.24933	1.62469	0.0
0.53288	1335	1331.809	1313.18	1335	0.23904	1.63444	0.0
0.63958	1349	1346.181	1328.712	1349	0.20897	1.50395	0.0
0.75260	1363	1360.831	1346.511	1363	0.15913	1.20976	0.0
0.87252	1377	1375.768	1367.063	1377	0.08950	0.72167	0.0
1.00000	1391	1391	1391	1391	0.00000	0.00000	0.0
	323.15K						
0.00000	1229	1229	1229	1229	0.00000	0.00000	0.0
0.07791	1243.5	1241.039	1236.109	1243.5	0.19792	0.59437	0.0
0.15975	1256	1253.259	1244.0159	1256	0.21823	0.95414	0.0
0.24581	1268.5	1265.662	1252.8406	1268.5	0.22370	1.23448	0.0
0.33642	1281.5	1278.253	1262.7283	1281.5	0.25341	1.46483	0.0
0.43198	1295	1291.038	1273.8593	1295	0.30598	1.63249	0.0
0.53288	1308	1304.019	1286.4489	1308	0.30439	1.64764	0.0
0.63958	1321	1317.2	1300.7671	1321	0.28766	1.53163	0.0
0.75260	1333	1330.587	1317.1544	1333	0.18100	1.18872	0.0
0.87252	1346	1344.185	1336.0443	1346	0.13482	0.73965	0.0
1.00000	1358	1358	1358	1358	0.00000	0.00000	0.0

Mole fraction, Experimental Ultrasonic Velocity, Theoretical Ultrasonic Velocities of Impedance Dependence Relation, Vandael Vangeal Relation, Free length Theory and Deviations a for acetophenone +benzene mixture at 303.15K, 313.15K, and 323.15K

FIGURES

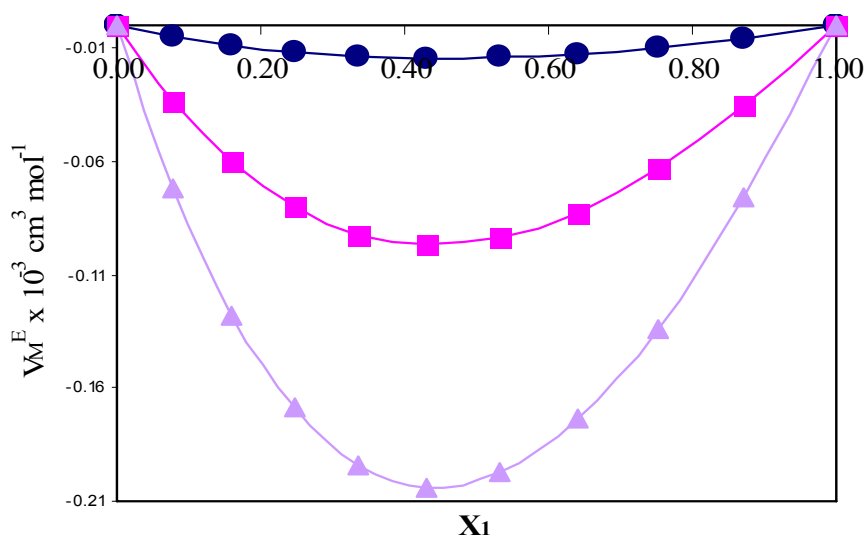


Figure 1. Plot of V_M^E against X_1 of Acetopenone, Acetopenone + Benzene at 303.15 K (●), 313.15 K (■) and 323.15 K (▲)

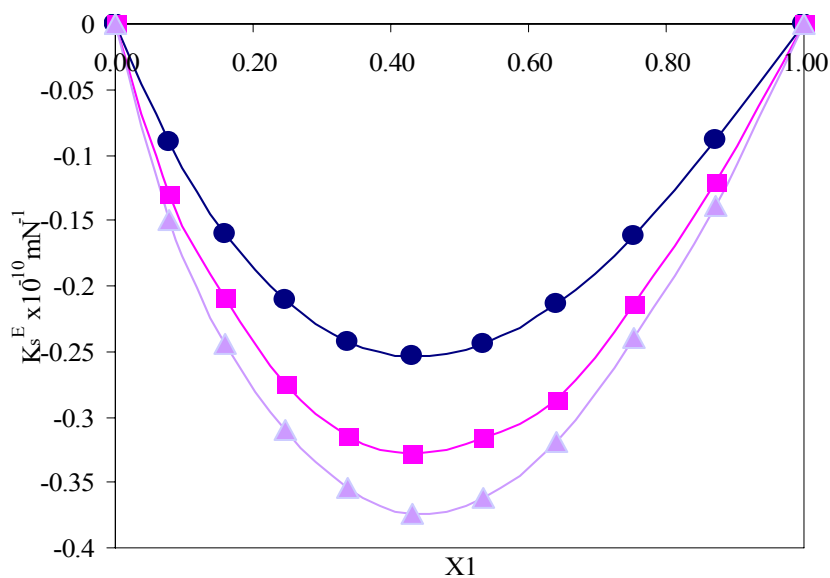


Figure 2. Plot of K_s^E against X_1 of Acetopenone, Acetopenone + Benzene at 303.15 K (●), 313.15 K (■) and 323.15 K (▲)

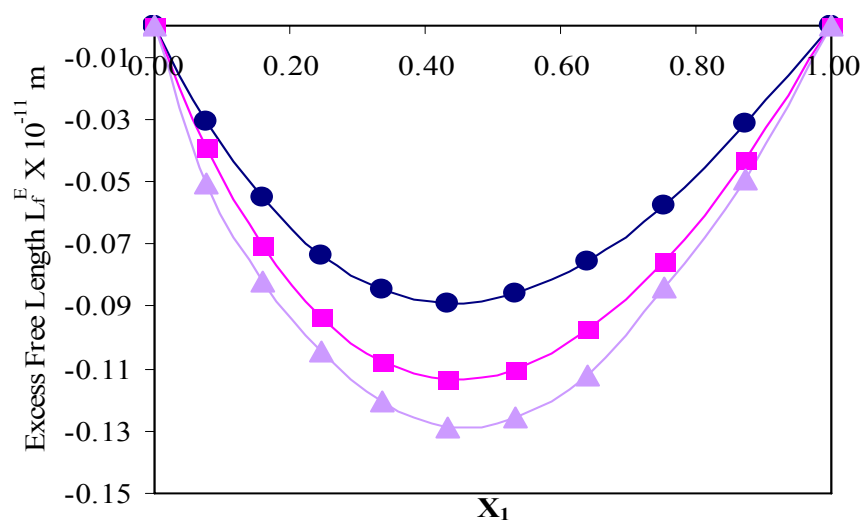


Figure 3. Plot of L_f^E against X_1 of Acetopenone, Acetopenone + Benzene at 303.15 K (●), 313.15 K (■) and 323.15 K (▲)

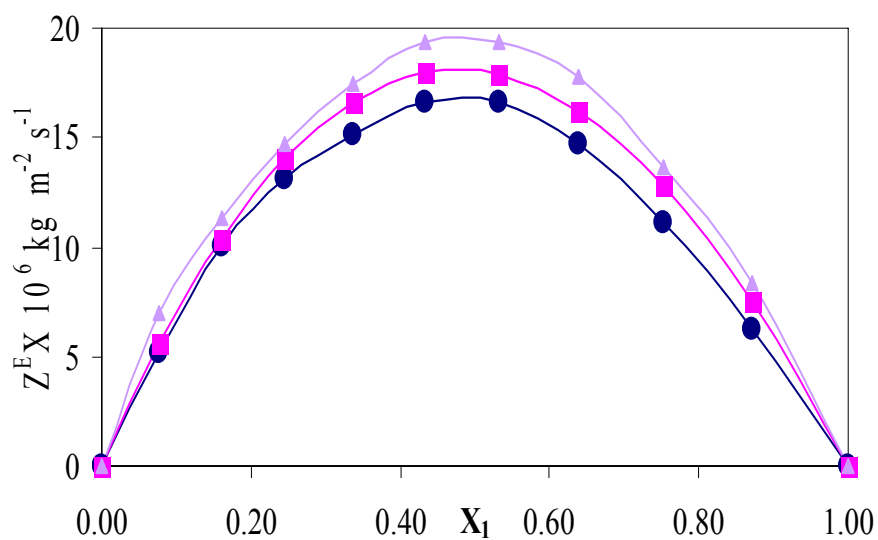


Figure 4. Plot of Z^E against X_1 of Acetopenone, Acetopenone + Benzene at 303.15 K (●), 313.15 K (■) and 323.15 K (▲)