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Molecular Interaction Studies on Some Binary Liquid Mixtures at 303.15, 308.15, 313.15 and 318.15 K

K. Narendra[1*], Ch. Srinivasu[2], Sk. Fakruddin[1] and P. Narayana Murthy[3]

[1]Department of Physics, V.R. Siddhartha Engineering College, Vijayawada, India
[2]Department of Physics, Andhra Loyola College, Vijayawada, India
[3]Department of Physics, Acharya Nagarjuna University, Guntur, India

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ABSTRACT

Density (ρ), viscosity (η) and ultrasonic velocity (u) of binary liquid mixtures of anisaldehyde with o-cresol, m-cresol and p-cresol over the entire composition range have been measured at 303.15, 308.15, 313.15 and 318.15 K. Experimental data have been used to evaluate the excess ultrasonic velocity (u^E), excess enthalpy (H^E) and excess free volume (V_f^E). The computed results were fitted to the Redlich–Kister polynomial equation. These results suggest that specific interactions are taking place in the components of liquid mixtures.

Key Words: Binary liquid mixture, enthalpy, internal pressure, anisaldehyde, cresol.

INTRODUCTION

The ultrasonic method plays an important role in understanding the physic-co-chemical behavior of liquids. The velocity gives information about the bonding between the molecule and formation of complexes at various temperatures through molecular interactions [1–3]. Properties such as densities, viscosities and ultrasonic velocities and their variation with temperature and composition of the binary mixture are useful to design engineering processes and in chemical and biological industries. The study on changes in these properties of mixtures has been found to be an excellent qualitative and quantitative way to bring out the information about molecular structure and intermolecular forces present in the liquid mixtures. In order to examine molecular interaction in the mixture of anisaldehyde with phenols through excess acoustical properties, we report here the density (ρ), viscosity (η) and ultrasonic velocity (*u*) of binary mixtures of anisaldehyde with o-cresol, m-cresol and p-cresol over the entire range of composition at T = 303.15, 308.15, 313.15 and 318.15 K. The experimental values of ρ, η and *u* were used to calculate the excess ultrasonic velocity (u^E), excess enthalpy (H^E) and excess free volume (V_f^E). These results have been used by several workers [4-6] to discuss the nature of interaction between unlike molecules in terms of hydrogen bonding, dipole– dipole interaction and dispersive forces. The results are explained in terms of intermolecular interactions occurring in these binary liquid mixtures.

EXPERIMENTAL SECTION

The mass fraction purity of the liquids (obtained from Merck) was as follows: o-cresol (0.990), m-cresol (0.990) and p-cresol (0.980) and the purity of the liquid (obtained from SRL chemicals) anisaldehyde (0.990). All the liquids used were further purified by standard procedure [7]. The purity of samples was checked by comparing experimental values of density, viscosity and ultrasonic velocity with those reported in the literature (Table 1). Job's method of continuous variation was used to prepare the mixtures of required proportions. The prepared mixtures were

preserved in well-Stoppard conical flasks. After mixing the liquids thoroughly, the flasks were left undisturbed to allow them to attain thermal equilibrium.

The densities of pure liquids and liquid mixtures were measured by using a specific gravity bottle with an accuracy of ± 0.5%. Weights were measured with an electronic digital balance (Shimadzu AUY220, Japan) capable of measuring up to 0.1 mg. An average of 4-5 measurements was taken for each sample. Viscosities were measured at the desired temperature using Ostwald's viscometer; the viscometer is calibrated using water and benzene. After the mixture had attained bath temperature, flow time has been measured. The flow measurements were made with an electronic stopwatch with a precision of 0.01 sec. The viscosity is determined using the relation

$$\eta = k\rho t \quad \ldots (1)$$

Where k, ρ and t are viscometric constant, density of liquid and time of efflux for a constant volume of liquid, respectively. The values are accurate to ± 0.001mPaS.

The ultrasonic velocities were measured by using single crystal ultrasonic pulse echo interferometer (Mittal Enterprises, New Delhi, Model: F-80X). It consists of a high frequency generator and a measuring cell. The measurements of ultrasonic velocities were made at a fixed frequency of 3MHz. The calibration of the equipment was done by measuring the velocity in carbon tetrachloride and benzene. The results are in good agreement with the literature values [8]. The ultrasonic velocity has an accuracy of ± 0.5 m/s. The temperature was controlled by circulating water around the liquid cell from thermostatically controlled constant temperature water bath (accuracy ± 0.1 K).

Theory

From the experimental data of density, viscosity and ultrasonic velocity various thermodynamic parameters are evaluated using stand equations:

$$\text{Free volume } V_f = [\, M_{eff}\, u / K\eta]^{3/2} \quad \ldots (2)$$

Where M_{eff} is the effective molecular weight and K is proportionality constant, which is sensitive to molecular phenomenon.

$$\text{Enthalpy } H = V_m \pi \quad \ldots (3)$$

Where V_m is the molar volume and π is the internal pressure.

The strength of interaction between the component molecules of binary mixtures is well reflected in the deviation of the excess functions from ideality [9]. The excess properties such as V_f^E, H^E and u^E have been calculated using the equation

$$Y^E = Y_{mix} - [x_1Y_1 + x_2Y_2] \quad \ldots (4)$$

Where Y^E is V_f^E or H^E or u^E and x represent mole fraction of the component and subscript 1 and 2 for the components 1 and 2.

The excess values of above parameters for each mixture have been fitted to Redlich-Kister [10] polynomial equation

$$Y^E = x_1 (1-x_1) \Sigma A_i (2x_1-1)^i \quad (i = 0, 1, 2) \quad \ldots (5)$$

The values of the coefficients A_i were calculated by method of least squares along with the standard deviation σ (Y^E). The coefficient is adjustable parameters for a better fit of the excess functions. The standard deviation values were obtained from

$$\sigma (Y^E) = [\, \Sigma (Y^E_{expt} - Y^E_{cal})^2 / (m-n)\,]^{1/2} \quad \ldots (6)$$

Where m is the number of experimental points, n is the number of parameters, Y_{expt} and Y_{cal} are the experimental and calculated parameters, respectively.

RESULTS AND DISCUSSION

The experimental values of density (ρ), viscosity (η) and ultrasonic velocity (*u*) for all the mixtures over the entire range of composition are presented in Table 2 at 303.15, 308.15, 313.15 and 318.15 K. The values of the Redlich–Kister polynomial coefficient A_i evaluated by the method of least squares along with standard deviation is given in Table 3. Plots of u^E, H^E and V_f^E against mole fraction of anisaldehyde for all the mixtures are given in Figs. 1-3, respectively.

Table-1 Comparison of experimental values of density (ρ), viscosity (η) and velocity (u) of pure liquids with literature values at 303.15 K.

Liquids	ρ/ (Kg m^{-3})		η/ (x 10^{-3} Nsm^{-2})		u/ (m s^{-1})	
	Expt.	Lit.	Expt.	Lit.	Expt.	Lit.
anisaldehyde	1125.2	1125.5[a]	3.2512	3.2753[a]	1694.3	1684[a]
o- cresol	1036.2	1036.9[b]	7.4791	4.243[c] (313.15) K	1485.3	1487[b]
m- cresol	1025.8	1026.1[b]	8.9290	6.252[c] (313.15) K	1464.2	1465[b]
p- cresol	1026.5	1026.3[b]	9.5398	6.661[c] (313.15) K	1468.4	1471[b]

Expt. – Experimental; Lit. – Literature; [a]Ref. 15; [b]Ref. 16; [c]Ref. 17

The values of u^E, H^E and V_f^E for the binary mixtures of anisaldehyde with o-cresol, m-cresol and p-cresol may be explained on the basis of various types of intermolecular interactions between components. According to Parveen *et.al.*,[11] the excess thermodynamic properties of the mixtures are influenced by three main types of contribution, viz. (i) physical: due to non-specific Vander Walls type forces (ii) chemical: due to hydrogen bonding, dipole–dipole, and donor–acceptor interaction between unlike molecules and (iii) structural: due to the fitting of smaller molecules into the voids created by the bigger molecules. The first effect leads to contraction in volume, hence leads to positive contribution towards H^E and V^E_f and negative contribution towards u^E. However, the remaining two effects lead to the contraction in volume, resulting in negative H^E, V_f^E values and positive u^E values.

From Fig.1 it can be observed that u^E values are positive for all the mixtures at all the temperatures studied. In the present investigation the magnitude of u^E values follows the sequence: o-cresol > p-cresol > m-cresol. The higher positive values of u^E for anisaldehyde + o-cresol mixture suggest that interaction between anisaldehyde and o-cresol is stronger as compared to that of between anisaldehyde and p-cresol or m-cresol. The effect of temperature on u^E values is not very significant in the case of anisaldehyde + o- cresol or + p-cresol mixtures. However, an appreciable change is observed in u^E values in anisaldehyde rich region. The plots of deviation in ultrasonic velocity u^E with mole fraction at all the four temperatures for all the three mixtures exhibit positive values. The positive values of u^E decrease with increase in temperature which indicates the decrease in strength of interaction with temperature in all the three mixtures. As anisaldehyde is an aprotic liquid and when it is mixed with phenols (protic liquids), it tends to break the associates present in the phenol molecules. The higher positive values of u^E in anisaldehyde + o-cresol mixture indicate the presence of strong intermolecular interaction [12].

Table-2 Values of density (ρ), viscosity (η) and velocity (u) of binary mixtures at different temperatures

x_1	ρ/ (Kg m^{-3})	η /(x 10^{-3} Nsm^{-2})	u/ (m s^{-1})	x_1	ρ/ (Kg m^{-3})	η /(x 10^{-3} Nsm^{-2})	u/ (m s^{-1})	x_1	ρ/ (Kg m^{-3})	η /(x 10^{-3} Nsm^{-2})	u/ (m s^{-1})
anisaldehyde + o- cresol 303.15 K				**anisaldehyde + m- cresol 303.15 K**				**anisaldehyde + p- cresol 303.15 K**			
0.0000	1036.2	7.4791	1485	0.0000	1025.8	8.9290	1464	0.0000	1026.5	9.5398	1468
0.0875	1039.2	7.1628	1507	0.0883	1031.6	8.5127	1487	0.0882	1032.1	9.1420	1492
0.1774	1044.2	6.8243	1526	0.1789	1037.8	8.0284	1507	0.1788	1038.5	8.6180	1511
0.2699	1050.1	6.5188	1545	0.2719	1044.0	7.5687	1528	0.2717	1044.6	8.0859	1532
0.3651	1058.5	6.2016	1564	0.3674	1052.6	7.0515	1550	0.3673	1053.0	7.5237	1553
0.4631	1067.1	5.7780	1585	0.4656	1060.7	6.5279	1572	0.4654	1061.2	7.0638	1575
0.5640	1074.3	5.3187	1611	0.5665	1068.0	5.9686	1595	0.5663	1068.4	6.5426	1599
0.6680	1081.3	4.8115	1636	0.6703	1076.4	5.3314	1619	0.6701	1076.7	5.7532	1622
0.7753	1093.2	4.2607	1658	0.7770	1088.0	4.5926	1643	0.7769	1089.3	5.0400	1646
0.8859	1106.6	3.7576	1681	0.8869	1104.5	3.9300	1668	0.8868	1105.6	4.2647	1671
1.0000	1125.2	3.2512	1694	1.0000	1125.2	3.2512	1694	1.0000	1125.2	3.2512	1694

308.15 K				308.15 K				308.15 K			
0.0000	1031.0	5.9629	1466	0.0000	1021.5	7.4121	1449	0.0000	1022.0	8.1190	1455
0.0875	1033.8	5.7620	1488	0.0883	1026.7	7.1076	1471	0.0882	1027.7	7.8243	1477
0.1774	1038.2	5.5404	1506	0.1789	1032.4	6.7474	1490	0.1788	1033.0	7.4188	1496
0.2699	1043.4	5.3613	1524	0.2719	1038.0	6.4210	1511	0.2717	1038.6	7.0015	1516
0.3651	1050.6	5.1677	1544	0.3674	1045.4	6.0458	1532	0.3673	1045.9	6.5680	1536
0.4631	1058.4	4.8739	1564	0.4656	1052.3	5.6585	1553	0.4654	1053.0	6.2185	1558
0.5640	1065.0	4.5597	1589	0.5665	1060.0	5.2373	1575	0.5663	1060.5	5.8261	1580
0.6680	1071.5	4.1963	1613	0.6703	1066.1	4.7414	1598	0.6701	1066.8	5.1576	1602
0.7753	1082.8	3.8152	1635	0.7770	1077.2	4.1515	1621	0.7769	1077.5	4.6038	1625
0.8859	1095.3	3.4751	1657	0.8869	1092.6	3.6476	1645	0.8868	1093.0	3.9654	1648
1.0000	1111.6	3.1306	1670	1.0000	1111.6	3.1306	1670	1.0000	1111.6	3.1306	1670
313.15 K				**313.15 K**				**313.15 K**			
00.000	1026.0	4.2380	1452	0.0000	1017.0	6.1160	1436	0.0000	1018.1	6.7410	1443
0.0875	1030.2	4.1621	1470	0.0883	1022.8	5.8936	1455	0.0882	1024.2	6.5293	1462
0.1774	1034.7	4.0725	1486	0.1789	1028.4	5.6289	1473	0.1788	1029.7	6.2416	1479
0.2699	1040.9	4.0075	1502	0.2719	1034.8	5.3930	1490	0.2717	1035.9	5.9127	1496
0.3651	1047.3	3.9364	1519	0.3674	1042.8	5.1298	1509	0.3673	1044.0	5.5817	1514
0.4631	1055.4	3.8060	1536	0.4656	1049.1	4.8580	1528	0.4654	1050.3	5.3386	1533
0.5640	1062.1	3.6728	1560	0.5665	1056.8	4.5554	1547	0.5663	1057.6	5.0700	1552
0.6680	1070.0	3.4940	1580	0.6703	1064.4	4.1814	1567	0.6701	1065.6	4.5412	1572
0.7753	1082.1	3.2908	1598	0.7770	1075.1	3.7240	1588	0.7769	1076.5	4.0989	1591
0.8859	1094.9	3.1260	1617	0.8869	1090.9	3.3400	1609	0.8868	1091.7	3.6092	1612
1.0000	1109.5	2.9614	1631	1.0000	1109.5	2.9614	1631	1.0000	1109.5	2.9614	1631
318.15 K				**318.15 K**				**318.15 K**			
0.0000	1021.1	2.2150	1437	0.0000	1013.5	5.0185	1424	0.0000	1013.9	5.4690	1432
0.0875	1026.3	2.2689	1449	0.0883	1019.2	4.8489	1437	0.0882	1020.0	5.3161	1445
0.1774	1031.9	2.3130	1460	0.1789	1026.5	4.6554	1449	0.1788	1027.2	5.1150	1456
0.2699	1038.3	2.3633	1470	0.2719	1033.4	4.4695	1461	0.2717	1033.9	4.8700	1467
0.3651	1044.3	2.4141	1482	0.3674	1041.6	4.2725	1474	0.3673	1042.1	4.6160	1479
0.4631	1052.8	2.4506	1493	0.4656	1048.2	4.0849	1486	0.4654	1048.9	4.4315	1492
0.5640	1059.5	2.4960	1511	0.5665	1055.2	3.8683	1500	0.5663	1055.4	4.2586	1505
0.6680	1067.7	2.5427	1524	0.6703	1062.5	3.5863	1513	0.6701	1063.0	3.8612	1518
0.7753	1078.8	2.5892	1536	0.7770	1073.3	3.2362	1527	0.7769	1073.7	3.5228	1531
0.8859	1090.1	2.6308	1549	0.8869	1088.4	2.9489	1542	0.8868	1088.9	3.1628	1544
1.0000	1104.7	2.6822	1557	1.0000	1104.7	2.6822	1557	1.0000	1104.7	2.6822	1557

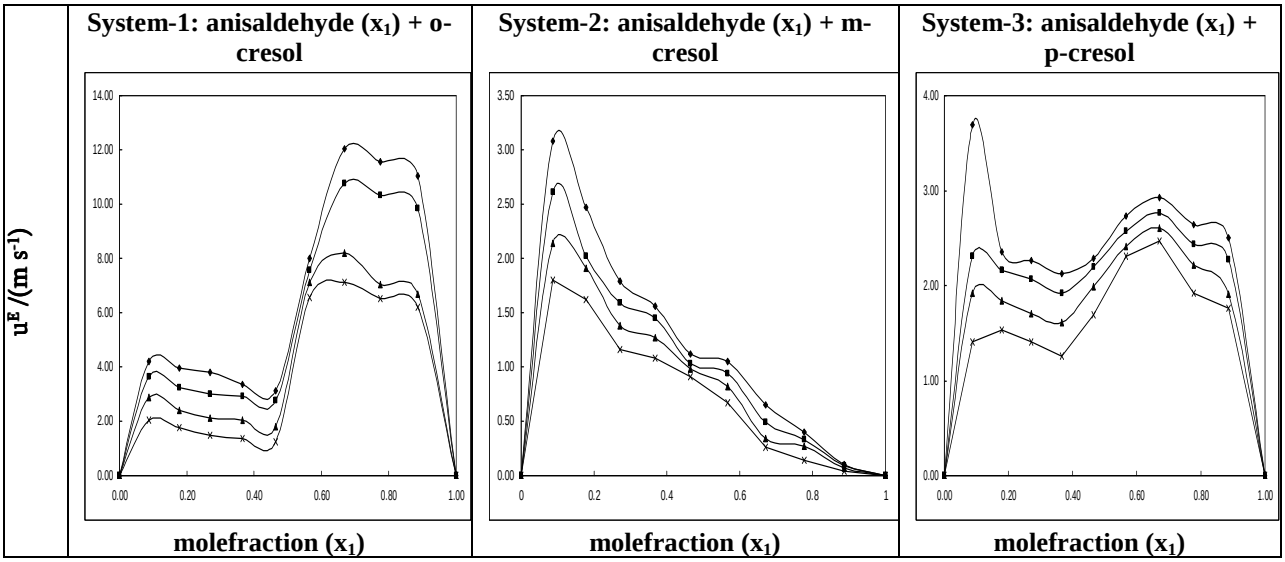

Fig. 1 The Variation of excess ultrasonic velocity with mole fraction of anisaldehyde (x_1) for (a) anisaldehyde + o-cresol (b) anisaldehyde + m-cresol and (c) anisaldehyde + p-cresol mixture at ♦303.15, ■308.15, ▲313.15 and ×318.15 K.

Table-3 The values of coefficient A_i from Equation (5) for u^E, H^E and V_f^E and standard deviation σ (Y^E) for binary liquids at varying temperatures.

System	Temp./ (K)	A_0	A_1	A_2	σ
u^E/ (m s^{-1})					
anisaldehyde + o-cresol	303.15	14.9396	41.2528	105.1554	1.4682
	308.15	13.3817	37.1995	92.5946	1.4062
	313.15	8.5686	22.4567	67.6270	1.7999
	318.15	6.6397	25.6170	58.4664	1.6076
H^E /(KJ mol^{-1})					
	303.15	29.7536	-3.6304	-25.4819	0.4929
	308.15	23.9862	-5.9947	-25.0264	0.5928
	313.15	16.7937	-6.0545	-19.6838	0.3432
	318.15	4.5765	-4.5792	-1.4176	0.1632
V_f^E / (x 10^{-6} m^3 mol^{-1})					
	303.15	-6.5197	-3.0307	-0.4890	0.0111
	308.15	-5.5015	-1.7744	0.3841	0.0146
	313.15	-3.6668	-0.4533	1.0215	0.0190
	318.15	-0.2544	0.5973	0.3009	0.0173
u^E/(m s^{-1})					
anisaldehyde + m-cresol	303.15	2.8627	-22.0698	25.4053	1.0603
	308.15	2.7539	-18.6926	21.0561	0.8826
	313.15	2.8020	-15.3940	16.3799	0.6574
	318.15	2.6941	-13.0999	13.0959	0.5558
H^E/(KJ mol^{-1})					
	303.15	33.7097	3.9058	-9.0662	0.6700
	308.15	30.354	0.3754	-13.7176	0.7002
	313.15	26.3186	-1.8996	-17.8573	0.8040
	318.15	21.0524	-4.8962	-18.6758	0.9687
V_f^E /(x 10^{-6} m^3 mol^{-1})					
	303.15	-7.6181	-5.0235	-2.2831	0.0282
	308.15	-6.9952	-3.8373	-1.3232	0.0212
	313.15	-6.3364	-2.7532	-0.4563	0.0329
	318.15	-5.8020	-1.8277	0.2973	0.0551
u^E/(m s^{-1})					
anisaldehyde + p-cresol	303.15	8.2434	-10.9640	42.1784	1.2867
	308.15	8.5463	-2.4236	26.8039	0.5705
	313.15	7.7196	-1.9636	21.4319	0.5362
	318.15	6.7658	0.7783	16.8180	0.4129
H^E/(KJ mol^{-1})					
	303.15	56.9269	39.9771	29.1427	1.3611
	308.15	52.6042	33.6175	25.7772	1.4075
	313.15	45.7201	26.0998	20.1988	1.4495
	318.15	36.8592	19.3744	19.2301	1.3058
V_f^E /(x 10^{-6} m^3 mol^{-1})					
	303.15	-8.4437	-8.3153	-5.5034	0.1445
	308.15	-8.0517	-7.3919	-4.7787	0.1224
	313.15	-7.5256	-6.2820	-3.9114	0.0954
	318.15	-7.0255	-5.3492	-3.2979	0.0764

The values of excess enthalpy H^E can be interpreted in terms of the formation of intermolecular hydrogen bonding and the breaking of associated structures of the anisaldehyde with phenols. From Fig.2 it is observed that the H^E values are positive for all the three mixtures taken up for study. The positive values of H^E in the mixture indicate the presence of strong interaction between unlike molecules [13]. The interaction between anisaldehyde and o-cresol or m-cresol or p-cresol may lead to dispersion type forces due to rupture of hydrogen bonded self-association in cresol molecules giving rise to positive values in H^E.

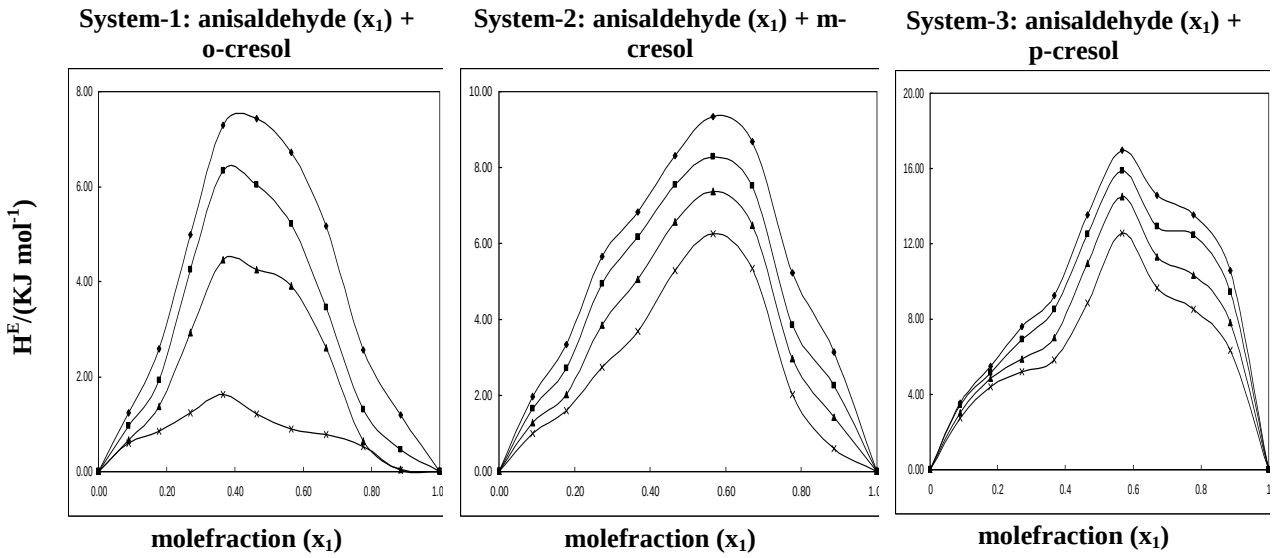

Fig. 2 The Variation of excess enthalpy with mole fraction of anisaldehyde (x_1) for (a) anisaldehyde + o-cresol (b) anisaldehyde + m-cresol and (c) anisaldehyde + p-cresol mixture at ♦303.15, ■308.15, ▲313.15 and ×318.15 K.

Excess free volume (V_f^E) is found to be negative (Fig.3) for all the binary mixtures over the entire composition range and absolute values of V_f^E increases as the temperature is raised, suggesting an increase in intermolecular interaction between unlike molecules due to thermal energy. The negative values of V_f^E suggest the existence of strong dipole–dipole type of interaction between anisaldehyde and cresols. This observation has been supported by Rama Rao *et.al*.[14].

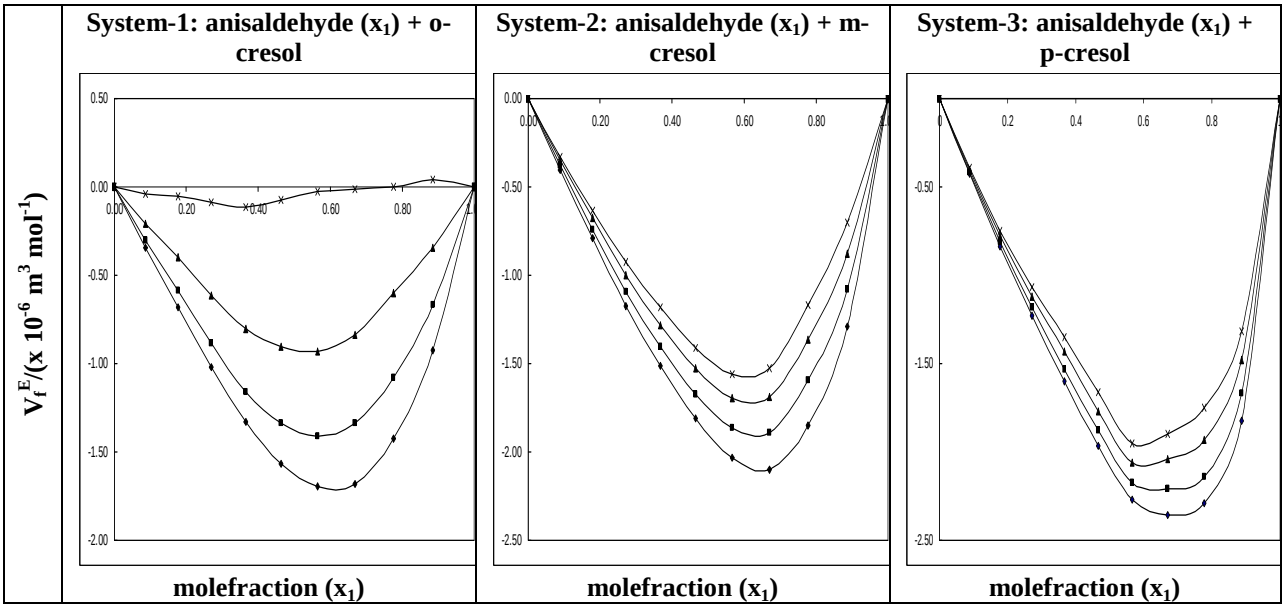

Fig. 3 Variation of excess free volume with mole fraction of anisaldehyde (x_1) for (a) anisaldehyde + o-cresol (b) anisaldehyde + m-cresol and (c) anisaldehyde + p-cresol mixture at ♦303.15, ■308.15, ▲313.15 and ×318.15 K.

CONCLUSION

The negative values of V_f^E and positive values of u^E and H^E in all the three binary mixtures support the existence of strong molecular interactions between the molecules of the mixtures taken up for study.

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