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Studies of Molecular Interaction in Binary Liquid Mixtures of O-Cresol and Nonanol at Different Temperatures

Narendra K^{*}, Tulasi K B B¹, Babu Rao K², Srinivas SSJ², Sarath Babu M²

^{*}Department of Physics, V.R. Siddhartha Engg. College, Vijayawada, A.P.

¹Department of Chemistry C.R Reddy College for women, Eluru, A.P

²Department of Chemistry, MIC College of Technology, Kanchikacherla, A.P

ABSTRACT

Various acoustic and thermodynamic parameters are calculated from the values of velocity, density and viscosity that were experimentally measured. Excess parameters such as excess adiabatic compressibility (β^E), excess free volume (V_f^E), excess enthalpy (H^E) and excess Gibbs free energy of activation (G^{*E}) are calculated at four temperatures 303.15, 308.15, 313.15 and 318.15 K, and the results are explained in the light of the molecular interactions. Theoretical values of ultrasonic speed in binary liquid mixtures are calculated using Nomoto's relation, Van Dael and Vangeel's ideal mixing relation, impedance relation, Rao's specific sound velocity relation and Junjie's equation. The relative merits of these theories and relations are also discussed.

Key words: Binary mixtures, Ultrasonic's, o-cresol, nonanol.

***Corresponding author:**

E-mail: narenk75@gmail.com

INTRODUCTION

Ultrasonic measurements are very useful in chemical and food processing, material testing, under water range cleaning. Ultrasonic's also has wide range of applications in the fields of physics, chemistry, biology and medicine. Ultrasonic vibrations are commonly employed in mechanical machinery of materials [1], preparation of colloids or emulsions, imaging of biological tissues and non-destructive testing (NDT). Ultrasonic AFM (Atomic force microscope) can improve fabrication technologies on nanometer scale [2] and ultrasound eliminates friction at a nanometer scale [3]. The properties of liquid mixtures are thermodynamically very important as part of studies of thermodynamic, acoustic and transport aspects. The intermolecular forces of liquids in a mixture show a considerable effect on the physical and chemical properties [4-6]. There is continuing need for reliable thermodynamic data of binary systems for chemical industries as the data is essential in the design of processes involving chemical separation, heat transfer, mass transfer and fluid flow.

Several researchers [7-11] have carried out ultrasonic investigations on liquid mixtures and correlated the experimental results with the theoretical relations of Nomoto [12], Van Dael and Vangeel [13], impedance relation [14], Rao's specific velocity [15] and Junjie [16]. In the present work the results are also interpreted in terms of molecular interactions.

MATERIALS AND METHODS

Experimental

Chemicals

The chemicals used in the present study are of AnalarR grade (99% of purity) and hence used without further purification.

Measurements

The ultrasonic velocity is measured by using ultrasonic interferometer (Mittal Enterprises, New Delhi) at a fixed frequency of 3MHz with an accuracy of $\pm 0.05\%$. The densities of liquid mixtures are measured using 10 ml specific gravity bottle and the weights are taken with an accuracy of $\pm 0.1\text{mg}$.

The viscosities are measured with Ostwald's viscometer. In this method, the time taken by a given volume of liquid to flow through a small capillary tube is measured. Similarly, the flow time with water of known viscosity is also measured. The ratio of flow time is equal to the ratio of kinematic viscosities. If the densities of the test liquid and water are known the dynamic viscosity of the experimental liquid can be calculated using the following expression.

$$\eta = (\rho t / \rho^1 t^1) \eta^1 \quad - \quad (1)$$

The accuracy in viscosity measurement is up to 0.01cp. The measurements are made at all the temperatures with the help of thermostat with an accuracy of $\pm 0.01K$.

THEORY

The acoustic and thermodynamic parameters are calculated by using the standard relations given elsewhere [17]. Excess values are calculated using the relation $Y^E = Y_{\text{exp}} - Y_{\text{ideal}}$, where Y^E is the excess value of the parameter Y , Y_{exp} is the experimental value of the parameter Y , $Y_{\text{ideal}} = X_1Y_1 + X_2Y_2$; X_1, X_2 are the mole fractions and Y_1 and Y_2 are the values of the parameter Y in the component liquids of the liquid mixture.

Assuming the linear dependence of the molar sound velocity (R) on concentration in mole fraction (X_1 and X_2) and the additivity of molar volume V , Nomoto established an empirical relation for ultrasonic velocity in binary liquid mixtures as

$$U_N = [(X_1R_1 + X_2R_2)/(X_1V_1 + X_2V_2)]^3 \quad - \quad (2)$$

Van Dael and Vangeel Ideal mixing relation is

$$U_{\text{Imx}} = [(X_1/M_1U_1^2 + X_2/M_2U_2^2)(X_1M_1 + X_2M_2)]^{-1/2} \quad - \quad (3)$$

Where U_{Imx} is the ideal mixing ultrasonic velocity in liquid mixture and U_1 and U_2 are ultrasonic velocities of individual compounds.

Impedance dependent relation is

$$U_{\text{Ir}} = \sum X_i Z_i / \sum X_i \rho_i \quad - \quad (4)$$

where X_i is the mole fraction, ρ_i the density of the mixture and Z_i is the acoustic impedance. Rao's specific sound velocity is

$$U_R = (\sum X_i r_i \rho_i)^3 \quad - \quad (5)$$

Where X_i is the mole fraction, U_i is the ultrasonic velocity, ρ_i the density of the mixture and r_i is the Rao's specific sound velocity = $U_i^{1/3} / \rho_i$ and Z_i is the acoustic impedance.

Jungie's equation is

$$U_J = (X_1M_1/\rho_1 + X_2M_2/\rho_2) / [\{X_1M_1 + X_2M_2\}^{1/2} \times \{X_1M_1/\rho_1U_1^2 + X_2M_2/\rho_2U_2^2\}^{1/2}] \quad - \quad (6)$$

Where M_1, M_2 are molecular weights of constituent components, ρ_1 and ρ_2 are the densities of constituent components.

RESULTS AND DISCUSSION

From table 1 it is observed that as the mole fraction of o-cresol increases, internal pressure increases whereas the free volume decreases. This suggests close packing of the molecules inside the shield, which may be due to increasing magnitude of interactions [18, 19]. Further it is also noticed that the internal pressure values shows exactly in a reverse trend with reference to that of free volume. The variation of β^E , V_f^E , H^E and G^{*E} with mole fraction of o-cresol for different temperatures are shown in figures 1-4. The experimentally measured values of ultrasonic velocity along with theoretical values at different temperatures are given in table 2. The % deviation between experimental and theoretical values of ultrasonic velocities at different temperatures is given in table 3.

Table1: Variation of Internal pressure (π) and free volume (V_f) with mole fraction of o-cresol at different temperatures.

X_1	π				V_f			
	303.15K	308.15K	313.15K	318.15K	303.15K	308.15K	313.15K	318.15K
0.0000	2222.12	2069.23	1942.22	1844.76	1.1969	1.5440	1.9404	2.3514
0.1575	2356.12	2168.81	2022.77	1908.13	1.1702	1.5681	2.0087	2.4800
0.2961	2470.35	2273.28	2076.81	1943.71	1.1330	1.5193	2.0735	2.6194
0.4190	2595.56	2389.10	2118.19	1967.35	1.1019	1.4776	2.1961	2.8223
0.5287	2700.47	2493.13	2162.30	1963.51	1.0906	1.4490	2.3105	3.2046
0.6273	2801.20	2568.62	2216.18	1970.85	1.0827	1.4670	2.3728	3.4981
0.7163	2894.43	2662.70	2280.47	1990.07	1.0832	1.4513	2.4065	3.7500
0.7970	2985.95	2721.17	2336.59	1985.40	1.0878	1.4975	2.4545	4.1328
0.8707	3079.88	2803.93	2392.75	1960.74	1.0791	1.4944	2.4971	4.7036
0.9381	3157.93	2865.96	2448.28	1922.22	1.0906	1.5256	2.5400	5.4397
1.0000	3210.48	2922.35	2508.18	1845.95	1.1239	1.5495	2.5473	6.6369

Table2: Experimental and theoretical values of ultrasonic velocity in the mixtures of o-cresol and nonanol.

X_1	U_{exp}	U_N	U_{Imx}	U_J	U_{ir}	U_R
303.15K						
0.0000	1348.42	1348.42	1348.42	1146.89	1348.42	1348.42
0.1575	1370.53	1361.71	1355.73	1258.29	1374.54	1369.39
0.2961	1380.00	1375.08	1365.91	1357.29	1395.86	1388.03
0.4190	1392.63	1388.55	1378.08	1446.24	1413.61	1404.69
0.5287	1402.10	1402.10	1391.63	1526.87	1428.61	1419.67
0.6273	1417.90	1415.74	1406.14	1600.50	1441.44	1433.22
0.7163	1427.37	1429.46	1421.33	1668.14	1452.56	1445.53
0.7970	1443.16	1443.28	1436.97	1730.59	1462.28	1456.77
0.8707	1458.95	1457.18	1452.91	1788.50	1470.85	1467.06
0.9381	1475.26	1471.18	1469.04	1842.43	1478.46	1476.53
1.0000	1485.26	1485.26	1485.26	1892.80	1485.26	1485.26
308.15K						
0.0000	1335.78	1335.78	1335.78	1410.31	1335.78	1335.78
0.1575	1355.57	1348.53	1342.59	1423.71	1360.78	1355.89
0.2961	1367.37	1361.36	1352.25	1439.07	1381.20	1373.74

0.4190	1373.68	1374.27	1363.87	1455.74	1398.19	1389.70
0.5287	1380.00	1387.25	1376.85	1473.29	1412.55	1404.05
0.6273	1398.95	1400.32	1390.79	1491.39	1424.85	1417.03
0.7163	1411.58	1413.46	1405.38	1509.85	1435.50	1428.82
0.7970	1436.84	1426.69	1420.41	1528.50	1444.81	1439.57
0.8707	1446.32	1439.99	1435.74	1547.22	1453.02	1449.42
0.9381	1458.95	1453.38	1451.25	1565.94	1460.31	1458.48
1.0000	1466.84	1466.84	1466.84	1584.59	1466.84	1466.84
313.15K						
0.0000	1310.53	1310.53	1310.53	1392.91	1310.53	1310.53
0.1575	1338.95	1324.26	1318.44	1404.59	1337.53	1332.20
0.2961	1348.42	1338.09	1329.15	1418.20	1359.59	1351.45
0.4190	1354.74	1352.01	1341.80	1433.08	1377.94	1368.68
0.5287	1365.53	1366.03	1355.80	1448.81	1393.46	1384.18
0.6273	1383.16	1380.14	1370.76	1465.08	1406.74	1398.21
0.7163	1398.95	1394.35	1386.38	1481.67	1418.25	1410.95
0.7970	1427.37	1408.64	1402.46	1498.43	1428.31	1422.59
0.8707	1430.53	1423.04	1418.85	1515.24	1437.18	1433.25
0.9381	1446.32	1437.53	1435.42	1532.03	1445.06	1443.06
1.0000	1452.11	1452.11	1452.11	1548.74	1452.11	1452.11
318.15K						
0.0000	1297.89	1297.89	1297.89	1373.56	1297.89	1297.89
0.1575	1315.05	1311.39	1305.62	1380.63	1324.44	1319.19
0.2961	1326.32	1324.99	1316.13	1389.57	1346.12	1338.12
0.4190	1336.11	1338.67	1328.56	1399.73	1364.16	1355.05
0.5287	1348.42	1352.45	1342.33	1410.69	1379.41	1370.29
0.6273	1364.21	1366.32	1357.03	1422.14	1392.47	1384.08
0.7163	1376.84	1380.28	1372.40	1433.89	1403.78	1396.61
0.7970	1398.63	1394.33	1388.22	1445.78	1413.67	1408.05
0.8707	1408.42	1408.48	1404.34	1457.71	1422.39	1418.53
0.9381	1424.21	1422.72	1420.65	1469.59	1430.13	1428.17
1.0000	1437.06	1437.06	1437.06	1481.38	1437.06	1437.06

Table3: Percentage deviations of theoretical velocities from experimental velocities.

X_1	%U _N	%U _{lmax}	%U _J	%U _{ir}	%U _R
303.15K					
0.0000	0.0000	0.0000	-	0.0000	0.0000
0.1575	-0.6437	-1.0801	-8.1894	0.2923	0.0829
0.2961	-0.3562	-1.0209	-1.6459	1.1496	0.5816
0.4190	-0.2932	-1.0449	3.8494	1.5065	0.8657
0.5287	-0.0004	-0.7472	8.8987	1.8901	1.2530
0.6273	-0.1523	-0.8290	12.8785	1.6608	1.0810
0.7163	0.1467	-0.4233	16.8678	1.7648	1.2726
0.7970	0.0083	-0.4289	19.9164	1.3247	0.9430
0.8707	-0.1211	-0.4138	22.5884	0.8154	0.5561
0.9381	-0.2768	-0.4217	24.8883	0.2167	0.0859
1.0000	0.0000	0.0000	27.4390	0.0000	0.0000
308.15K					

0.0000	0.0000	0.0000	5.5798	0.0000	0.0000
0.1575	-0.5193	-0.9574	5.0269	0.3842	0.0233
0.2961	-0.4395	-1.1056	5.2440	1.0113	0.4660
0.4190	0.0426	-0.7141	5.9740	1.7841	1.1663
0.5287	0.5255	-0.2281	6.7598	2.3586	1.7431
0.6273	0.0977	-0.5836	6.6080	1.8512	1.2924
0.7163	0.1335	-0.4393	6.9618	1.6945	1.2213
0.7970	-0.7067	-1.1432	6.3791	0.5546	0.1901
0.8707	-0.4373	-0.7310	6.9768	0.4635	0.2148
0.9381	-0.3821	-0.5279	7.3333	0.0935	0.0322
1.0000	0.0000	0.0000	8.0273	0.0000	0.0000
313.15K					
0.0000	0.0000	0.0000	6.2859	0.0000	0.0000
0.1575	-1.0968	-1.5321	4.9024	0.1059	0.5045
0.2961	-0.7659	-1.4293	5.1748	0.8283	0.2248
0.4190	-0.2012	-0.9555	5.7829	1.7129	1.0289
0.5287	0.0367	-0.7126	6.0988	2.0453	1.3660
0.6273	-0.2183	-0.8969	5.9224	1.7051	1.0878
0.7163	-0.3291	-0.8987	5.9127	1.3795	0.8580
0.7970	-1.3119	-1.7453	4.9781	0.0657	0.3350
0.8707	-0.5236	-0.8168	5.9217	0.4647	0.1903
0.9381	-0.6078	-0.7533	5.9263	0.0872	0.2254
1.0000	0.0000	0.0000	6.6544	0.0000	0.0000
318.15K					
0.0000	0.0000	0.0000	5.8303	0.0000	0.0000
0.1575	-0.2782	-0.7169	4.9870	0.7137	0.3146
0.2961	-0.1006	-0.7681	4.7686	1.4928	0.8896
0.4190	0.1917	-0.5652	4.7616	2.0997	1.4179
0.5287	0.2987	-0.4519	4.6178	2.2986	1.6223
0.6273	0.1545	-0.5260	4.2468	2.0718	1.4566
0.7163	0.2498	-0.3224	4.1437	1.9567	1.4359
0.7970	-0.3072	-0.7443	3.3714	1.0752	0.6732
0.8707	0.0044	-0.2897	3.4996	0.9917	0.7176
0.9381	-0.1044	-0.2501	3.1865	0.4158	0.2778
1.0000	0.0000	0.0000	3.0841	0.0000	0.0000

The adiabatic compressibility is a measure of ease with which the system can be compressed. The variation of excess compressibility (β^E) at temperatures 303.15 K, 308.15 K, 313.15 K and 318.15 K is presented in figure 1. The values are positive at intermediate concentration and both positive and negative at higher concentration where as these values are negative at lower concentration of o-cresol. The negative values of excess adiabatic compressibility indicate strong specific interactions between component molecules of the liquid mixtures. As the temperature increases it is observed that the excess compressibility values become less negative and it indicates that the interactions decrease with increase of temperature [20].

The excess free volume (V_f^E) at different temperatures is shown in figure 2. And it is observed that these values are almost negative over the entire range of composition. This suggests that the component molecules are closer in the liquid mixture than in the pure liquids that form the mixture which indicates strong interactions as suggested by Baluja and Oza [21] between component molecules.

From figure 3 it is observed that the excess enthalpy (H^E) values are almost positive except at 313.15K over the entire composition range and these values suggest that there exist strong interaction between component molecules of the mixture as reported by Parveen et al.[22].

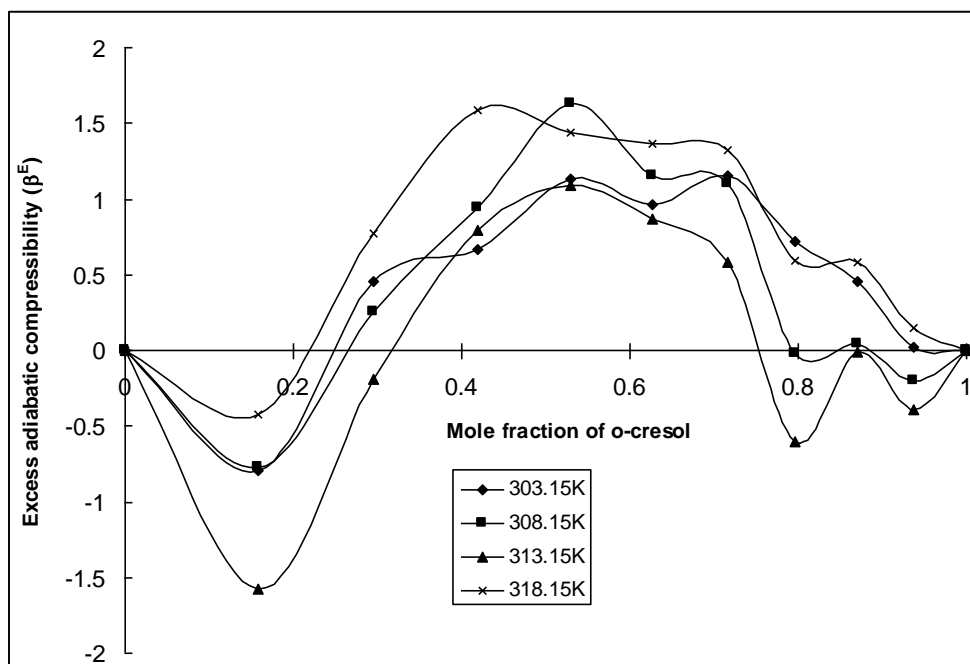


Figure1: Excess adiabatic compressibility of nonanol with o-cresol

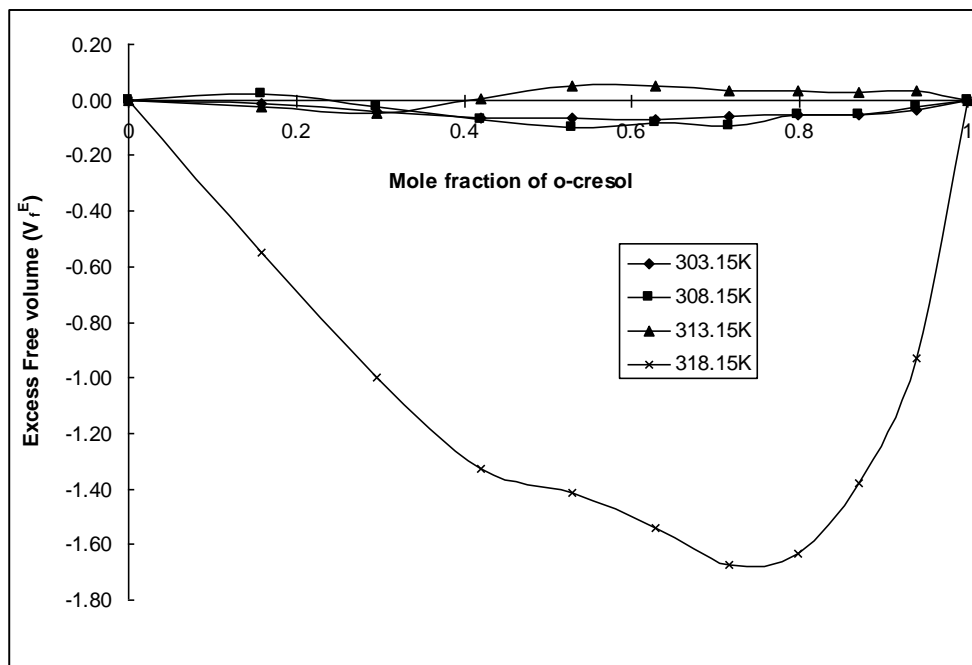


Figure2: Excess free volume of nonanol with o-cresol

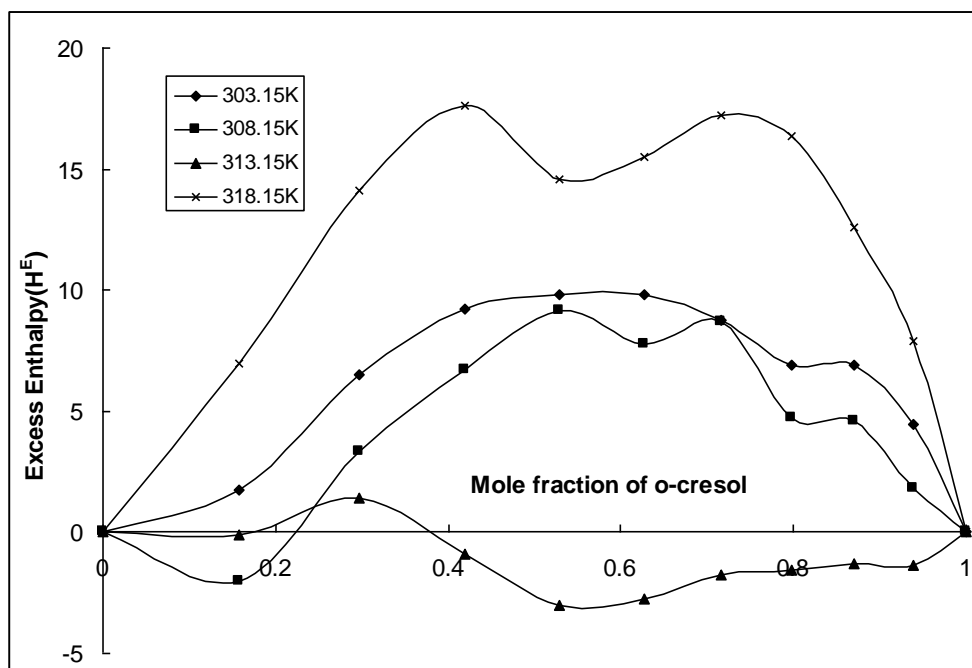


Figure3: Excess enthalpy of nonanol with o-cresol

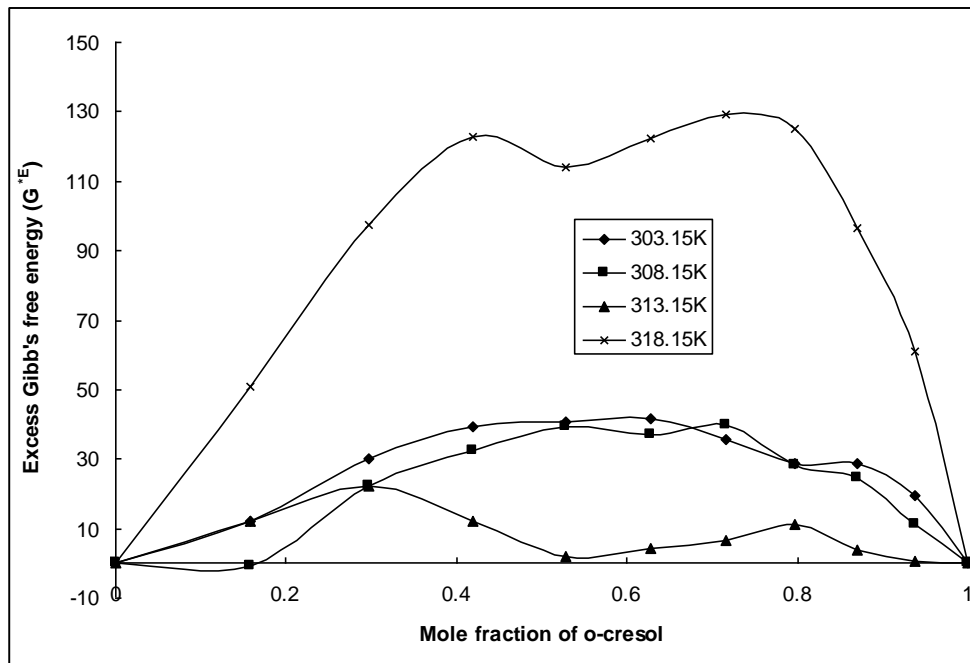


Figure4: Excess Gibb's free energy of nonanol with o-cresol

From figure 4 it is observed that the excess Gibb's free energy of activation (G^{*E}) values are positive and these values also indicate strong interaction between the component molecules [23, 24]. It is found that at higher temperatures the values become more positive.

It can be seen from table 2 that the theoretical values of ultrasonic velocity calculated from various theories show deviations from experimental values and the limitations and approximations used in these theories are accountable for the same. The deviations of theoretical values from experimental values indicate that the molecular interactions take place between the unlike molecules in the liquid mixture.

Table 3 presents a good agreement between the experimental and theoretical values calculated by Nomoto's relation, ideal mixing relation, Rao's relation and Impedance relation. It is also observed that Nomoto's relation provides better results than those of ideal mixing relations at all temperatures. Nevertheless, higher deviations are observed in Junjie's theory. The agreement between experimental and theoretical velocities of Nomoto's relation suggests that R is an additive property. Baluja and Karia [25] reported that, the higher deviations in some intermediate concentrations are due to the existence of strong interactions between component molecules.

CONCLUSION

The excess parameters such as adiabatic compressibility, free volume, enthalpy and Gibb's free energy of activation are calculated from the experimental measured values of density, ultrasonic velocity and viscosity. From the results it is concluded that there exist strong intermolecular interactions between the component molecules of the mixture. The ultrasonic

velocity values measured experimentally are compared with several empirical/semi empirical relations and it is observed that Nomoto's relation gives best results when compared to other relations for the present system.

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