



Excess Molar Volumes and Viscosity Studies of Binary Mixtures of *o*-Cresol and Nonanol at Different Temperatures

K. NARENDRA^{1,*}, B. TULASI KOTESWARI BAI², K. BABU RAO³, S.S.J. SRINIVAS³ and M. SARATH BABU³

¹Department of Physics, V.R. Siddhartha Engineering College, Vijayawada-520 007, India

²Department of Chemistry, Sir C.R. Reddy College for Women, Eluru-500 026, India

³Department of Chemistry, MIC College of Technology, Kanchikacherla-521 180, India

*Corresponding author: E-mail: narenk75@gmail.com

(Received: 29 August 2011;

Accepted: 21 March 2012)

AJC-11208

Ultrasonic velocity, density and viscosity have been measured for the binary mixtures of *o*-cresol and nonanol at 303.15, 308.15, 313.15 and 318.15 K and at atmospheric pressure. The experimental data obtained has been used to calculate the acoustical parameters namely adiabatic compressibility (β), free length (L_f), free volume (V_f), internal pressure (π), acoustic impedance (Z) and molar volume (V_m). The excess values like excess molar volume and excess viscosity were evaluated and the results were fitted into Redlich-Kister equation. The results were also used to explain the molecular interaction between the components of these mixtures.

Key Words: Ultrasonic velocity, Density, Viscosity, Acoustic parameters, *o*-Cresol and nonanol.

INTRODUCTION

Acoustic properties of the systems containing aromatic hydrocarbons have attracted the attention of researchers in the recent years¹⁻⁴. An attempt has been made to record the ultrasonic velocities, densities and viscosities of the binary mixtures of *o*-cresol and nonanol at different temperatures and at atmospheric pressure. Various acoustic parameters were calculated using the experimental data while so excess molar volume and excess viscosity were also calculated and the results were fitted into Redlich-Kister equation⁵.

Acoustic and thermodynamic parameters have been used to understand different kinds of association *viz.*, the molecular motion, molecular packing, various types of intermolecular interactions and their strengths that are influenced by the size and shape in pure components as well as in the mixtures⁶. These acoustic and thermodynamic parameters derived offer a convenient method for the study of thermodynamic properties of liquid mixtures that are not easily obtained by other means. It is well known that alcohols are self associated liquids and a three dimensional network of hydrogen bond is believed to be present in them.

EXPERIMENTAL

The chemicals *o*-cresol and nonanol were supplied by Merck chemicals. The purity of these substances ranged between 0.990 to 0.995 by mass fraction. The purities of pure

liquids taken for study were ascertained by comparing the experimentally measured values with the values available in the literature⁷⁻⁹ and there has been a good agreement between the two.

The mixtures of various concentrations in mole fraction were prepared by taking purified AnalaR grade samples. In all the mixtures the mole fraction of the compound *o*-cresol has been increased from 0 to 1. The ultrasonic velocity in liquid mixtures has been measured using an ultrasonic interferometer (Mittal Enterprises, Model F-80X) working at 3 MHz frequency with an accuracy $\pm 0.5 \text{ ms}^{-1}$. The densities (ρ) of these liquids were measured using 10 mL specific gravity bottle in an electronic balance precisely within $\pm 0.01 \text{ mg}$ accuracy. Ostwald viscometer of accuracy $\pm 0.002 \text{ cP}$ was used to measure the viscosities of the liquids.

In all the above apparatus the temperature was maintained constant at 303.15, 308.15, 313.15 and 318.15 K using proportional temperature controller of accuracy $\pm 0.01 \text{ K}$.

Theoretical data: From the experimentally measured values of ultrasonic velocity (U), density (ρ) and viscosity (η), various acoustic parameters can be calculated and they have been dealt elsewhere in detail¹⁰.

Excess molar volume V_m^E is given by:

$$V_m^E = V_{\text{exp}} - V_{\text{ideal}} = V_{\text{exp}} - (x_1 V_{m1} + x_2 V_{m2})$$

where, V_{exp} is the molar volume of the mixture, V_{m1} and V_{m2} are the molar volumes of the pure components 1 and 2 respectively.

TABLE-1
COMPARISON OF EXPERIMENTAL RESULTS FOR PURE COMPONENT
AT 303.15 K WITH DATA REPORTED IN THE LITERATURE

U (m s ⁻¹)		ρ (g cm ⁻³)		η (mPa s)	
Experimental	Literature	Experimental	Literature	Experimental	Literature
<i>o</i> -cresol					
1485.26	1487.00 ⁷	1.0362	1.0369 ⁷	7.4791	4.2430 ⁸ (313.15K)
Nonanol					
1348.42	1347.42 ⁹	0.8214	0.8210 ⁹	8.6861	7.9940 ⁹

TABLE-2
EXPERIMENTAL VALUES OF ULTRASONIC VELOCITY, DENSITY AND VISCOSITY FOR *o*-CRESOL
+ NONANOL BINARY MIXTURES AT 303.15, 308.15, 313.15 AND 318.15 K

x ₁	303.15 K			308.15 K		
	U (m s ⁻¹)	ρ (g cm ⁻³)	η (mPa s)	U (m s ⁻¹)	ρ (g cm ⁻³)	η (mPa s)
0.0000	1348.42	0.8214	8.6861	1335.78	0.8180	7.2612
0.1575	1370.53	0.8518	8.6088	1355.57	0.8497	7.0053
0.2961	1380.00	0.8673	8.5369	1367.37	0.8651	6.9560
0.4190	1392.63	0.8906	8.4847	1373.68	0.8886	6.8825
0.5287	1402.10	0.9114	8.3375	1380.00	0.9093	6.7898
0.6273	1417.90	0.9321	8.2312	1398.95	0.9296	6.6327
0.7163	1427.37	0.9533	8.0651	1411.58	0.9500	6.5626
0.7970	1443.16	0.9763	7.9307	1436.84	0.9724	6.3807
0.8707	1458.95	0.9952	7.8747	1446.32	0.9927	6.2833
0.9381	1475.26	1.0163	7.7363	1458.95	1.0141	6.1167
1.0000	1485.26	1.0362	7.4791	1466.84	1.0310	5.9629
	313.15 K			318.15 K		
0.0000	1310.53	0.8140	6.1173	1297.89	0.8100	5.3300
0.1575	1338.95	0.8455	5.8665	1315.05	0.8406	5.0065
0.2961	1348.42	0.8614	5.5753	1326.32	0.8561	4.6928
0.4190	1354.74	0.8828	5.2119	1336.11	0.8748	4.3485
0.5287	1365.53	0.9053	4.9226	1348.42	0.9009	3.9085
0.6273	1383.16	0.9248	4.7592	1364.21	0.9196	3.6238
0.7163	1398.95	0.9465	4.6424	1376.84	0.9406	3.3994
0.7970	1427.37	0.9670	4.5596	1398.63	0.9597	3.1567
0.8707	1430.53	0.9874	4.4135	1408.42	0.9817	2.8490
0.9381	1446.32	1.0085	4.3166	1424.21	1.0026	2.5583
1.0000	1452.11	1.0260	4.2380	1437.06	1.0211	2.2150

Similarly excess viscosity η^E is given by:

$$\eta^E = \eta_{\text{exp}} - \eta_{\text{ideal}} = \eta_{\text{exp}} - (x_1\eta_1 + x_2\eta_2)$$

where, η_{exp} is the viscosity of the mixture, η_1 and η_2 are the viscosities of the pure components 1 and 2 respectively. x_1 and x_2 are the mole fractions of 1st and 2nd components respectively.

RESULTS AND DISCUSSION

The experimentally determined values of ultrasonic velocity (U), density (ρ) and viscosity (η) of the pure compounds are compared with the values in the literature and are given in Table-1. The U, ρ and η values of binary mixtures measured at different temperatures for the entire mole fractions are given in Table-2. The acoustical parameters are calculated by using the above data and the results are given in Table-3. The excess molar volume and excess viscosity are calculated and the results are fitted into Redlich-Kister equation and the corresponding coefficients and standard deviation values are presented in Table-4.

The variations of excess molar volume and excess viscosity with mole fraction of *o*-cresol for different temperatures are shown in Figs. 1 and 2 respectively. It is observed from Table-2 that the values of U and ρ increase with mole fraction

of *o*-cresol whereas the values of η show reverse trend and same is observed at all the temperatures studied and this can be attributed to intermolecular interactions in the binary mixtures studied¹¹. The properties adiabatic compressibility (β) and intermolecular free length (L_f) show a reverse trend.

As mole fraction of *o*-cresol increases the values of β as well as L_f decrease and such a decrease suggests that the hydrogen bonding gradually strengthens with the addition of *o*-cresol, which leads to decrease in molar volume (V_m) as observed in Table-3.

Further, the decrease in free volume and increase in internal pressure with increase in mole fraction of *o*-cresol clearly show the increasing magnitude of interactions¹². Also, increase in the values of internal pressure indicates association through hydrogen bonding¹³. The increase in the values of β and L_f with increase in temperatures clearly indicate that the interaction becomes weaker at high temperatures. Acoustic impedance values are observed to be increasing with mole fraction of *o*-cresol and it supports the possibility of molecular interactions between the unlike molecules.

The observed V^E values may be due to (1) decrease in dipolar association of the components (2) interstitial accommodation and (3) weak hydrogen bonding interaction. The factor

TABLE-3
VALUES OF ADIABATIC COMPRESSIBILITY (β), FREE LENGTH (L_f), FREE VOLUME (V_f), INTERNAL PRESSURE (π),
ACOUSTIC IMPEDANCE (Z) AND MOLAR VOLUME (V_m) AT 303.15, 308.15, 313.15 AND 318.15 K

x_1	$\beta \times 10^{11} (\text{m}^2 \text{N}^{-1})$	$L_f (\text{Å}^\circ)$	$V_f \times 10^{-6} (\text{m}^3 \text{mol}^{-1})$	$\pi \times 10^{-5} (\text{N m}^2)$	$Z (\text{Kg m}^{-2}\text{s}^{-1})$	$V_m \times 10^{-6} (\text{m}^3 \text{mol}^{-1})$
303.15 K						
0.0000	66.9568	0.5131	1.1969	2222.12	1107.59	175.6270
0.1575	62.5025	0.4957	1.1702	2356.12	1167.39	162.6835
0.2961	60.5435	0.4879	1.1330	2470.35	1196.89	153.9978
0.4190	57.8983	0.4771	1.1019	2595.56	1240.22	144.9933
0.5287	55.8142	0.4684	1.0906	2700.47	1277.84	137.3343
0.6273	53.3651	0.4580	1.0827	2801.20	1321.59	130.4642
0.7163	51.4870	0.4499	1.0832	2894.43	1360.71	124.1885
0.7970	49.1776	0.4397	1.0878	2985.95	1409.02	118.2691
0.8707	47.2059	0.4308	1.0791	3079.88	1451.99	113.3527
0.9381	45.2087	0.4216	1.0906	3157.93	1499.37	108.6020
1.0000	43.7473	0.4147	1.1239	3210.48	1539.03	104.3621
308.15 K						
0.0000	68.5136	0.5227	1.5440	2069.23	1092.67	176.3570
0.1575	64.0457	0.5054	1.5681	2168.81	1151.83	163.0809
0.2961	61.8244	0.4965	1.5193	2273.28	1182.92	154.3901
0.4190	59.6367	0.4877	1.4776	2389.10	1220.68	145.3098
0.5287	57.7481	0.4799	1.4490	2493.13	1254.83	137.6480
0.6273	54.9689	0.4682	1.4670	2568.62	1300.41	130.8176
0.7163	52.8263	0.4590	1.4513	2662.70	1341.05	124.6152
0.7970	49.8108	0.4457	1.4975	2721.17	1397.23	118.7449
0.8707	48.1564	0.4382	1.4944	2803.93	1435.76	113.6411
0.9381	46.3280	0.4298	1.5256	2865.96	1479.50	108.8438
1.0000	45.0792	0.4240	1.5495	2922.35	1512.31	104.8885
313.15 K						
0.0000	71.5289	0.5379	1.9404	1942.22	1066.77	177.2236
0.1575	65.9687	0.5166	2.0087	2022.77	1132.13	163.8838
0.2961	63.8446	0.5082	2.0735	2076.81	1161.58	155.0471
0.4190	61.7192	0.4997	2.1961	2118.19	1195.98	146.2657
0.5287	59.2388	0.4895	2.3105	2162.30	1236.21	138.2556
0.6273	56.5179	0.4781	2.3728	2216.18	1279.21	131.4849
0.7163	53.9840	0.4673	2.4065	2280.47	1324.14	125.0779
0.7970	50.7585	0.4531	2.4545	2336.59	1380.24	119.4145
0.8707	49.4875	0.4474	2.4971	2392.75	1412.56	114.2467
0.9381	47.4015	0.4379	2.5400	2448.28	1458.63	109.4459
1.0000	46.2225	0.4324	2.5473	2508.18	1489.86	105.3996
318.15 K						
0.0000	73.2891	0.5483	2.3514	1844.76	1051.29	178.0988
0.1575	68.7925	0.5312	2.4800	1908.13	1105.39	164.8523
0.2961	66.4049	0.5219	2.6194	1943.71	1135.41	156.0219
0.4190	64.0345	0.5125	2.8223	1967.35	1168.81	147.6078
0.5287	61.0482	0.5004	3.2046	1963.51	1214.79	138.9303
0.6273	58.4286	0.4896	3.4981	1970.85	1254.57	132.2310
0.7163	56.0837	0.4797	3.7500	1990.07	1295.03	125.8678
0.7970	53.2664	0.4675	4.1328	1985.40	1342.28	120.3189
0.8707	51.3531	0.4590	4.7036	1960.74	1382.62	114.9173
0.9381	49.1712	0.4491	5.4397	1922.22	1427.96	110.0874
1.0000	47.4223	0.4411	6.6369	1845.95	1467.38	105.9054

(1) leads to expansion in volume while factors (2) and (3) contribute to contraction. From Fig. 1 it is observed that excess molar volumes are negative over the entire mole fraction range. The deviations in excess molar volumes are negative at 303.15 K and continue to be more negative as the temperature is increased to 313.15 K. This shows that as the temperature increases the hydrogen bonding formation between hetero molecules gets predominant.

The excess viscosity variation gives a qualitative estimation of the strength of intermolecular interactions. The excess viscosities may be explained in general by considering the following factors:

(1) The difference in size and shape of the component molecules and the loss of dipolar association in pure component may contribute to a decrease in viscosity.

(2) Specific interactions between unlike molecules such as hydrogen bond formation and charge transfer complexes may cause increase in viscosity and the latter effect produces positive deviation in excess viscosity. From Fig. 2, it is observed that the excess viscosity values are almost positive at all temperatures studied except at 313.15 K and it confirms that there exist specific interactions between unlike molecules of the mixture.

TABLE-4
COEFFICIENTS OF THE REDLICH-KISTER EQUATION
AND STANDARD DEVIATION OF EXCESS FUNCTIONS
FOR *o*-CRESOL + NONANOL BINARY MIXTURES
AT 303.15, 308.15, 313.15 AND 318.15 K

	a_0	a_1	a_2	σ
303.15 K				
η^E	0.8931	1.1610	1.6032	0.083
V_m^E	-3.4557	8.0024	-8.5327	0.456
308.15 K				
η^E	0.5310	1.1195	-0.3230	0.048
V_m^E	-3.9740	7.1289	-13.5294	0.408
313.15 K				
η^E	-0.6192	-0.8029	0.8750	0.034
V_m^E	-4.0925	7.7346	-12.5163	0.416
318.15 K				
η^E	0.8149	0.5242	1.7139	0.061
V_m^E	-3.8167	7.8589	-10.4895	0.558

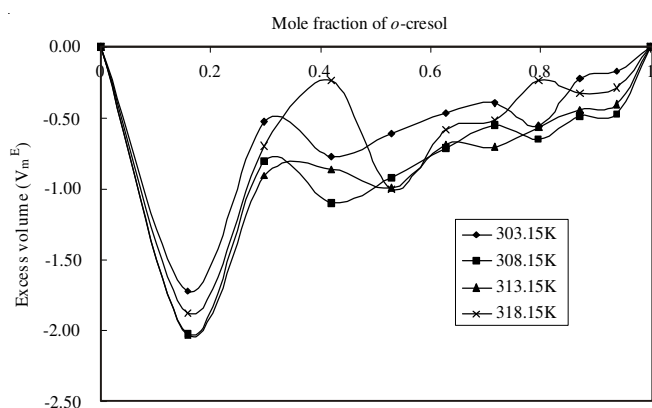


Fig. 1. Variation of Excess molar volume with mole fraction of *o*-cresol at different temperatures

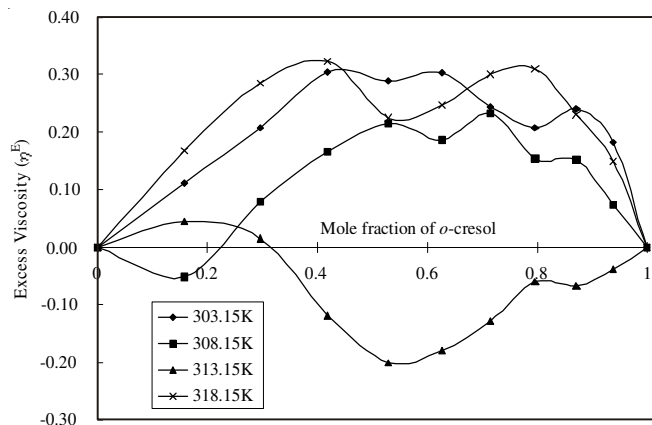


Fig. 2. Variation of excess viscosity with mole fraction of *o*-cresol at different temperatures

Conclusion

Acoustic parameters are calculated by using the values obtained through experiments on ultrasonic velocity, density and viscosity and in turn the data is used to calculate excess molar volume and excess viscosity. From these results it is observed that there exists intermolecular interactions in the binary mixtures selected for the work and also that the interactions get weakened in magnitude as the temperature increases.

REFERENCES

1. K.P. Rao and K.S. Reddy, *Phys. Chem. Liqs.*, **15**, 147 (1985).
2. A.N. Kannappan and V. Rajendran, *Indian J. Pure Appl. Phys.*, **29**, 465 (1991).
3. C. Chennarayappa, K. Rambabu, P. Venkateshwarla and G.K. Raman, *Acoustics Lett.*, **15**, 83 (1991).
4. S. Thirumaran and S.S. Devi, *Arch. Appl. Sci. Res.*, **1**, 128 (2009).
5. O. Redlich and A.T. Kister, *Ind. Eng. Chem.*, **40**, 345 (1948).
6. S. Gokhan and A. Ertunc, *Indian Acad. Sci.*, **66**, 435 (2006).
7. C.S. Bhatia, R. Rani and R. Bhatia, *J. Chem. Eng. Data*, **56**, 1669 (2011).
8. R. Rosal, I. Medina, E. Forster and J. MacInnes, *Fluid Phase Equilib.*, **211**, 143 (2003).
9. E. Zorebski and B. Lubowiecka-Kostka, *J. Chem. Thermodyn.*, **41**, 197 (2009).
10. K. Narendra, Ch. Srinivasu and P.N. Murthy, *Asian J. Chem.*, **23**, 752 (2011).
11. A.N. Kannappan and L. Palaniappan, *Indian J. Phys.*, **73B**, 531 (1999).
12. D. Anbanathan, *J. Acoustic Soc. India*, **7**, 123 (1979).
13. J.D. Pandey, N.A. Hassan, J.N. Shukla and R. Dey, *Acoustic Lett.*, **23**, 06 (1999).