Study of molecular interactions in binary liquid mixture containing quinoline and cresol by using excess thermodynamic parameters at different temperatures

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Abstract

In this paper , we have measured the values of ultrasonic velocity, density and viscosity in binary liquid mixtures of a heterocyclic aromatic compound quinoline which is readily soluble in organic solvents cresol at different temperatures over the entire range of composition. From these measured values excess thermodynamic parameters like excess adiabatic compressibility (β^E), excess intermolecular free length(L_f^E), excess acoustic impedance(Z^E), and excess ultrasonic velocity(U^E) have been calculated. The calculated deviations in excess thermodynamic parameters have been explained on the basis of the intermolecular interactions present in these mixture.

Key word: Viscosity, density,excess adiabatic compressibility, excess intermolecular free length, quinoline and cresol.

Introduction:

When two or more liquids are mixed, there occur some changes in physical and thermodynamic properties because of change in molecular orientations. The measurement of physical properties like ultrasonic velocity, density and viscosity are all very much important to explain the interactions between different component molecules.These interactions can be explained on the basis of excess thermodynamic parameters [1-4].Molecular interaction in liquid mixtures has been extensively studied using ultrasonic technique by many workers [5], because mixed solvents find practical applications in many chemical, biological and industrial processes. Quinoline is a colourless liquid with strong odor and widely used in manufacturing of dyes, pesticides and solvent for resins and terpenes. Cresol is widely used for phonograph records, wood preservatives and selective weed killing. As a part of today's progressive and ongoing research [6] on thermoacoustic properties of binary liquid mixtures, we report here the results of study on binary liquid mixture of quinoline with cresol over the entire range of composition at different temperatures T= 303.15K, 308.15K, 313.15K and 318.15K. By using the experimentally measured values of ultrasonic velocity (u), density (ρ) and viscosity (η) various excess parameters like excess adiabatic compressibility (β^E), excess intermolecular free length(L_f^E), excess acoustic impedance(Z^E), and excess ultrasonic velocity(U^E) have been calculated for the liquid mixture.

Experimental Procedure:

By using Standard procedure we have purified chemicals[7].The ultrasonic velocities were measured by using single crystal ultrasonic pulse echo interferometer of Mittal enterprises**,** India with model number 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 densities of pure liquids and liquid mixture were measured by using a specific gravity bottle with an accuracy of ± 0.5%. Weights were measured with an electronic balance namely Shimadzu AUY220, Japan capable of measuring up to 0.1mg. An average of 4 to 5 measurements was taken for each sample.Viscosities were measured at

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the desired temperature using Ostwald's viscometer calibrated using water and benzene. The flow time has been measured after the attainment of bath temperature by each mixture. The flow measurements were made with an electronic stopwatch with a precision of 0.01 s. For all pure compounds and mixtures, 4 to 5 measurements were performed and the average of these values was used in all the calculations.

Theory:

From the experimentally measured values of ultrasonic velocity (u), density (ρ) and viscosity (η), various thermoacoustical parameters such as adiabatic compressibility (β), intermolecular free length (L_f) and acoustic impedance (Z) are calculated using the following equations:

$$\beta = 1/\rho u^2 \quad --- \quad (1)$$

$$L_f = K_T\beta^{1/2} \quad --- \quad (2)$$

$$Z = \rho U \quad --- \quad (3)$$

where ρ is density ,U is ultrasonic velocity and K_T is the temperature dependent constant.
The strength of interaction between the component molecules of binary mixtures is well reflected in the deviation of the excess functions from ideality. The excess thermodynamic properties such as β^E, Lf^E, Z^E, and u^E have been calculated using

$$Y^E = Y_{mix} - [X_1Y_1 + X_2Y_2] \quad --- \quad (4)$$

where Y^E is β^E, Lf^E, Z^E, or u^E and x represents mole fraction of the component and subscript 1 and 2 for the components 1 and 2, respectively.

Results and Discussion:

The values of ultrasonic velocities and densities for pure liquids are experimentally measured and are compared with the literature values and they are good agreement with each other as given in the below table-1.The values of densities, viscosities and ultrasonic velocities for the binary liquid mixture at different temperatures is given in table-2.

Table-1: Comparison of experimental densities ρ and ultrasonic velocities U of pure liquids with literature values.

Liquids	Density 'ρ' ($kg . m^{-3}$)		Ultrasonic Velocity 'U' ($m . s^{-1}$)	
	Expt	Lit	Expt	Lit
Quinoline	1085	1085.82[8]	1554	1547[8]
Cresol	1026	1026.3[9]	1468	1471[9]

[8]Jagan Nath.

[9]Bhatia et al.

Table-2: Values of density (ρ), viscosity (η) and ultrasonic velocity (u) for the binary mixtures of quinoline + cresol at T = 303.15K, 308.15K, 313.15K and 318.15K.

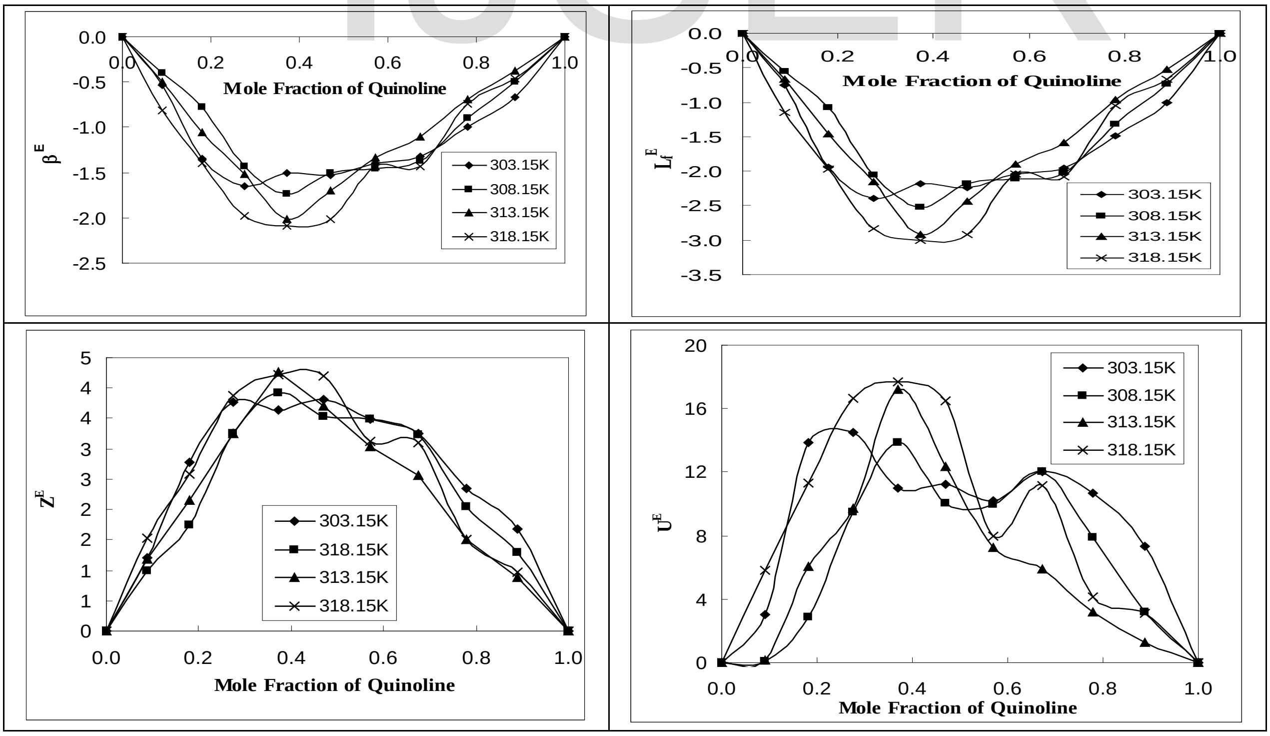
Molefraction(x)	ρ (kgm^{-3})	ηX10^{-3} (Nsm^{-2})	u (ms^{-1})	ρ (kgm^{-3})	ηX10^{-3} (Nsm^{-2})	u (ms^{-1})
	at T=303.15K			at T=308.15K		
0.0000	1026.50	9.540	1461	1022.00	8.119	1449
0.0896	1038.15	25.040	1472	1034.49	23.431	1458
0.1812	1046.69	21.706	1491	1043.33	20.325	1470
0.2751	1058.49	18.790	1500	1054.60	17.519	1486
0.3711	1065.72	16.696	1505	1061.70	15.641	1500
0.4696	1072.43	13.636	1514	1067.70	12.680	1506
0.5704	1076.81	9.272	1522	1073.38	8.596	1516
0.6738	1079.86	6.879	1533	1076.13	6.234	1528
0.7798	1080.88	4.672	1541	1077.34	4.280	1535
0.8885	1084.94	3.500	1547	1081.91	3.249	1541
1.0000	1085.45	2.932	1550	1082.11	2.707	1549
Molefraction(x)	at T=313.15K			at T=318.15K		
0.0000	1018.10	6.741	1436	1013.90	5.469	1424
0.0896	1031.92	21.767	1446	1026.31	23.899	1440
0.1812	1040.14	18.821	1462	1035.44	18.905	1456
0.2751	1050.90	16.227	1476	1046.39	16.221	1472
0.3711	1058.20	14.449	1494	1053.69	14.472	1484
0.4696	1063.68	11.763	1500	1060.39	11.741	1494
0.5704	1068.76	7.928	1506	1065.16	7.852	1497
0.6738	1072.61	5.701	1516	1068.70	5.649	1512
0.7798	1073.63	3.879	1525	1069.41	3.788	1517
0.8885	1077.18	2.890	1535	1072.84	2.872	1528
1.0000	1078.60	2.447	1545	1074.99	2.430	1538

The calculated values of excess thermodynamic parameters like excess adiabatic compressibility(β^E),excess intermolecular free length(L_f^E),excess acoustic impedance(Z^E) and excess ultrasonic velocicities(U^E) for the binary liquid mixture at different temperatures is given in the table-3. The variations of the excess parameters with the mole fraction of quinoline in the binary liquid mixture at different temperatures are represented in the Figure-1.

Molefraction of Quinoline	β^E				L_f^E			
	303.15K	308.15K	313.15K	318.15K	303.15K	308.15K	313.15K	318.15K
0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.0896	-0.5309	-0.4048	-0.4937	-0.8159	-0.7489	-0.5517	-0.6730	-1.1412
0.1812	-1.3420	-0.7816	-1.0504	-1.3946	-1.9437	-1.0818	-1.4661	-1.9683
0.2751	-1.6452	-1.4366	-1.5217	-1.9723	-2.3979	-2.0558	-2.1602	-2.8275
0.3711	-1.5056	-1.7394	-2.0125	-2.0886	-2.1862	-2.5210	-2.9143	-3.0099
0.4696	-1.5351	-1.5092	-1.6966	-2.0153	-2.2434	-2.1775	-2.4407	-2.9157
0.5704	-1.3896	-1.4523	-1.3339	-1.4335	-2.0375	-2.1121	-1.9004	-2.0375
0.6738	-1.3207	-1.3740	-1.1087	-1.4343	-1.9602	-2.0249	-1.5833	-2.0817
0.7798	-0.9952	-0.8962	-0.6869	-0.7437	-1.4852	-1.3136	-0.9640	-1.0424
0.8885	-0.6647	-0.4965	-0.3762	-0.4640	-1.0078	-0.7314	-0.5297	-0.6636
1.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Molefraction of Quinoline	Z^E				U^E			
	303.15K	308.15K	313.15K	318.15K	303.15K	308.15K	313.15K	318.15K
0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.0896	1.2074	0.9900	1.1756	1.5300	3.0300	0.0400	0.1500	5.7900
0.1812	2.7791	1.7400	2.1446	2.5800	13.8700	2.8800	6.0700	11.3400
0.2751	3.7764	3.2500	3.2601	3.8900	14.5200	9.4900	9.7400	16.6400
0.3711	3.6368	3.9200	4.2684	4.2100	10.9700	13.8900	17.1700	17.6900
0.4696	3.8138	3.5400	3.7023	4.2000	11.2100	10.0400	12.3500	16.4700
0.5704	3.4946	3.5000	3.0318	3.1200	10.2300	9.9600	7.2500	7.9700
0.6738	3.2580	3.2300	2.5606	3.0900	12.0300	12.0400	5.8800	11.1900
0.7798	2.3477	2.0400	1.5027	1.5100	10.6500	7.9100	3.2200	4.1000
0.8885	1.6737	1.2900	0.8876	0.9800	7.2900	3.2000	1.2700	3.1300
1.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000

Table-3: Excess thermodynamic parameters of quinoline+ cresol system

Figure-1: Variations of excess parameters with the molefractions of quinoline in quinoline + cresol system



The excess thermodynamic properties of the mixtures are influenced by three main types of contributions, namely, (i) due to non specific Van der Waals type forces, (ii) due to hydrogen bonding, dipole-dipole, and donor-acceptor interaction between unlike molecules, and (iii) 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 negative contribution towards u^E and positive contribution towards β^E. However, the second effect leads to negative contribution towards β^E and positive contribution towards u^E. For the liquid mixtures, the results of the excess adiabatic compressibility β^E plotted in Figure-1 are negative at all the temperatures studied. The negative values of β^E suggest that the mixture is less compressible than the corresponding ideal mixture. According to Fort and Moore [10], the liquids of different molecular size usually mix with decrease in volume yielding negative β^E values. The strength of the interactions between component molecules increases when excess values tend to become increasingly negative. As the temperature increases, the β^E values also increase in the liquid mixture systems, suggesting that the thermal energy activates the molecules towards complex formation between unlike molecules [11]. Also from Figures-1 it is observed that $L_f{}^E$ values are negative for the entire mole fraction range, for all the four temperatures in case of the mixture. The $L_f{}^E$ values are increasingly negative as the strength of interaction between component molecules increases [12]. The excess values of Z^E which are plotted in Figures -1 are all positive in the liquid system over the entire composition range and for all the four temperatures studied. The positive excess values of Z^E clearly suggest that there exist strong molecular interactions between the molecules of the mixture [13].Further the results for the excess ultrasonic velocity u^E plotted in Figures -1 are positive for the mixtures at all the temperatures studied. The positive values of u^E increase with the increase in temperature which indicates the increase in strength of interaction with temperature in the liquid mixture.

5. Conclusions:

we have calculated the excess thermodynamic parameters in the binary liquid mixtures of quinoline with cresol at different temperatures T = 303.15, 308.15, 313.15, and 318.15 K over the entire range of composition from the measured values of ultrasonic velocity, density and viscosity. It is observed from the excess thermodynamic parameters is that there exists a strong molecular interaction between the unlike molecules in the liquid mixture .

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