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Excess parameters of binary mixtures of quinoline with o-cresol, m-cresol and p-cresol at T = (303.15, 308.15, 313.15, and 318.15) K

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ABSTRACT

Densities, ultrasonic velocities and viscosities of binary mixtures of (quinoline + o-cresol, or + m-cresol, or + p-cresol) have been measured over the entire range of composition at T = (303.15, 308.15, 313.15, and 318.15) K. From the experimental data, the excess molar volume, V^E, viscosity deviation, $\Delta\eta$ and excess Gibb's free energy of activation for viscous flow, ΔG^{*E} have been calculated. The calculated excess and deviation functions have been fitted to the Redlich-Kister polynomial equation. The negative and positive values of excess or deviation parameters observed have been explained on the basis of the intermolecular interactions present in these binary liquid mixtures.
Keywords: Excess Volume, Viscosity, Density, Quinoline, Cresol.

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INTRODUCTION

When two or more liquids are mixed, there occur some changes in physical and thermodynamic properties because of free volume change, change in energy and change in molecular orientations. Excess and deviation properties of liquid mixtures are useful in the study of molecular interactions and arrangements. The results from intermolecular interactions [1] obtained by volumetric properties of the liquid mixtures are proved to be a useful indicator of the existence of significant effects. A survey of the literature [2] shows that a very few attempts have been made to study excess properties for mixtures containing quinoline. Knowledge of the physicochemical properties of the binary liquid mixtures has relevance in theoretical and applied areas of research and such results are frequently used in process designing in many chemical and industrial processes. Phenols are widely used for phonograph records, wood preservatives and selective weed killing. Quinoline is widely used in manufacturing of dyes, pesticides and solvent for resins and terpenes. In the present study, the densities and viscosities of the binary mixtures of (quinoline + cresols) over the entire composition range at different temperatures of T= (303.15, 308.15, 313.15 and 318.15) K, are presented. From the experimental results, the values of excess volume and viscosity deviation over entire mole fraction range were calculated. These values are fitted to the Redlich-Kister type polynomial equation to derive the binary coefficients and the standard deviations between experimental and theoretical results.

MATERIALS AND METHODS

Chemicals

The mass fractions of the liquids, cresols (obtained from Merck) are as follows: o-cresol (0.990), m-cresol (0.990) and p-cresol (0.980) and that of the liquid, quinoline (obtained from SDFCL Chemicals) is 0.97. All the liquids obtained from the suppliers were further purified by standard procedure [3]. A comparison of the experimental values of density, viscosity and ultrasonic velocity obtained in the present study with the values reported in literature [4-6] is presented in Table 1, which shows good agreement.

Table1: Comparison of experimental densities, ρ, ultrasonic velocities, u, and viscosities, η, of pure liquids with literature values.

Liquids	T/K	ρ / (kg . m^{-3})		u / (m . s^{-1})		$10^3.\eta$ / (kg . m^{-1}. s^{-1})	
		Experimental	Literature	Experimental	Literature	Experimental	Literature
Quinoline	303.15	1085	1085.82[a]	1554	1547[a]	2.932	-
o-Cresol	303.15	1036	1036.9[b]	1485	1487[b]	7.479	4.243[c] 313.15/K
m-Cresol	303.15	1025	1026.1[b]	1464	1465[b]	8.929	6.252[c] 313.15/K
p-Cresol	303.15	1026	1026.3[b]	1468	1471[b]	9.540	6.661[c] 313.15/K

[a] Jagan Nath.[4]. [b] Bhatia et al.[5]. [c] Rosal et al.[6].

Measurements

Job's method of continuous variation was used to prepare the mixtures in the required proportions. The mixtures were preserved in well-stoppered conical flasks. After thorough mixing of the liquids, the flasks were left undisturbed to allow them to attain thermal equilibrium.

An electronic balance (Shimadzu AUY220, Japan), with a precision of ± 0.1 mg was used for the mass measurements. The densities of pure liquids and liquid mixtures were measured by using a specific gravity bottle with an accuracy of ± 0.5%.

Viscosities were measured at 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, 5 to 7 measurements were performed and the average of these values was used in all the calculations. The values are accurate to ± 10^{-3} mPa.s.

The ultrasonic velocities were measured by using a single crystal ultrasonic pulse echo interferometer (Model: F-80X Mittal enterprises, India), equipped with a high frequency generator and a measuring cell. The measurements of ultrasonic velocities were made at a fixed frequency of 3 MHz. The equipment was calibrated by measuring the velocity in carbon tetrachloride and benzene. The results are in good agreement with the literature reports [7]. The error in velocity measurement is ± 0.5 %. The temperature was controlled through the water circulation around the liquid cell using thermostatically controlled constant temperature water bath with an accuracy of ± 0.01 K.

The experimental values of density (ρ), viscosity (η) and ultrasonic velocity (u) for all the mixtures over the entire range of composition and at 303.15, 308.15, 313.15 and 318.15 K are presented in Table 2.

THEORY

The parameters are evaluated from the experimental values, by using the standard equations [8].The strength of interaction between the component molecules of the binary mixtures is well reflected in the deviation of the excess functions from ideality. The excess properties such as V^E, viscosity deviation $\Delta\eta$ and excess Gibb's free energy of activation for viscous flow, ΔG^{*E} have been calculated using the standard equations [9] and have been fitted to the polynomial equation [10].

$$Y^E = x_1 (1-x_1) \sum A_i (2x_1-1)^i \qquad (i = 0, 1, 2) \qquad\qquad (1)$$

Table2: Densities, ρ, viscosities, η, and ultrasonic velocities, u, for binary mixtures at T = (303.15, 308.15, 313.15 and 318.15) K.

x_1	T=303.15K			T=308.15K			T=313.15K			T=318.15K		
	$\rho/$ (kg.m^{-3})	$10^3.\eta/$ (kg.m^{-1}.s^{-1})	$u/$ (m.s^{-1})	$\rho/$ (kg.m^{-3})	$10^3.\eta/$ (kg.m^{-1}.s^{-1})	$u/$ (m.s^{-1})	$\rho/$ (kg.m^{-3})	$10^3.\eta/$ (kg.m^{-1}.s^{-1})	$u/$ (m.s^{-1})	$\rho/$ (kg.m^{-3})	$10^3.\eta/$ (kg.m^{-1}.s^{-1})	$u/$ (m.s^{-1})
(Quinoline(1) + o-Cresol(2))												
0.0000	1036.20	7.479	1485	1031.00	5.963	1467	1026.00	4.238	1452	1021.10	2.125	1437
0.0888	1048.32	13.382	1500	1044.34	12.507	1494	1041.76	11.459	1487	1038.39	11.185	1481
0.1798	1055.14	13.432	1509	1052.57	12.512	1506	1049.98	11.469	1503	1047.71	11.218	1494
0.2732	1063.07	13.437	1515	1060.08	12.519	1513	1056.07	11.475	1508	1054.91	11.240	1500
0.3690	1070.40	13.377	1525	1066.17	12.448	1519	1063.07	11.499	1509	1059.78	11.467	1503
0.4672	1075.08	13.016	1532	1071.76	12.179	1522	1069.57	11.204	1514	1066.17	11.082	1506
0.5681	1078.84	9.322	1534	1073.80	8.670	1529	1072.90	7.950	1516	1069.00	7.921	1509
0.6717	1080.77	6.585	1538	1076.13	6.051	1534	1074.35	5.422	1520	1071.04	5.303	1516
0.7782	1081.18	4.639	1544	1078.43	4.262	1540	1076.61	3.950	1525	1069.62	3.799	1520
0.8876	1084.33	3.795	1551	1081.20	3.448	1546	1077.28	3.103	1536	1073.37	2.927	1528
1.0000	1085.45	2.932	1554	1082.11	2.707	1551	1078.60	2.447	1548	1074.99	2.430	1541
(Quinoline(1) + m-Cresol(2))												
0.0000	1025.80	8.929	1464	1021.50	7.412	1456	1017.00	6.116	1444	1013.50	5.019	1433
0.0896	1043.54	19.344	1488	1040.68	18.111	1484	1035.77	16.614	1481	1031.28	16.294	1475
0.1813	1047.10	18.546	1496	1043.32	17.354	1487	1039.33	15.925	1484	1034.63	15.729	1478
0.2752	1056.46	17.706	1509	1052.76	16.437	1494	1049.58	15.122	1491	1044.77	15.039	1481
0.3713	1061.45	16.364	1519	1057.94	15.303	1500	1055.06	14.091	1497	1051.16	14.049	1487
0.4697	1068.06	12.925	1528	1065.46	12.037	1513	1062.97	11.029	1503	1059.43	10.891	1497
0.5706	1075.49	9.257	1532	1072.38	8.669	1522	1069.16	7.957	1516	1065.36	7.806	1506
0.6740	1077.82	6.715	1544	1075.21	6.211	1539	1073.53	5.579	1521	1070.53	5.463	1514
0.7799	1079.88	4.841	1547	1076.43	4.456	1540	1074.24	4.029	1528	1071.45	3.854	1519
0.8886	1083.86	3.534	1549	1081.40	3.263	1544	1078.30	2.864	1538	1073.78	2.656	1532
1.0000	1085.45	2.932	1552	1082.11	2.707	1550	1078.60	2.447	1546	1074.99	2.403	1540
(Quinoline(1) + p-Cresol(2))												
0.0000	1026.50	9.540	1461	1022.00	8.119	1449	1018.10	6.741	1436	1013.90	5.469	1424
0.0896	1038.15	25.040	1472	1034.49	23.431	1458	1031.92	21.767	1446	1026.31	23.899	1440
0.1812	1046.69	21.706	1491	1043.33	20.325	1470	1040.14	18.821	1462	1035.44	18.905	1456
0.2751	1058.49	18.790	1500	1054.60	17.519	1486	1050.90	16.227	1476	1046.39	16.221	1472
0.3711	1065.72	16.696	1505	1061.70	15.641	1500	1058.20	14.449	1494	1053.69	14.472	1484
0.4696	1072.43	13.636	1514	1067.70	12.680	1506	1063.68	11.763	1500	1060.39	11.741	1494
0.5704	1076.81	9.272	1522	1073.38	8.596	1516	1068.76	7.928	1506	1065.16	7.852	1497

0.6738	1079.86	6.879	1533	1076.13	6.234	1528	1072.61	5.701	1516	1068.70	5.649	1512
0.7798	1080.88	4.672	1541	1077.34	4.280	1535	1073.63	3.879	1525	1069.41	3.788	1517
0.8885	1084.94	3.500	1547	1081.91	3.249	1541	1077.18	2.890	1535	1072.84	2.872	1528
1.0000	1085.45	2.932	1550	1082.11	2.707	1549	1078.60	2.447	1545	1074.99	2.430	1538

Table3: Coefficients of Redlich-Kister equation, A_i, and standard deviations, σ, for excess molar volume, V^E, viscosity deviation, $\Delta\eta$, and excess Gibb's free energy of activation for viscous flow,ΔG^{*E}, for binary liquid mixtures.

Properties	A_0	A_1	A_2	σ	A_0	A_1	A_2	σ
(Quinoline(1) + o-Cresol(2))								
303.15 K					308.15 K			
V^E / (m^3.mol^{-1})	-0.5713	0.2960	-0.1183	0.0139	-0.6124	0.3501	-0.1964	0.0135
$10^3\Delta\eta$ / (kg.m^{-1}.s^{-1})	2.7680	-4.5696	1.8756	0.5892	2.7720	-4.9388	2.3820	0.6103
ΔG^{*E}/ (j.mol^{-1})	2.1698	-2.4129	0.9848	0.4369	2.3405	-3.0539	1.5258	0.4920
313.15 K					318.15 K			
V^E / (m^3.mol^{-1})	-0.6911	0.5469	-0.2794	0.0243	-0.7250	0.6657	-0.3661	0.0222
$10^3\Delta\eta$ / (kg.m^{-1}.s^{-1})	2.7732	-5.2845	2.9594	0.6359	3.0972	-6.4626	4.0684	0.7495
ΔG^{*E}/ (j.mol^{-1})	2.6171	-3.9792	2.4860	0.5840	3.2922	-6.5383	4.9141	0.8227
(Quinoline(1) + m-Cresol(2))								
303.15 K					308.15 K			
V^E / (m^3.mol^{-1})	-0.4834	0.5904	-0.7504	0.0460	-0.5937	-0.2507	0.3304	0.0399
$10^3\Delta\eta$ / (kg.m^{-1}.s^{-1})	2.2168	-8.1515	6.7069	0.7902	2.2211	-8.2090	6.9377	0.7945
ΔG^{*E}/ (j.mol^{-1})	1.8743	-3.6039	2.1208	0.4711	1.9978	-4.0401	2.5863	0.5144
313.15 K					318.15 K			
V^E / (m^3.mol^{-1})	-0.6089	0.5632	-0.7919	0.0503	-0.6145	0.5615	-0.6183	0.05627
$10^3\Delta\eta$ / (kg.m^{-1}.s^{-1})	2.1546	-8.0063	6.7483	0.7723	2.3067	-8.5444	7.1093	0.8261
ΔG^{*E}/ (j.mol^{-1})	2.1097	-4.5479	2.8596	0.5541	2.2954	-5.4079	3.2947	0.6215
(Quinoline(1) + p-Cresol(2))								
303.15 K					308.15 K			
V^E / (m^3.mol^{-1})	-0.6827	0.0863	0.0449	0.0139	-0.6526	0.1090	-0.1177	0.0130
$10^3\Delta\eta$ / (kg.m^{-1}.s^{-1})	2.1212	-1.1946	1.1578	0.9480	2.1000	-1.1659	1.1423	0.9430
ΔG^{*E}/ (j.mol^{-1})	1.8466	-4.5495	3.2045	0.4951	1.9466	-4.8744	3.5966	0.5290
313.15 K					318.15 K			
V^E / (m^3.mol^{-1})	-0.6336	0.2914	-0.1765	0.0119	-0.6689	0.2352	0.0730	0.00897
$10^3\Delta\eta$ / (kg.m^{-1}.s^{-1})	2.0940	-1.1361	1.1092	0.9147	2.2080	-1.3667	1.4103	0.9390
ΔG^{*E}/ (j.mol^{-1})	2.0860	-5.3510	3.9239	0.5721	2.2762	-6.5003	5.3225	0.6579

The values of the coefficients A_i were calculated by the 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

$$\sigma\ (Y^E) = [\Sigma\ (Y^E_{expt} - Y^E_{cal})^2\ /\ (m\text{-}n)\ ]^{1/2} \tag{2}$$

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.

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.

RESULTS AND DISCUSSION

Plots of V^E, $\Delta\eta$, and ΔG^{*E} against mole fraction of quinoline at temperatures 303.15 to 313.15 K for all the mixtures are given in Figs. 1 to 3, respectively. The values of V^E, $\Delta\eta$, and ΔG^{*E} for the binary mixtures of quinoline with o-cresol, m-cresol and p-cresol may be explained on the basis of various types of intermolecular interactions between components. The excess properties of the mixtures [11] 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.

Figure 1(a) : Excess molar volume, V^E quinoline with o-cresol
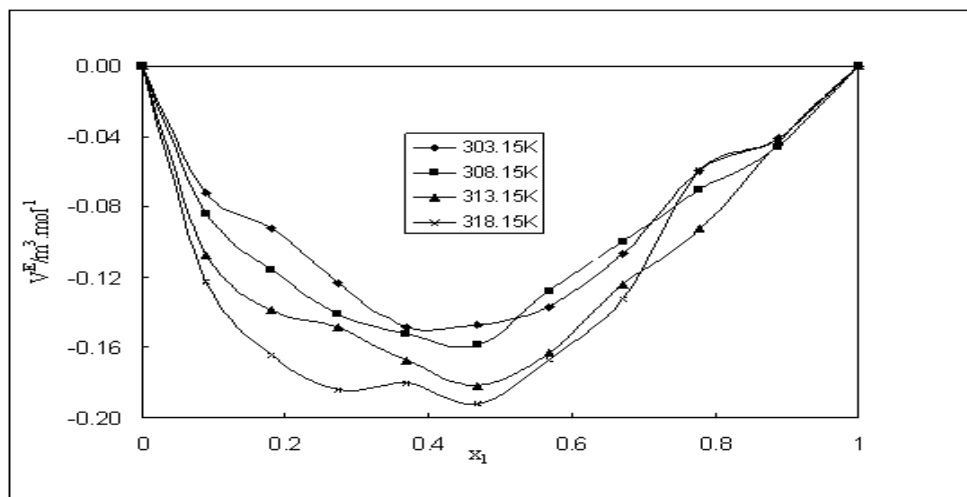
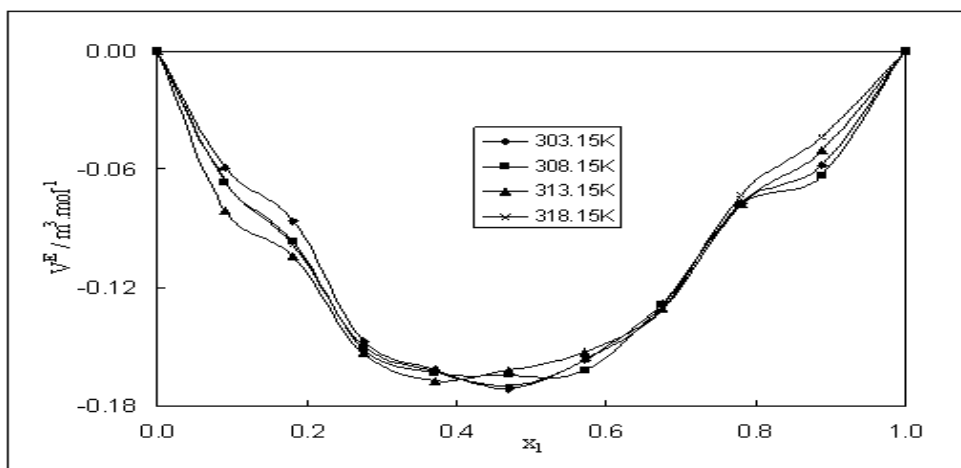**Figure 1(b) : Excess molar volume, V^E of quinoline with m-cresol**

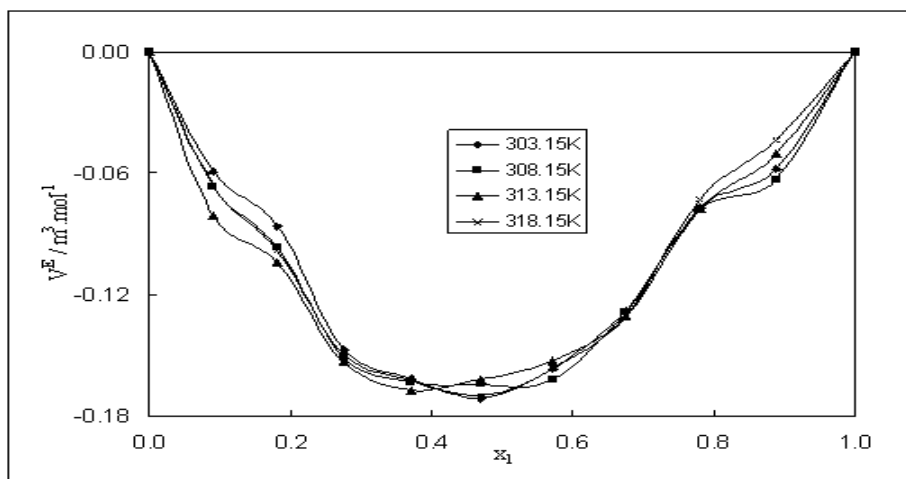**Figure 1(c) : Excess molar volume, V^E of quinoline with p-cresol**

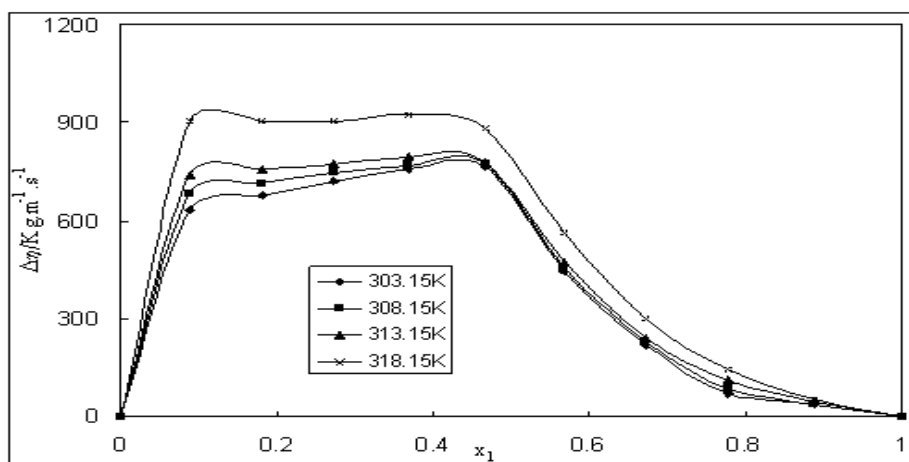**Figure 2(a) : Deviation in viscosity, $\Delta\eta$ of quinoline with o-cresol**

Figure 2(b) : Deviation in viscosity, Δη of quinoline with m-cresol

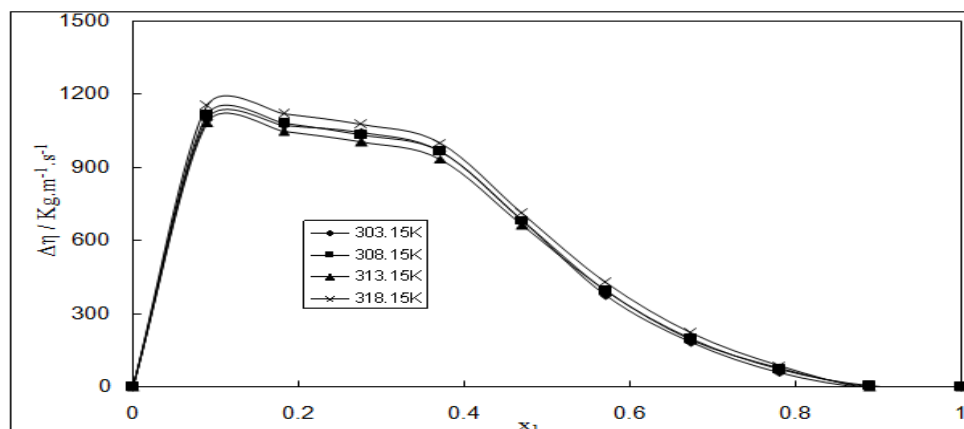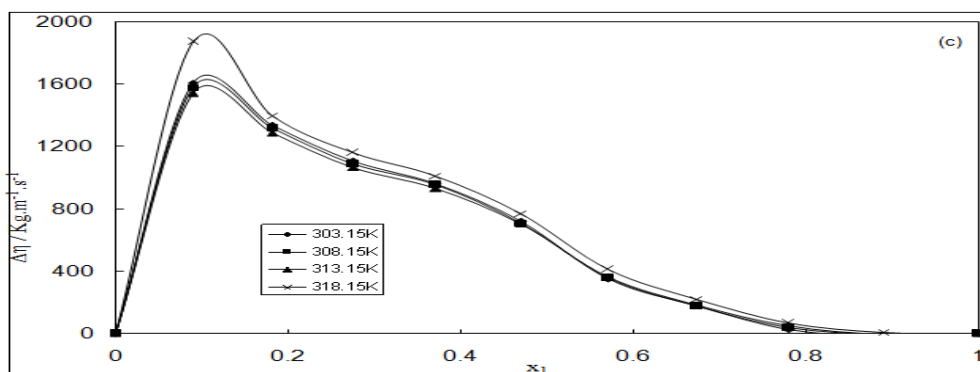**Figure 2(c) : Deviation in viscosity, Δη of quinoline with p-cresol**

Figure 3(a): Excess Gibb's energy of activation for viscous flow, ΔG^{*E} of quinoline with o-cresol
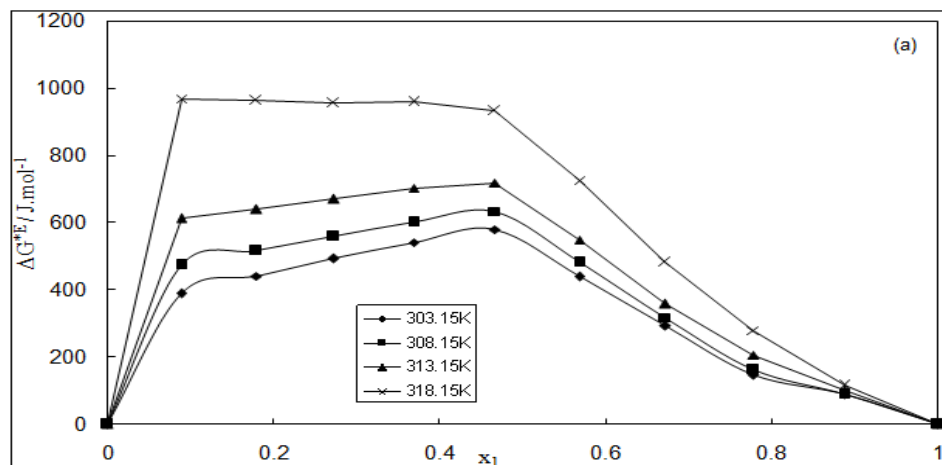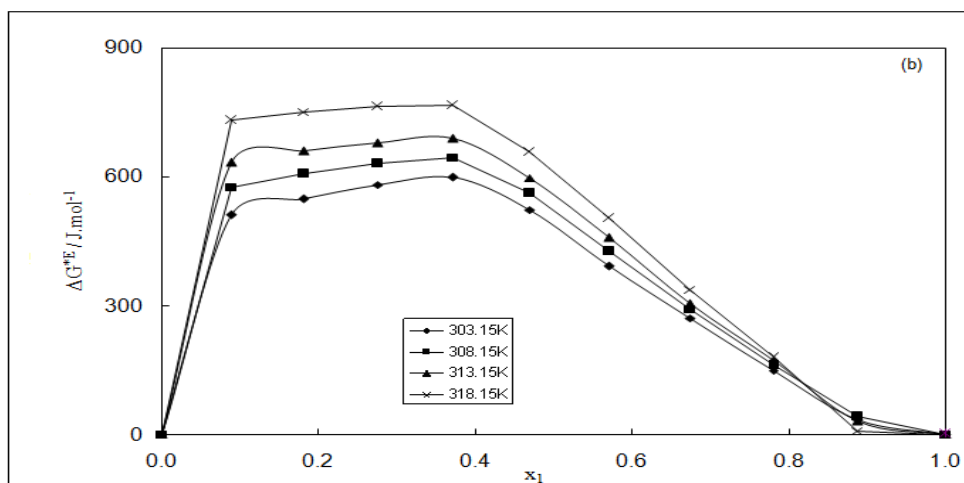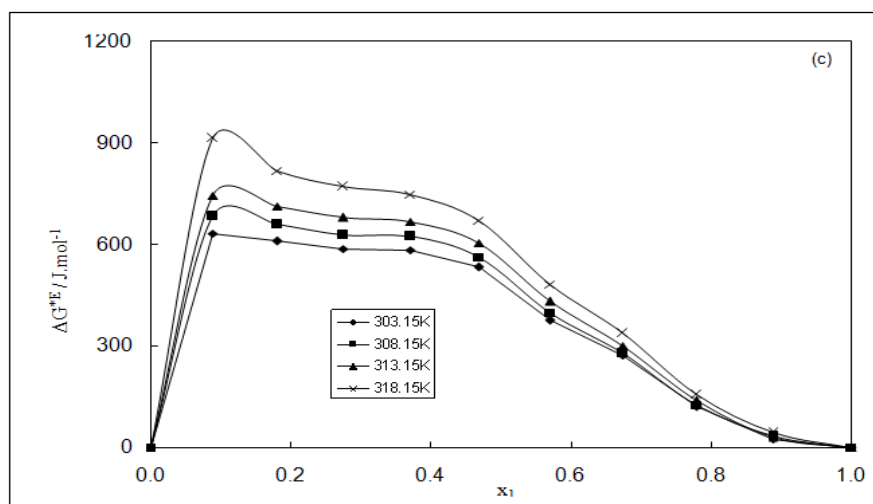
Figure 3(b): Excess Gibb's energy of activation for viscous flow, ΔG^{*E} of quinoline with m-cresol

Figure 3(c): Excess Gibb's energy of activation for viscous flow, ΔG^{*E} of quinoline with p-cresol

The excess molar volume, V^E, versus mole fraction, x_1, is plotted and shown in figures 1(a) to 1(c) over the entire composition range and at T = (303.15, 308.15, 313.15 and 318.15) K. The V^E values are found to be negative for all the three systems over the entire range of composition. The deviations in excess molar volume are mainly due to the mutual dissociation of component molecules and the formation of hydrogen bonds between unlike molecules. The former effect leads to positive excess volume and the latter effect to negative excess volume. The actual change in volume would depend upon the relative strengths of the two effects. The observed negative values show that the main contribution of V^E is due to hydrogen bond formation between unlike molecules. The negative values of V^E fall in the sequence, quinoline + m-cresol > quinoline + p-cresol > quinoline + o-cresol. It is also observed that the magnitude of V^E decreases with increase in temperature. The contraction in molar volume is due to the presence of strong intermolecular forces of attraction [12]. With increase in temperature,

interactions between the unlike molecules become weaker and the V^E values become less negative for all the systems studied.

Figures 2(a) to 2(c) show viscosity deviation, $\Delta\eta$, against mole fraction, x_1, over the entire composition range at T= (303.15, 308.15, 313.15 and 318.15) K. $\Delta\eta$ values are positive over the whole composition range for all the systems under study. A correlation between the signs of $\Delta\eta$, V^E has been observed for a number of binary systems. $\Delta\eta$ is positive, where V^E is negative and vice-versa. In general, for systems where dispersion and dipolar interactions are operating, $\Delta\eta$ values are found to be negative whereas charge transfer and hydrogen bonding interactions lead to the formation of complex species between unlike molecules thereby resulting in positive $\Delta\eta$ values. The maximum deviation is observed in quinoline + p-cresol system. It is observed that the deviations in viscosities are in the order of quinoline + p-cresol > quinoline + m-cresol > quinoline + o-cresol.

Figures 3(a) to 3(c) show excess Gibb's energy, ΔG^{*E}, against the mole fraction, x_1, over the entire composition range at T= (303.15, 308.15, 313.15 and 318.15) K. It can be seen from these figures that the ΔG^{*E} values are positive at all temperatures and the entire range of the mole fraction. These positive values indicate the existence of strong intermolecular interaction [13] between the components of the mixtures considered for the study. The maximum deviation is observed in the case of quinoline + p-cresol. From the above results, it is inferred that strong interactions are present between the molecules of the mixture viz., quinoline + p-cresol when compared with the other two mixtures investigated in the present study.

From the above results it is evident that the presence of strong interactions between unlike molecules is predominant and characterized by the negative V^E and positive $\Delta\eta$ and ΔG^{*E} values.

CONCLUSIONS

Ultrasonic velocity, density and viscosity values are used to calculate various thermodynamic parameters. The negative values of V^E and positive values of $\Delta\eta$ and ΔG^{*E} in all the three binary mixtures support the existence of strong molecular interactions between the molecules of the mixtures taken up for study.

ACKNOWLEDGEMENT

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