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Excess Isentropic Compressibilities, Excess Molar Volumes, Refractive Index Deviations of Diethyl Carbonate + Nitrobenzene, + Chlorobenzene, and + Ethylbenzene at T = (293.25, 303.15, 313.15 and 323.15) K

KEYWORDS: speed of sound, refractive index, isentropic compressibility, diethyl carbonate

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ABSTRACT *Densities, speeds of sound and refractive indices of diethyl carbonate + nitrobenzene, + chlorobenzene, and + ethylbenzene have been measured at (293.25, 303.15, 313.15 and 323.15) K over the entire composition range and at atmospheric pressure. From these measurements, excess molar isentropic compressibilities ( ), excess molar volumes (VE) and refractive index deviations (ΔnD) were calculated. The results were fitted to the Redlich-Kister polynomial equation in order to derive the adjustable parameters and standard deviations to study the nature of the molecular interactions in the mixtures.*

Introduction:- For investigating the properties of pure components and the nature of intermolecular interactions between the components of liquid mixtures, data of physical properties such as density, speed of sound and refractive index of pure components and their binary mixtures are being increasingly used as tools [1]. For understanding the molecular interactions, excess thermodynamic parameters are used as important parameters. Diethyl carbonate (DEC) is a solvent of both extraction and reaction used in many industries such as agrochemicals, pharmaceuticals and hydrocarbon refinery. It can make dyeing uniformity and increase fading against sunshine. DEC was also proposed as lubricant of the new refrigerant, hydrofluorocarbon and as paint remover in the paint industry.

Benzene derivatives such as nitrobenzene (NB), chlorobenzene (CB) and ethylbenzene (EB) are important liquids which find variety of applications such as solvent for lacquers, oils and resins. Several researchers [2-5] studied the molecular interactions in binary liquid mixtures containing diethyl carbonate by measuring the values of density, speed of sound and refractive index. As a part of the experimental investigation of the excess thermodynamic properties of industrially important liquids like diethyl carbonate, here we report the densities, speeds of sound, refractive indices, excess molar isentropic compressibilities (K_s^E), excess molar volumes (V^E) and refractive index deviations (Δn_D) for binary mixtures of the above mentioned systems at (293.15, 303.15, 313.15 and 323.15) K over the entire composition range.

Experimental Procedure:-

All the chemicals used in this study were purchased from Aldrich Chemicals Company. According to the manufacturer, the purities of these compounds were >99%. The purity of the samples was checked by comparing the observed values of densities, speeds of sound and refractive

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indices with those reported in literature and were used as such without further purification.The measured values are included in table 1 along with the values reported in literature.

Anton Paar DSA 5000 density and sound analyser provided with two Pt 100 platinum thermometer was used for measuring the densities and speeds of sound of pure liquids and liquid mixtures. The density is extremely sensitive to temperature, so the apparatus was controlled to ±0.001 K by a built-in solid state thermostat. The stated accuracy in density and speed of sound are $5x10^{-3}$ kgm^{-3} and 0.5 m/s respectively.

The binary liquid mixtures were prepared by mixing known masses of pure liquids in airtight-stoppered bottles to minimize evaporation losses. The weighings were done with an electronic balance with a precision of ±0.01mg.

Refractive indices of the mixtures at the sodium D-line were determined with an Abbemat heavy duty line refractometer equipped with a circulating water bath permitting to maintain the sample at constant temperature to within ±0.002K. The instrument was calibrates by measuring the refractive index of deionised water. The sample support was rinsed with acetone and dried with a paper towel. The stated accuracy in refractive index is ±0.00002 nD.

Results and discussion:-

Density, speed of sound and refractive index of pure DEC, NB, CB and EB were measured at (293.15, 303.15, 313.15 and 323.15) K and at atmospheric pressure. The same conditions of pressure and temperature were applied in the determination of experimental density, speed of sound and refractive index of the three binary systems studied in this work: (DEC+NB), (DEC+CB) and (DEC+EB).

Table 2 lists the experimental values of densities, ρ, speeds of sound, u, and refractive indices, n_D, of binary mixtures of diethyl carbonate + nitro benzene,

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chloro benzene, and ethyl benzene at different temperatures.

The values of speed of sound, u, and density, ρ, were used to calculate the isentropic compressibility, k_s, by using the following relation,

$$k_s = u^{-2} \rho^{-1} \quad \text{---(1)}$$

The excess isentropic compressibility,

$$k_s^E = k_s - k_s^{id} \quad \text{---(2)}$$

k_s^{id} was calculated from the relations

$$k_s^{id} = \sum_{i=1}^{2} \phi_i [k_{s,i} + TV_i(\alpha_i^2)/C_{p,i}] - \{T(\sum_{i=1}^{2} x_i V_i)(\phi_i \alpha_i)^2 / \sum_{i=1}^{2} x_i C_{p,i}\} \quad \text{---(3)}$$

$$\text{and } \phi_i = x_i V_i / (\sum_{i=1}^{2} x_i V_i) \quad \text{---(4)}$$

where ϕ_i is the volume fraction, V_i is the molar volume, α_i is the isobaric thermal expansion coefficient (calculated from the measured densities of the pure components at different temperatures) and $C_{p,i}$ is the molar heat capacity of i^{th} component. $C_{p,i}$ values at different temperatures are taken from the literature.

The excess molar volume was calculated from the relation

$$V^E = [(x_1M_1 + x_2M_2)/\rho - x_1M_1/\rho_1 - x_2M_2/\rho_2] \quad \text{---(5)}$$

where x_1, x_2, M_1, M_2, ρ_1 and ρ_2 represent the mole fraction, molar masses and densities of pure components respectively and ρ is the density of liquid mixture.

The refractive index deviations, Δn_D, were obtained from the relation

$$\Delta n_D = n_D - x_1 n_{D1} - x_2 n_{D2} \quad \text{---(6)}$$

The calculated k_s^E values and Δn_D values were correlated by the Redlich-Kister polynomial [12] by using the relation

$$\Delta Y = x_1 x_2 \sum_{i=0}^{n} a_i (x_1 - x_2)^i \quad \text{---(7)}$$

The coefficients, a_i, in eq 7 were estimated by the least-squares fitting method, and the standard deviation, σ, was calculated by using the relation

$$\sigma = \left[\sum_{i=0}^{D} \frac{(\Delta Y_{expt} - \Delta Y_{cal})^2}{(D - N)} \right]^{1/2} \quad \text{---(8)}$$

where D and N are the number of data points and parameters respectively.

Regression results for k_s^E, V_m^E and Δn_D of three binary mixtures at different temperatures are reported in table 3.

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Table 1

Comparison of Experimental densities, ρ, speeds of sound, u, and refractive indices, n_D, of pure liquids with literature values

Liquid	T/K	ρ/(kgm^{-3})		u/(ms^{-1})		n_D		α/(10^{-}	C_p/(J.mol^{-}
		Expt.	Lit.	Expt.	Lit.	Expt.	Lit.	Expt.	Lit.
Diethyl carbonate	303.15	963.47	963.00[6]	1156.9	--	1.3802	1.3801[6]	1.17653	221.6[11]
Nitrobenzene	303.15	1192.3	1193.4[7]	1438.3	1444.3[8]	1.5418	1.5420[9]	0.83386	142[11]
Chlorobenzene	303.15	1095.5	1095.0[7]	1248.9	1252.0[9]	1.5187	1.5191[9]	0.79213	129.4[11]
Ethylbenzene	303.15	859.29	858.10[10]	1297.7	--	1.4898	1.4906[10]	1.03971	171.1[11]

Table 2

Densities, ρ, speeds of sound, u, and refractive indices, n_D, for binary mixtures at T = (293.15, 303.15, 313.15 and 323.15) K

x_1	ρ/(kgm^{-3})	u/(ms^{-1})	n_D	ρ/(kgm^{-3})	u/(ms^{-1})	n_D
{Diethyl carbonate + Nitrobenzene}						
	T = 293.15 K			T = 303.15 K		
0.000000	1202.238	1474.07	1.552334	1192.297	1438.30	1.541859
0.093671	1179.555	1447.27	1.529004	1169.588	1410.67	1.521554
0.167813	1161.679	1426.18	1.514038	1151.720	1389.12	1.506858
0.271534	1137.613	1396.76	1.494745	1127.312	1359.07	1.487897
0.357663	1117.218	1372.21	1.479554	1106.804	1334.20	1.473076
0.454745	1094.887	1345.12	1.463265	1084.371	1306.65	1.457079
0.614931	1059.198	1300.95	1.438064	1048.576	1261.57	1.433029
0.660560	1049.223	1288.49	1.431038	1038.529	1248.79	1.426519
0.772188	1024.734	1258.34	1.414238	1013.802	1217.90	1.410186
0.890681	998.715	1227.05	1.397277	987.638	1186.02	1.393785
1.000000	974.699	1198.01	1.384701	963.468	1156.96	1.380107
	T = 313.15 K			T = 323.15 K		
0.000000	1182.355	1402.70	1.541592	1172.408	1367.68	1.536476
0.093671	1159.516	1374.35	1.522334	1149.425	1338.01	1.518865
0.167813	1141.539	1352.09	1.507705	1131.336	1315.56	1.504782
0.271534	1116.988	1321.57	1.489083	1106.631	1284.56	1.485873
0.357663	1096.362	1296.42	1.474016	1085.885	1259.01	1.470715
0.454745	1073.821	1268.35	1.457526	1063.228	1230.48	1.454296
0.614931	1037.908	1222.43	1.432184	1027.192	1183.83	1.429345
0.660560	1027.777	1209.39	1.425164	1016.861	1170.60	1.422388
0.772188	1002.798	1177.88	1.408514	991.710	1138.44	1.405523
0.890681	976.470	1145.16	1.391256	965.209	1105.09	1.387562
1.000000	952.134	1116.45	1.375586	940.691	1076.66	1.370953
{Diethyl Carbonate + Chlorobenzene}						
	T = 293.15 K			T = 303.15 K		
0.000000	1106.296	1285.71	1.525885	1095.506	1248.92	1.518758
0.083980	1093.410	1278.03	1.510295	1083.340	1240.65	1.504221
0.177393	1079.990	1269.70	1.495487	1069.756	1231.85	1.489550
0.268224	1067.467	1261.68	1.481793	1057.263	1223.40	1.476075
0.359118	1055.470	1253.71	1.468440	1044.924	1215.05	1.462824

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0.461705	1042.065	1244.74	1.453798	1031.473	1205.63	1.448401
0.584550	1026.122	1233.99	1.436603	1015.282	1194.41	1.431435
0.629016	1020.399	1230.10	1.430510	1009.559	1190.34	1.425625
0.760177	1003.870	1218.65	1.413358	993.289	1178.36	1.408761
0.869399	990.570	1209.19	1.399621	979.863	1168.49	1.395352
1.000000	974.699	1198.01	1.384712	963.468	1156.96	1.380170
	T = 313.15 K			T = 323.15 K		
0.000000	1084.665	1212.19	1.513081	1073.772	1175.99	1.507462
0.083980	1072.811	1203.40	1.499142	1063.319	1166.60	1.494266
0.177393	1059.358	1194.10	1.484589	1049.487	1156.89	1.479959
0.268224	1046.598	1185.27	1.471204	1036.561	1147.68	1.466516
0.359118	1034.307	1176.51	1.458110	1023.897	1138.56	1.453416
0.461705	1021.001	1166.71	1.443659	1010.039	1128.40	1.438994
0.584550	1004.858	1155.04	1.426854	994.139	1116.30	1.422246
0.629016	999.120	1150.82	1.420970	988.282	1111.95	1.416463
0.760177	982.408	1138.42	1.404182	971.629	1099.17	1.399815
0.869399	968.857	1128.29	1.390757	958.042	1088.75	1.386509
1.000000	952.134	1116.45	1.375586	940.691	1076.66	1.370953
{Diethyl carbonate + Ethylbenzene}						
	T = 293.15 K			T = 303.15 K		
0.000000	867.108	1339.57	1.495667	859.298	1297.66	1.489875
0.093846	876.520	1325.27	1.485453	868.379	1283.22	1.479993
0.201961	887.574	1308.78	1.473774	879.016	1266.82	1.468464
0.302935	898.346	1293.32	1.462796	889.357	1251.48	1.457663
0.410995	909.808	1277.50	1.450783	900.494	1235.75	1.445804
0.507910	920.304	1263.68	1.439877	910.617	1222.02	1.435038
0.606418	931.199	1249.71	1.428816	921.207	1208.17	1.424122
0.703041	941.886	1236.40	1.418001	931.594	1194.91	1.413366
0.803457	953.022	1223.08	1.406738	942.403	1181.65	1.402156
0.891381	962.851	1211.55	1.396883	951.975	1170.12	1.392367
1.000000	974.699	1198.01	1.384700	963.468	1156.96	1.380170
	T = 313.15 K			T = 323.15 K		
0.000000	849.437	1256.38	1.484108	840.519	1215.77	1.478449
0.093846	858.279	1241.91	1.474546	848.819	1201.17	1.469293
0.201961	868.702	1225.50	1.463294	859.017	1184.76	1.458323
0.302935	878.853	1210.22	1.452594	869.101	1169.61	1.447660
0.410995	889.890	1194.58	1.440907	879.840	1154.04	1.436046
0.507910	899.807	1180.92	1.430305	889.474	1140.52	1.425491
0.606418	910.234	1167.19	1.419435	899.616	1126.88	1.414689
0.703041	920.571	1154.02	1.408751	909.725	1113.82	1.404090
0.803457	931.192	1140.88	1.397603	920.187	1100.60	1.392993
0.891381	940.696	1129.49	1.387807	929.462	1089.37	1.383201
1.000000	952.134	1116.45	1.375586	940.691	1076.66	1.370953

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Table 3

Value of Coefficients, a_i, of the Redlich-Kister Polynomial and standard deviations, σ, for binary mixtures at T = (293.15, 303.15, 313.15 and 323.15) K

Parameter	T/K	a_0	a_1	a_2	a_3	σ
{Diethyl carbonate + Nitrobenzene}						
$k_s^E/(TPa^{-1})$	293.15	-1.55263	-0.39039	-0.10425	-0.01583	0.00008
	303.15	-1.14283	-0.27257	-0.07682	-0.01707	0.00010
	313.15	-0.70130	-0.13187	-0.03617	-0.02115	0.00009
	323.15	-0.49290	-0.05267	-0.00625	-0.02392	0.00021
$V^E/(10^{-6}.m^3.mol^-$	293.15	-2.45970	0.65333	-0.54837	0.06764	0.01491
	303.15	-2.62486	0.78122	-0.63388	-0.26308	0.01347
	313.15	-2.81853	0.90696	-0.59587	-0.44027	0.01498
	323.15	-3.02331	1.00000	-0.56049	-0.54204	0.01611
Δn_D	293.15	-0.04878	-0.01416	-0.03383	-0.00411	0.00029
	303.15	-0.04253	-0.01634	-0.01152	0.00777	0.00016
	313.15	-0.03312	-0.00920	-0.00237	-0.00495	0.00012
	323.15	-0.02615	-0.01301	0.00963	0.01028	0.00008
{Diethyl carbonate + Chlorobenzene}						
$k_s^E/(TPa^{-1})$	293.15	-0.13552	-2.37623	-0.31480	-0.03602	0.00006
	303.15	-14.15086	-2.49983	-0.33635	-0.03786	0.00010
	313.15	-14.54438	-2.58469	-0.34888	-0.04312	0.00011
	323.15	-15.30378	-2.74523	-0.38185	-0.05062	0.00016
$V^E/(10^{-6}.m^3.mol^-$	293.15	-4.92800	-1.99433	3.89032	-1.32081	0.40554
	303.15	-5.15663	-2.07659	3.13780	-1.24603	0.41205
	313.15	-5.54323	-1.80320	3.15773	-1.93574	0.41430
	323.15	-5.82514	-1.77380	1.92533	-2.65455	0.42310
Δn_D	293.15	-0.02744	-0.00034	-0.01509	-0.01356	0.00013
	303.15	-0.02557	-0.00058	-0.00748	-0.00998	0.00006
	313.15	-0.02382	-0.00001	-0.00543	-0.00639	0.00004
	323.15	-0.02208	0.00049	0.00144	-0.00418	0.00004
{Diethyl carbonate + Ethylbenzene}						
$k_s^E/(TPa^{-1})$	293.15	-4.14002	-0.49174	-0.06361	-0.01022	0.00006
	303.15	-4.73298	-0.59130	-0.07623	-0.01570	0.00007
	313.15	-6.10609	-0.80877	-0.12874	-0.00175	0.00221
	323.15	-6.98011	-0.96152	-0.12839	-0.02460	0.00004
$V^E/(10^{-6}.m^3.mol^-$	293.15	0.60660	0.42610	-0.10318	0.23531	0.00655
	303.15	0.73017	0.47402	-0.16643	0.17065	0.00605
	313.15	0.85431	0.48891	-0.08120	0.19927	0.00769
	323.15	0.95445	0.35915	0.20493	0.89645	0.00951
Δn_D	293.15	0.00249	0.00288	-0.00049	-0.00362	0.00003
	303.15	0.00372	0.00263	0.00020	-0.00238	0.00003
	313.15	0.00531	0.00263	0.00087	-0.00144	0.00001
	323.15	0.00664	0.00349	0.00300	-0.00054	0.00001

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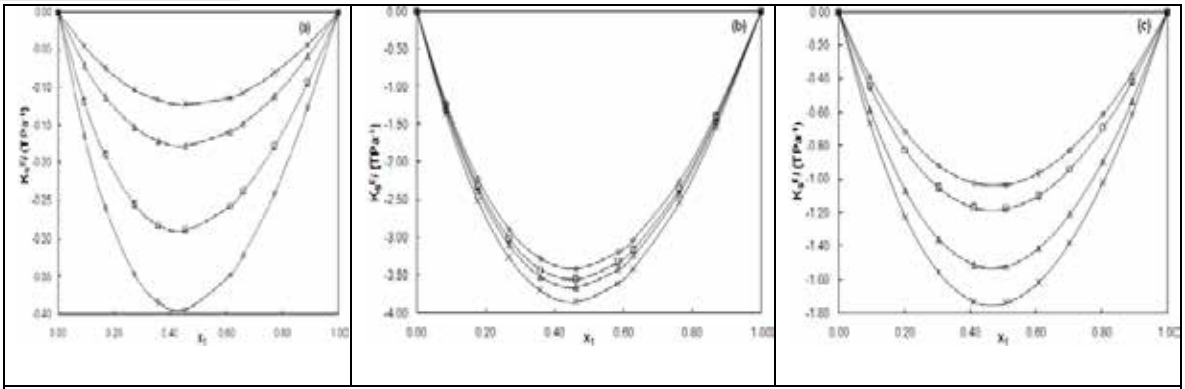

Figure 1. Plot of the excess isentropic compressibility, K_s^E, versus mole fraction, x_1, for binary liquid mixtures of diethyl carbonate with (a) nitrobenzene (b) chlorobenzene and (c) ethylbenzene at temperatures: ◊, 293.15 K; □, 303.15 K; Δ, 313.15 K; and ×, 323.15K.

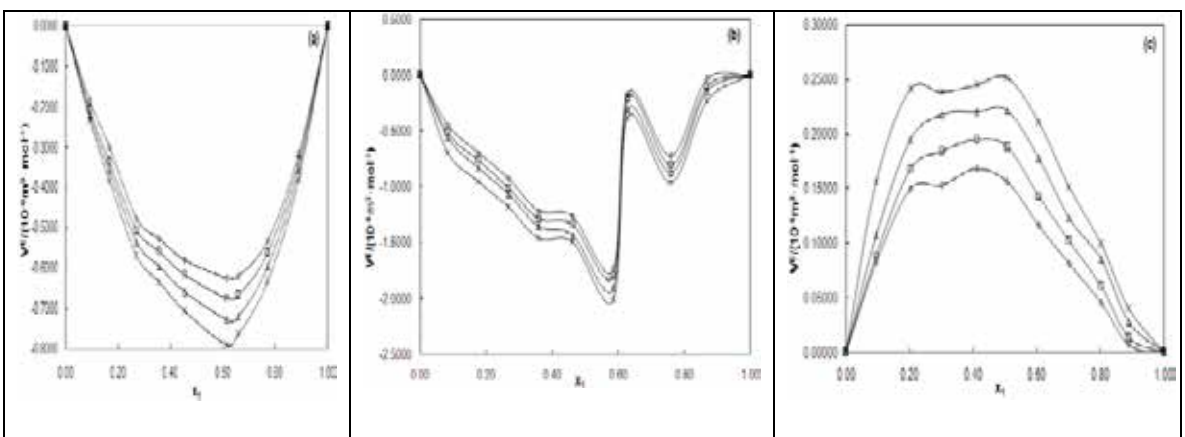

Figure 2. Plot of the excess molar volume, V^E, versus mole fraction, x_1, for binary liquid mixtures of diethyl carbonate with (a) nitrobenzene (b) chlorobenzene and (c) ethylbenzene at temperatures: ◊, 293.15 K; □, 303.15 K; Δ, 313.15 K; and ×, 323.15K.

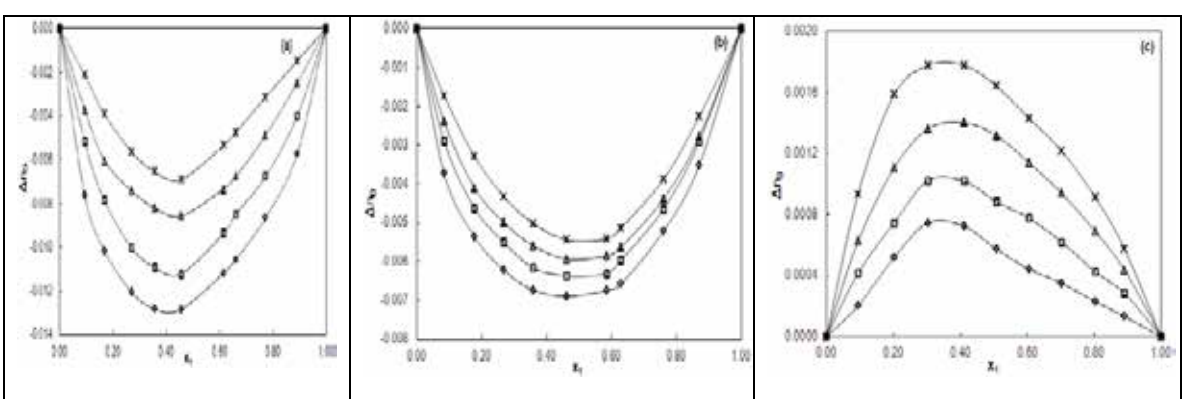

Figure 3. Plot of the refractive index deviations, Δn_D, versus mole fraction, x_1, for binary liquid mixtures of diethyl carbonate with (a) nitrobenzene (b) chlorobenzene and (c) ethylbenzene at temperatures: ◊, 293.15 K; □, 303.15 K; Δ, 313.15 K; and ×, 323.15K.

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The graphical variations of k_s^E, V_m^E and Δn_D with the mole fraction of diethyl carbonate for the three binary mixtures at T = (293.15, 303.15, 313.15 and 323.15) K are shown in figures 1(a) to 1(c), 2 (a) to 2(c) and 3 (a) to 3(c) respectively. The k_s^E values depend upon the relative strengths of several opposing effects that include (a) structural, (b) chemical and (c) physical contributions [13]. (a) The structural contribution involves the geometric effect allowing the fitting of molecules of two different sizes into each others' structure resulting in negative contribution to k_s^E, (b) The physical contribution consists of dispersion forces or weak dipole-dipole interactions that lead to positive contribution towards k_s^E and (c) Chemical contribution includes specific interactions such as formation of hydrogen bonds, formation of charge transfer complexes and other complex forming interactions including strong dipole-dipole interactions between component molecules result in negative k_s^E values. From figures 1(a to c), the k_s^E values are observed to be negative. In DEC + CB and DEC + EB mixtures as the temperature increases the k_s^E values are observed to be more negative. The more negative k_s^E values in the profiles, followed the trend, DEC + CB > DEC + EB > DEC+ NB. The observed negative k_s^E values for all the three systems under study, indicate that the mixture is less compressible than the corresponding ideal mixture, suggesting that significant interactions occurred between the unlike molecules of the mixture.

The variations of V^E for all of the systems, at different temperatures, are shown in figures 2(a to c). From figure 2(a), the values of V^E are found to be negative over the entire mole fraction range for the system DEC + NB, for DEC + EB (Figure 2(c)) these values are found to be positive whereas these values are found to be negative for the system DEC + CB except at higher mole fraction and at higher

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temperature. From figures 2(a and b) it is observed that as the temperature of the system increases excess molar volumes become less negative, indicating a decrease in interactions between the unlike molecules. The V^E values are observed to be less negative in case of DEC + NB when compared to DEC + CB. It suggests that the interactions are strong in DEC + CB when compared to DEC + NB. This is due to the predominance of physical interactions over chemical interactions between the unlike molecules. In other words, smaller molecules are geometrically fitting into the voids created by the larger molecules among the molecular components of liquid mixtures. Similar interpretation was reported by the researchers in the field [14,15].

The values of Δn_D are found to be negative (figure 3 (a to c)) over the entire mole fraction range for the systems DEC + NB, + CB whereas for DEC+ EB these values are positive. The values are found to be more negative in case of DEC+NB when compared to DEC+CB.The maxima of Δn_D values for the DEC+EB system occurs at 0.3 mole fraction, whereas that for the DEC+NB and DEC+CB systems the minima of Δn_D occurs at 0.4 mole fraction. The strength of interactions in the mixtures follows the order DEC + EB >DEC + CB > DEC + NB.

Conclusion :-

Density, speed of sound and refractive index data are reported for the binary mixtures of DEC + NB, or + CB, or + EB at T = (293.15, 303.15, 313.15 and 323.15) K and at atmospheric pressure. Excess isentropic compressibility, excess molar volume and deviation in refractive index were also studied in all mole fraction and temperature ranges. To obtain an adequate description of thermophysical behaviour of mixtures containing DEC + benzene derivatives these data are useful in fuel industry.

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