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Excess thermodynamic and other allied parameters in the binary mixtures of cresols and azo compounds with benzyl benzoate as common component

J.Nageswara Rao¹, N.Jaya Madhuri¹, J.Glory¹, P.S.Naidu^{2*}, K.Ravindra Prasad¹

¹Department of Physics, S.V.U.P.G.Centre, Kavali-524 201, A.P., (INDIA)

²Department of Physics, Jawahar Bharati Degree and P.G.College, Kavali-524 201, A.P., (INDIA)

E-mail : psnaidujb@yahoo.co.in

ABSTRACT

Ultrasonic velocity, density and viscosity have been measured in six binary mixtures of o-cresol, m-cresol, p-cresol, 1,4 dioxane, aniline and pyridine with benzyl benzoate as common component at 30°C. From the measured data, thermodynamic and other allied parameters have been computed and the intermolecular interactions are estimated in the light of the excess parameters. Also theoretical velocities are evaluated from a knowledge of the five theories FLT, CFT, NOMOTO, VANDAEL and JUNJIE. FLT, CFT, NOMOTO and JUNJIE appear to agree well with the experiment. In the mixtures of o-cresol, weak interactions and m-cresol and p-cresol, strong molecular interactions are suggested. In 1,4 dioxane system, weak interactions and dispersive forces and in the other two systems, strong AB interactions besides dipole-dipole type are suggested.

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KEYWORDS

Binary mixtures;
Cresols;
Benzyl benzoate;
Velocity;
Molecular interactions.

INTRODUCTION

In the recent years, ultrasonic methods have been accepted as an important tool in predicting the molecular interactions in the binary mixtures and these techniques are comparable to other techniques. Though several binary mixtures have been studied, the binary mixtures with atleast one component as cresol or benzyl benzoate or azo compound have been referred^[1-13] owing to the nature of the liquids in our present investigation. In the present investigation, the binary mixtures of the three cresols with benzyl benzoate as common component have been chosen owing to their importance in medicine and chemistry. Benzyl benzoate is used as an anti parasitic insecticide, as a food addi-

tive in artificial flavor, and as a solubilizing agent in the preparation of oily injections. Above all it is a good solvent for various chemical reactions. Cresols are used as disinfectants and deodorizers. Some of them are found in many foods, wood and tobacco smokes. p-cresol attracts the archid bee *Euglossa cyamura* to capture and study the species. m-cresol is used in some insulin solutions. 1,4 dioxane is used as solvent for a variety of liquids and a stabilizer for the solvent trichloro ethane. Pyridine acts as a precursor to agro chemicals and pharmaceuticals and a solvent and a reagent. Aniline is known for its precious nature for all reactions. Ultrasonic velocity, density and viscosity have been measured in the binary mixtures of benzyl benzoate with o-cresol, m-cresol and p-cresol and 1,

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4 dioxane, aniline and pyridine at 30°C. From the thermodynamic and other parameters computed from the measured data, excess parameters have been calculated and the intermolecular interactions have been estimated. Theoretical evaluation of velocities has also been made and CFT, NOMOTO & JUNJIE have been found to be better.

EXPERIMENTAL

The chemicals used in the present investigation are of analar grade/ fine grade. The binary mixtures were prepared by mixing the weighted quantities of the pure liquids. Ultrasonic velocity has been measured using a single crystal interferometer working at 2MHz with an accuracy of $\pm 0.05\%$. Density has been measured employing a double stem capillary type pycnometer with an accuracy of 2 parts in 10^5 . Weights are taken using an electronic single pan balance with an accuracy of ± 0.05 mg. Ostwald viscometer yielding an accuracy of $\pm 0.1\%$ has been employed for viscosity measurements. Temperature is maintained to within ± 0.01 K employing an electronically controlled water bath. All the three measuring devices – interferometer, pycnometer and viscometer are standardized with triply distilled water as reference liquid before carrying out all the measurements in the test liquids.

THEORETICAL

Theoretical velocities have been computed employing the following relations.

$$U_{FLT} = \frac{K}{L_f \rho_{mix}^{1/2}} \quad (1)$$

$$U_{CFT} = \frac{U_{\infty} S_{mix} B_{mix}}{V_T^M} \quad (2)$$

$$U_{NOMOTO} = \left(\frac{R}{V}\right)^3 = \left[\frac{(X_A R_A + X_B R_B)}{(X_A V_A + X_B V_B)}\right]^3 \quad (3)$$

$$U_{VANDAEL} = \frac{1}{\left[(X_A M_A + X_B M_B) \left(\frac{X_A}{M_A U_A^2} + \frac{X_B}{M_B U_B^2}\right)\right]^{1/2}} \quad (4)$$

$$U_{JUNJIE} = \frac{\frac{X_A M_A}{\rho_A} + \frac{X_B M_B}{\rho_B}}{\left[(X_A M_A + X_B M_B) \left(\frac{X_A M_A}{V_A^2 \rho_A} + \frac{X_B M_B}{V_B^2 \rho_B}\right)\right]^{1/2}} \quad (5)$$

Viscosity(η) and Surface tension(σ) in the mixture due to JOUYBAN – ACREE is given by

$$\ln \eta_{JA} = X_1 \ln \eta_1 + X_2 \ln \eta_2 + (X_1 X_2 / T) [A_0 + A_1 (X_1 - X_2) + A_2 (X_1 - X_2)^2] \quad (6)$$

$$\ln \sigma_{JA} = \phi_1 \ln \sigma_1 + \phi_2 \ln \sigma_2 + (\phi_1 \phi_2 / T) [A_0 + A_1 (\phi_1 - \phi_2) + A_2 (\phi_1 - \phi_2)^2] \quad (7)$$

The thermodynamic/acoustic and other related parameters can be computed from the following relations.

$$\text{Adiabatic Compressibility } \beta = \frac{1}{U_{\text{exp}}^2 \rho_{\text{exp}}} \quad (8)$$

$$\text{Internal pressure } \pi = bRT [K\eta/U]^{3/2} \rho^{2/3} / M^{7/6} \quad (9)$$

$$\text{Free volume } V_f = (M_{\text{eff}} U / K \eta)^{3/2} \quad (10)$$

$$\text{Enthalpy } H = \pi V_M \quad (11)$$

$$\text{Activation Energy } G = RT [\ln \eta V_M] \quad (12)$$

The excess parameters employ the following relations in general.

$$A^E = A^{\text{exp}} - A^{\text{ideal}} = [A^{\text{exp}} - (X_1 A_1 + X_2 A_2)] \quad (13)$$

X_1 and X_2 are the mole fractions of the two compounds. For β^E (excess adiabatic compressibility) volume fractions are employed. All these are explained elsewhere⁶¹.

RESULTS AND DISCUSSION

Study in cresol systems of benzyl benzoate

Ultrasonic velocity, density and viscosity have been measured in three binary mixtures of benzyl benzoate with o-, m- and p-cresols over the entire composition range of benzyl benzoate at 30°C and are presented in TABLE 1. Velocities have also been evaluated theoretically with the five standard theories CFT, FLT, NOMOTO, VANDAEL & JUNJIE and are presented in Figure 1 along with their experimental values. From TABLE 1 and Figure 1, it is seen that m-cresol has the lowest velocity while benzoate shows largest velocity. The velocity increases from cresols to benzoate in all the three mixtures. The maximum percentage deviations observed for all the three mixtures with o-cresol, m-cresol and p-cresol are 0.62, -0.91, 0.44, -5.42 and 0.44; -0.68, -1.12, 0.20, -6.18 and 0.17 and 0.60, -

TABLE 1 : Ultrasonic velocity, density and viscosity in the mixtures of cresols

Mole fraction of Benzyl benzoate	Velocity (ms ⁻¹)	Density (kgm ³)	Viscosity (mill.Pa.s)
Benzyl benzoate + o-Cresol			
0.0000	1484.4	1035.19	5.96365
0.1118	1485.1	1051.96	6.37361
0.1775	1486.9	1061.03	7.03346
0.2513	1487.8	1068.02	7.60907
0.3349	1488.1	1073.96	8.00701
0.4303	1491.9	1081.42	8.15400
0.5402	1493.8	1087.75	8.06752
0.6683	1496.0	1095.64	7.95027
0.8192	1501.0	1099.50	7.45858
0.9054	1502.3	1103.38	7.26191
1.0000	1506.0	1119.35	6.53251
Benzyl benzoate + m-Cresol			
0.0000	1464.2	1024.79	10.67127
0.1117	1471.4	1047.46	9.77912
0.1773	1473.3	1053.87	9.46463
0.2511	1479.8	1063.86	9.19167
0.3347	1481.0	1069.68	8.76395
0.4300	1488.9	1078.44	8.57926
0.5400	1492.9	1087.46	8.31459
0.6680	1498.2	1091.83	8.10402
0.8191	1503.8	1100.37	7.86483
0.9053	1504.9	1102.96	7.59263
1.0000	1506.0	1119.35	6.53251
Benzyl benzoate + p-Cresol			
0.0000	1471.2	1025.03	11.19358
0.1132	1478.8	1045.97	10.91278
0.1795	1482.8	1055.31	10.77452
0.2539	1484.4	1063.49	10.54531
0.3379	1487.5	1071.05	9.99765
0.4336	1492.7	1078.66	9.14847
0.5436	1494.6	1086.62	8.3735
0.6712	1498.2	1092.59	7.96253
0.8212	1501.1	1100.88	7.49263
0.9065	1502.8	1103.60	7.35462
1.0000	1506.0	1119.35	6.53251

0.36, 0.18, -9.56 and 0.17 in FLT, CFT, NOMOTO, VANDAEL & JUNJIE respectively. It may be envisaged that all the four theories (except VANDEAL) have a sharp edge with deviations less than unity.

The thermodynamic, acoustic and other related pa-

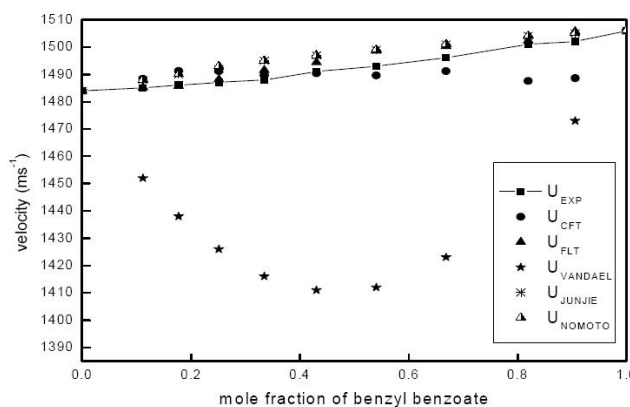


Figure 1 : Variation of theoretical velocities with mole fraction of benzyl benzoate at 30°C in the mixture : Benzyl benzoate + o-cresol system

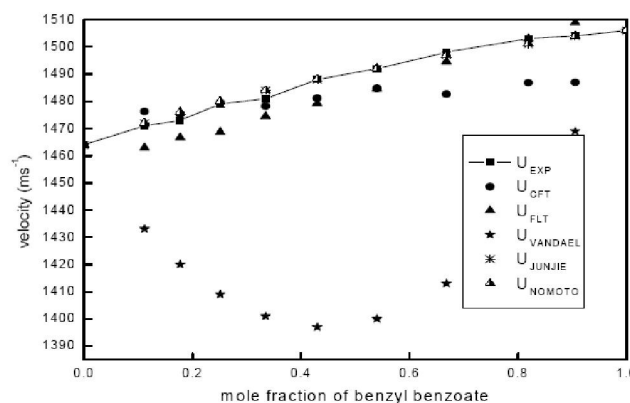


Figure 2 : Variation of theoretical velocities with mole fraction of benzyl benzoate at 30°C in the mixture : Benzyl benzoate + m-cresol system

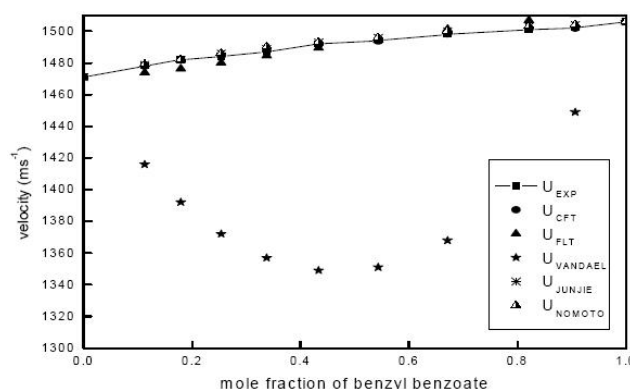


Figure 3 : Variation of theoretical velocities with mole fraction of benzyl benzoate at 30°C in the mixture : Benzyl benzoate + p-cresol system

rameters computed from the standard relations are presented in TABLE 2. In all the three cresol systems, adiabatic compressibility (β), internal pressure (π), free length (L_f) and enthalpy (H) decrease with the concentration of benzyl benzoate while molar volume (V_M) and activation energy (G) show increase with the increase

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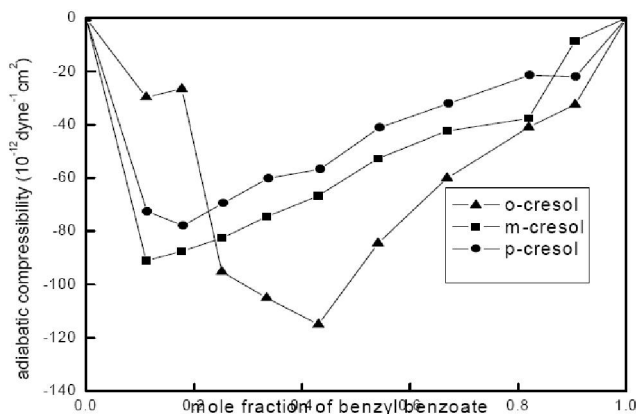


Figure 4 : Variation of excess adiabatic compressibility with mole fraction of benzyl benzoate at 30°C in the mixture : Benzyl benzoate + cresol systems

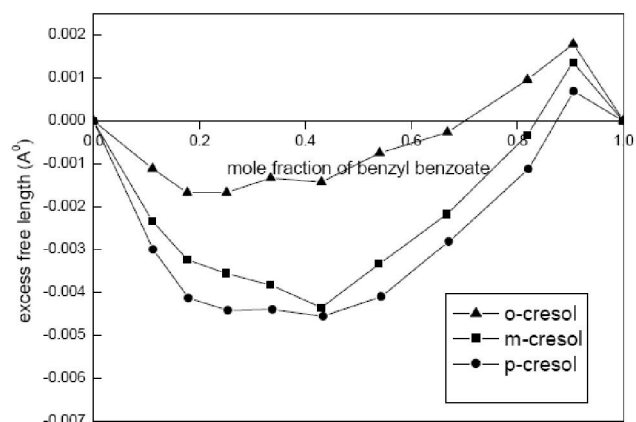


Figure 5 : Variation of excess free length with mole fraction of benzyl benzoate at 30°C in the mixture : Benzyl benzoate + cresol systems

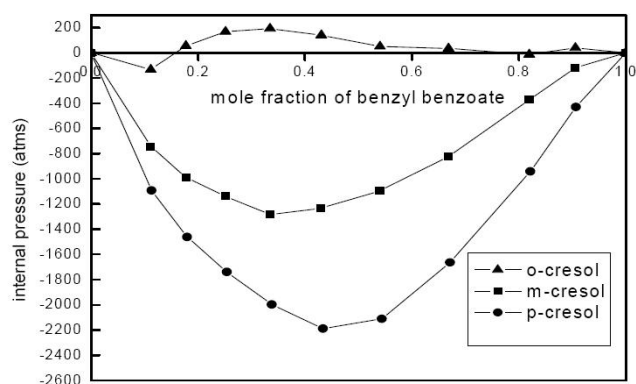


Figure 6 Variation of excess internal pressure with mole fraction of benzyl benzoate at 30°C in the mixture : Benzyl benzoate + cresol systems

of the concentration.

In order to estimate the molecular interactions in the binary system, it is desirable to have the variation of excess parameters with concentration of benzoate. Hence all the excess parameters are computed for all

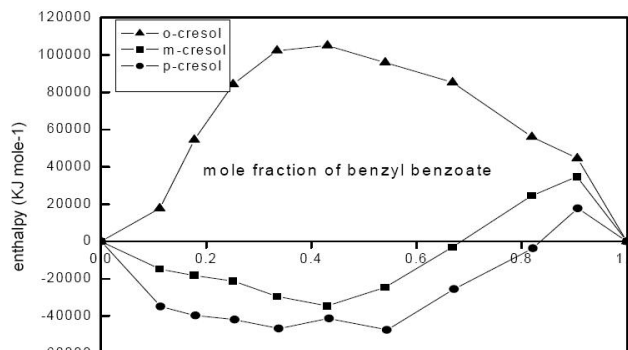


Figure 7 : Variation of excess enthalpy with mole fraction of benzyl benzoate at 30°C in the mixture : Benzyl benzoate + cresol systems

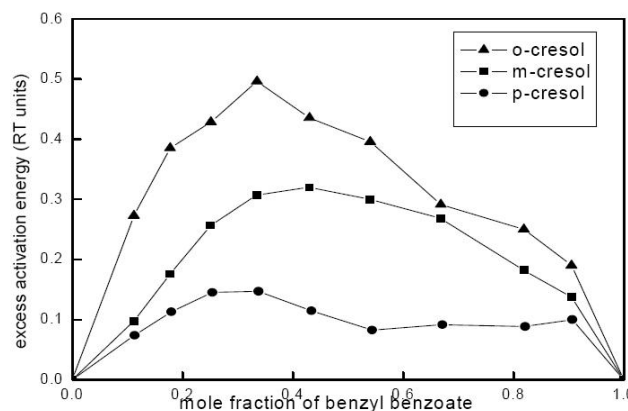


Figure 8 : Variation of excess activation energy with mole fraction of benzyl benzoate at 30°C in the mixture : Benzyl benzoate + cresol systems

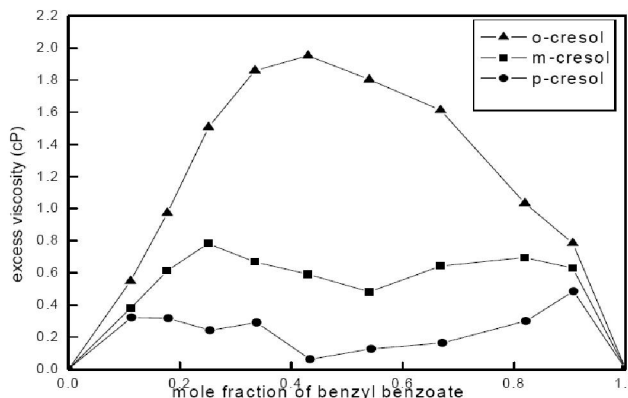


Figure 9 : Variation of excess viscosity with mole fraction of benzyl benzoate at 30°C in the mixture : Benzyl benzoate + cresol systems

the systems and are presented in Figures 2-8. From Figure 2, it is noticed that β^E is negative throughout the concentration range. For o-cresol, it is more negative at high concentrations. L_f^E is also negative – more negative for p-cresol system with a minimum at $\sim 0.4m$. Figure 4 reveals that o-cresol shows slightly positive π^E while it is negative for the other two m-cresol and p-

TABLE 2 : Thermodynamic parameters in the mixtures of cresols

Mole fraction of Benzyl benzoate	Adiabatic Compressibility ($10^{-12} \text{N}^{-1} \text{cm}^2$)	Internal pressure (atms)	Molar volume (ml.mole^{-1})	Free length (Å^0)	Enthalpy (KJ.mole^{-1})	Activation Energy (RT units)
o-Cresol						
0.0000	4.38	7960	104.46	0.4178	832	6.43
0.1118	4.31	7380	113.86	0.41425	840	6.59
0.1775	4.27	7306	119.34	0.41226	872	6.73
0.2513	4.24	7124	125.75	0.41065	896	6.86
0.3349	4.21	6814	133.16	0.40918	907	6.97
0.4303	4.16	6381	141.42	0.407	902	7.05
0.5402	4.13	5854	151.12	0.40529	885	7.11
0.6683	4.08	5326	162.20	0.40297	864	7.16
0.8192	4.04	4676	175.92	0.40092	823	7.18
0.9054	4.02	4385	183.44	0.39987	804	7.19
1.0000	3.94	3967	189.62	0.39602	752	7.12
m-Cresol						
0	4.55	10649	105.52	0.42572	1124	7.03
0.1117	4.41	9159	114.34	0.41901	1047	7.02
0.1773	4.37	8475	120.13	0.41721	1018	7.04
0.2511	4.3	7832	126.22	0.4137	989	7.06
0.3347	4.26	7128	133.67	0.41194	953	7.07
0.43	4.19	6542	141.79	0.40838	928	7.1
0.54	4.13	5945	151.14	0.40558	898	7.14
0.668	4.08	5362	162.74	0.40307	873	7.18
0.8191	4.02	4802	175.77	0.40027	844	7.23
0.9053	4.01	4480	183.5	0.39952	822	7.24
1	3.94	3967	189.62	0.39602	752	7.12
p-Cresol						
0	4.51	13819	85.96	0.42362	1188	6.87
0.1132	4.38	11612	97.67	0.4175	1134	6.97
0.1795	4.32	10589	104.6	0.41453	1108	7.03
0.2539	4.27	9579	112.48	0.4122	1078	7.08
0.3379	4.22	8492	121.43	0.40989	1031	7.1
0.4336	4.17	7360	131.59	0.4073	968	7.09
0.5436	4.13	6353	143.18	0.40528	910	7.09
0.6712	4.08	5544	156.91	0.40292	870	7.13
0.8212	4.03	4788	172.63	0.40063	827	7.17
0.9065	4.02	4459	181.81	0.39996	811	7.2
1	3.94	3967	189.62	0.39602	752	7.12

cresol systems. H^E also shows similar variation (having maximum at $\sim 0.5m$ for o-cresols and minimum at $\sim 0.5m$ for the other two). From these excess parameters, it may be said that in o-cresol system weak interactions and dispersive forces predominate while in the other two m- and p-cresol systems, strong interactions be-

tween the constituent unlike molecules (AB interactions) besides dipole-dipole interactions are predominant. It can also be mentioned that the strength of interactions follow the order: o-cresol < m-cresol < p-cresol. No complex formation is suggested in any system.

From the variation of G^E and η^E (excess viscosity)

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TABLE 3 : Ultrasonic velocity, density and viscosity of mixtures dioxane, aniline and pyridine

Mole fraction of Benzyl benzoate	Velocity (ms ⁻¹)	Density (kgm ³)	Viscosity (mill.Pa.s)
Benzyl benzoate + 1,4 diaxane			
0	1320.8	1020.39	1.01902
0.094	1358.5	1044.76	1.4822
0.151	1376.2	1052.99	1.71337
0.2166	1397.4	1061.62	1.91222
0.2932	1413.8	1070.03	2.4073
0.3836	1432.1	1078.84	3.01819
0.4919	1447.2	1086.43	3.51223
0.624	1466.4	1093.81	4.13747
0.7887	1480.8	1100.17	4.77321
0.8874	1487.8	1104.41	5.61315
1	1506	1119.35	6.53251
Benzyl benzoate + aniline			
0	1621.7	1011.88	3.08451
0.1086	1580	1028.76	3.46384
0.1727	1564.2	1042.84	3.76986
0.2452	1555.3	1051.85	3.99518
0.3276	1549.4	1061.4	4.41272
0.4222	1542	1072.25	4.79811
0.532	1532.2	1081.11	5.19408
0.6609	1520.4	1090.07	5.46524
0.8143	1512.9	1099.58	5.89675
0.9025	1507.3	1107.65	6.40452
1	1506	1119.35	6.53251
Benzyl benzoate + pyridine			
0	1397.6	970.68	0.78723
0.0974	1415.5	1001.85	1.10826
0.156	1421.1	1012.18	1.22128
0.2233	1432.8	1024.71	1.42958
0.3014	1443.2	1039.56	1.73434
0.3928	1455.3	1059.17	2.30259
0.5016	1467.4	1069.89	3.02915
0.6331	1476.9	1083.03	3.54381
0.7787	1485.8	1092.49	4.32895
0.8913	1493.9	1098.46	5.12677
1	1506	1119.35	6.53251

which is positive throughout in all the three systems, it may be that endothermic type of chemical reaction exists in all the systems and the strength of chemical reaction is in the order o-cresol > m-cresol > p-cresol. Other parameters like relaxation strength, relaxation time and classical absorption are also computed and presented

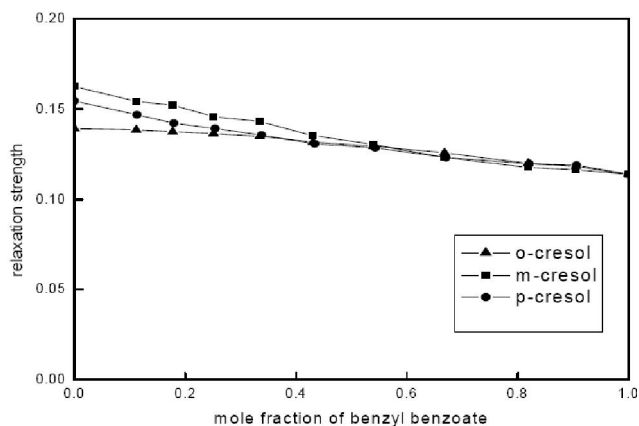


Figure 10 : Variation of relaxation strength with mole fraction of benzyl benzoate at 30°C in the mixture : Benzyl benzoate + cresol systems

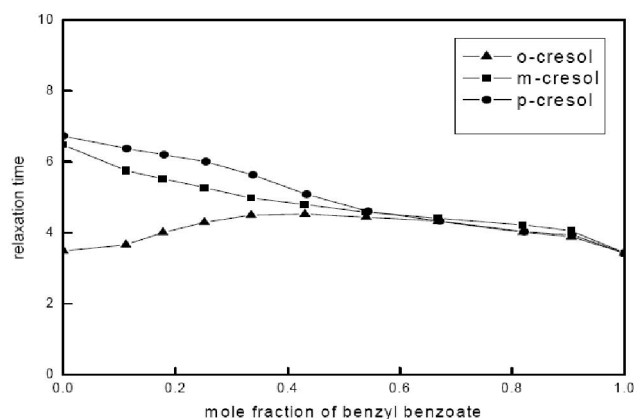


Figure 11 : Variation of relaxation time with mole fraction of benzyl benzoate at 30°C in the mixture : Benzyl benzoate + cresol systems

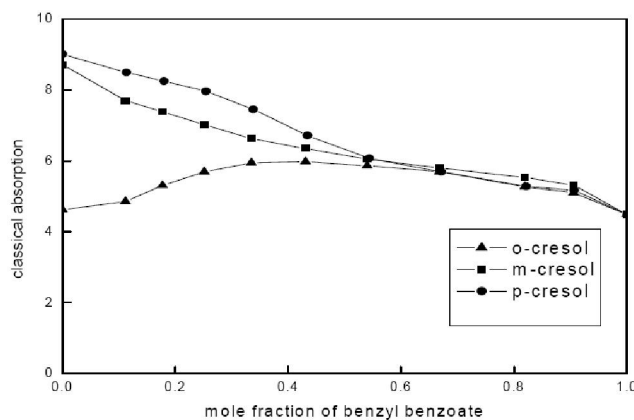


Figure 12 : Variation of absorption coefficient with mole fraction of benzyl benzoate at 30°C in the mixture : Benzyl benzoate + cresol systems

in Figures 9-11. Classical absorption and relaxation strength show decreasing trend with the addition of benzoate – which results in the formation of aggregates of solvent molecules around the solvent due to which

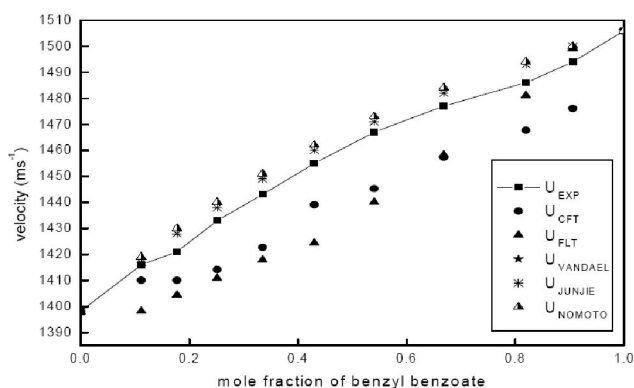


Figure 13 : Variation of theoretical velocities with mole fraction of benzyl benzoate at 30°C in the mixture: Benzyl benzoate + pyridine

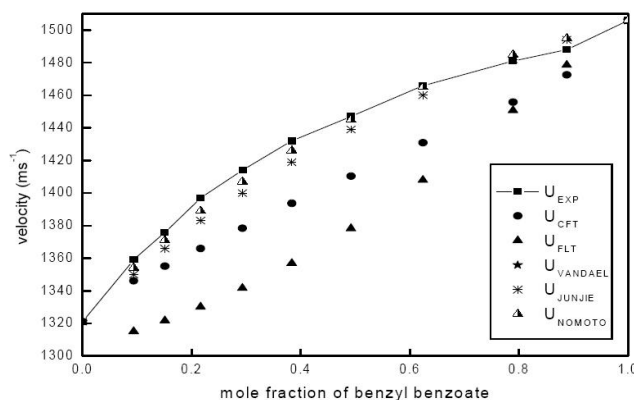


Figure 14 : Variation of theoretical velocities with mole fraction of benzyl benzoate at 30°C in the mixture : Benzyl benzoate + 1,4 dioxane

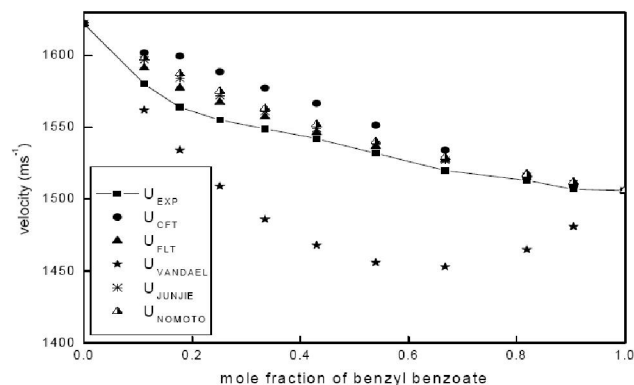


Figure 15 : Variation of theoretical velocities with mole fraction of benzyl benzoate at 30°C in the mixture : Benzyl benzoate + aniline system

structural arrangement is affected in the system. The behavior of absorption and relaxation time also indicate similar type of reactions suggested by excess parameters.

Redlich-Kister polynomial ($A^E = x_1x_2[A_0 + A_1(x_1 - x_2) + A_2(x_1 - x_2)^2 + A_3(x_1 - x_2)^3]$) of 3rd order is fitted to the excess parameters and the constants A_0, A_1, A_2 & A_3

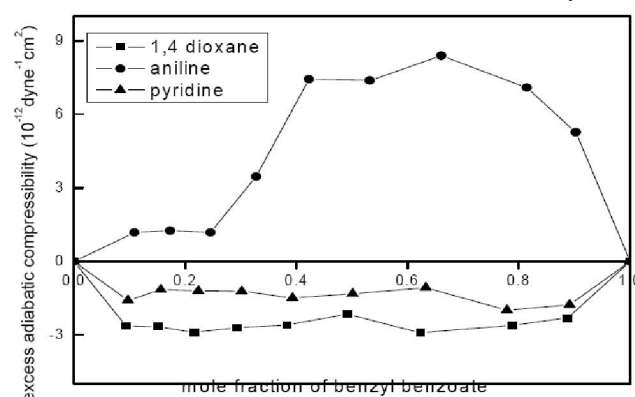


Figure 16 : Variation of excess adiabatic compressibility with mole fraction of benzyl benzoate at 30°C in the second type of mixtures

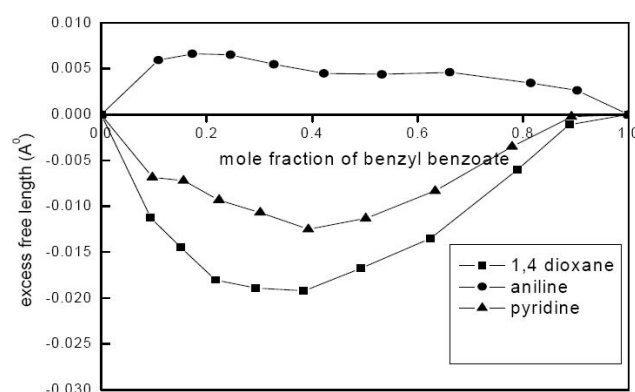


Figure 17 : Variation of excess free length with mole fraction of benzyl benzoate at 30°C in the second type of mixtures.

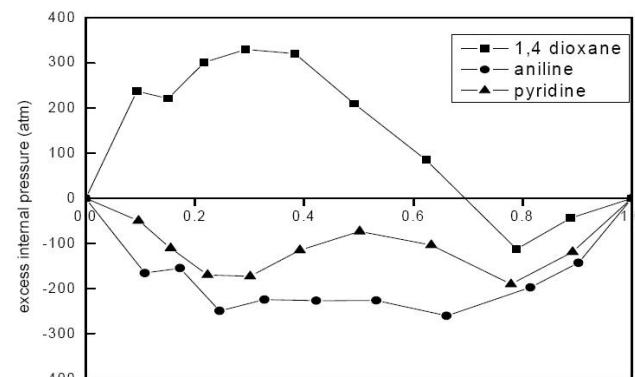


Figure 18 : Variation of excess internal pressure with mole fraction of benzyl benzoate at 30°C in the second type of mixtures

are presented in TABLE 4.

Study in systems of benzyl benzoate with 1,4 dioxane, aniline and pyridine

Ultrasonic velocity, density and viscosity have been measured in the three binary mixtures of the type II (with aromatic azo compounds and dioxane) at 30°C and are presented in TABLE 2. Velocities have also

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TABLE 4 : Thermodynamic parameters in mixtures of dioxane, aniline and pyridine

Mole fraction of Benzyl benzoate	Adiabatic Compressibility ($10^{-12} \text{ N}^{-1} \text{ cm}^2$)	Internal pressure (atms)	Molar volume (ml.mole^{-1})	Free length (A^0)	Enthalpy (KJ.mole^{-1})	Activation Energy (RT units)
BB+1,4 dioxane						
0	5.62	4387	86.35	0.47293	379	4.48
0.094	5.19	4584	95.5	0.45442	438	4.95
0.151	5.01	4545	101.48	0.44683	461	5.16
0.2166	4.82	4397	108.32	0.43824	476	5.33
0.2932	4.68	4494	116.36	0.43147	523	5.64
0.3836	4.52	4546	125.81	0.4242	572	5.94
0.4919	4.39	4390	137.31	0.41831	603	6.18
0.624	4.25	4210	151.37	0.41143	637	6.44
0.7887	4.15	3943	169.08	0.40625	667	6.69
0.8874	4.09	3970	179.53	0.40358	713	6.92
1	3.94	3967	189.62	0.39602	752	7.12
BB+aniline						
0	3.76	6421	92.04	0.3868	591	5.65
0.1086	3.89	5989	103.1	0.39374	617	5.88
0.1727	3.92	5843	109.03	0.39502	637	6.02
0.2452	3.93	5570	116.31	0.39557	648	6.14
0.3276	3.92	5393	124.51	0.39531	671	6.31
0.4222	3.92	5159	133.76	0.39519	690	6.46
0.532	3.94	4890	144.76	0.39608	708	6.62
0.6609	3.96	4539	157.66	0.3975	716	6.76
0.8143	3.97	4226	172.91	0.39776	731	6.93
0.9025	3.97	4164	181.14	0.39776	754	7.06
1	3.94	3967	189.62	0.39602	752	7.12
BB+pyridine						
0	5.27	4112	81.49	0.45826	335	4.16
0.0974	4.98	4148	91.89	0.44536	381	4.62
0.156	4.89	3979	98.67	0.44133	393	4.79
0.2233	4.75	3910	106.21	0.43505	415	5.02
0.3014	4.62	3896	114.69	0.42881	447	5.29
0.3928	4.46	4041	124.06	0.42129	501	5.65
0.5016	4.34	4113	136.36	0.41573	561	6.02
0.6331	4.23	3917	150.87	0.41054	591	6.28
0.7787	4.15	3809	167.3	0.4063	637	6.59
0.8913	4.08	3784	180.04	0.40301	681	6.83
1	3.94	3967	189.62	0.39602	752	7.12

been evaluated theoretically using five theories FLT, CFT, NOMOTO, VANDEAL and JUNJIE and have been shown in Figure 12 along with the experimental values. As followed from the figure, the velocity increases with the concentration of benzoate in the mixtures with pyridine and 1, 4 dioxane but decreases in aniline mixture.

The maximum percentage deviations are -5.26, -2.68, -0.60, -13.98 and -1.06 in 1, 4 dioxane system; -2.13, -1.51, 0.60, -13.63 and 0.48 in pyridine system and 2.26, 0.84, 1.42, -4.99 and 1.28 in aniline system in FLT, CFT, NOMOTO, VANDEAL and JUNJIE respectively. Maximum deviations are observed in

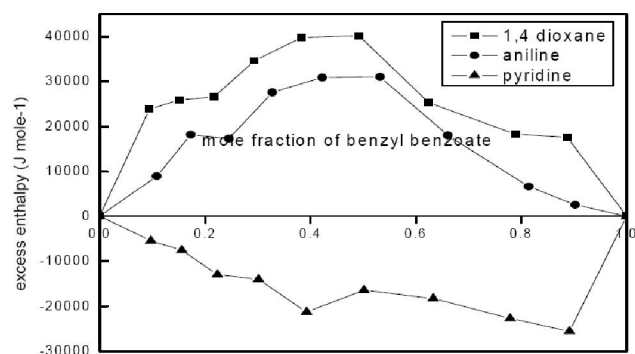


Figure 19 : Variation of excess enthalpy with mole fraction of benzyl benzoate at 30°C in the second type of mixtures

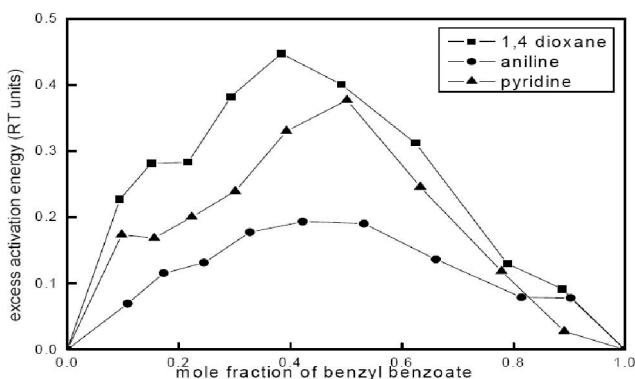


Figure 20 : Variation of excess activation energy with mole fraction of benzyl benzoate at 30°C in the second type of mixtures

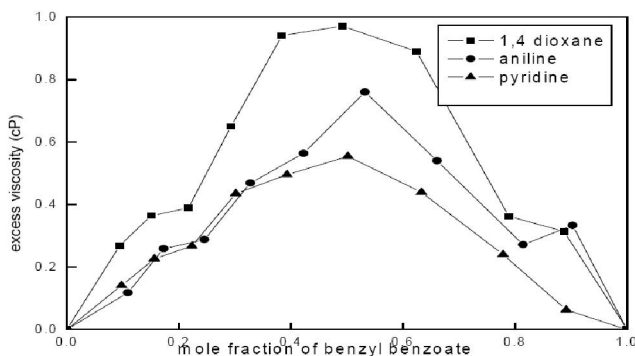


Figure 21 : Variation of excess viscosity with mole fraction of benzyl benzoate at 30°C in the second type of mixtures

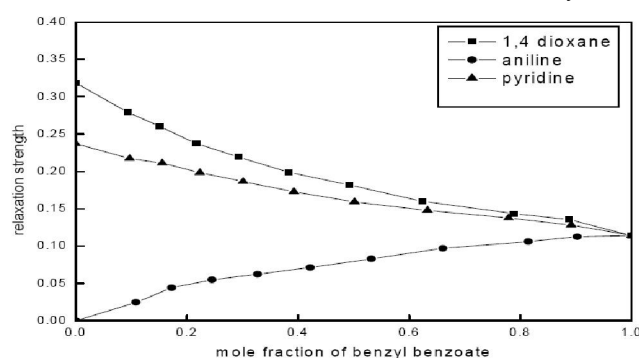


Figure 22 : Variation of relaxation strength with mole fraction of benzyl benzoate at 30°C in the second type of mixtures

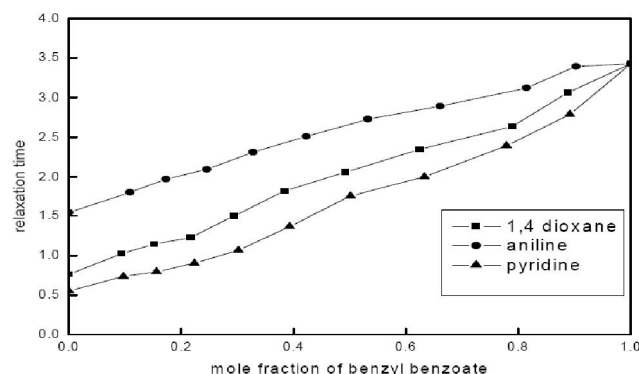


Figure 23 : Variation of relaxation time with mole fraction of benzyl benzoate at 30°C in the second type of mixtures

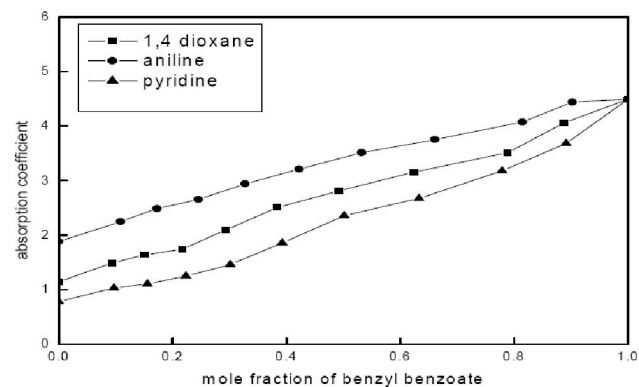


Figure 24 : Variation of absorption coefficient with mole fraction of benzyl benzoate at 30°C in the second type of mixtures

TABLE 5 : Jouyban-Acree model constants

Name of the System	A ₀	A ₁	A ₂	PMD	A ₀	A ₁	A ₂	PMD*
	(Surface Tension correlation)				(Viscosity correlation)			
Benzyl benzoate + o-cresol	-2.8	-19.68	-55.32	-0.7	340.4	58.2	-65.9	-3.69
Benzyl benzoate + m-cresol	2.49	-15.3	-38.12	-0.735	1.89	241.25	194.9	2.45
Benzyl benzoate + p-cresol	6.14	-20.79	-50.47	-0.617	28.44	11.1	230.5	-2.74
Benzyl benzoate + 1,4 dioxane	17.03	-29.78	-88.72	1.21	351.9	-293.7	53.2	7.54
Benzyl benzoate + aniline	-15.58	10.15	59.34	-0.416	134.3	-0.7	-3.4	2.96
Benzyl benzoate + pyridine	0.58	-22.32	-88.42	1.215	251.6	-204.8	-149.2	-7.58

PMD* : Percentage maximum deviation

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TABLE 6 : Redlich – Kister parameters A_0, A_1, A_2 along with standard deviation σ

Name of the system	$\beta^E (10^{11} \text{ N}^{-1} \text{ m}^2)$					$\pi^E (\text{atm})$					$H^E (\text{kJ mole}^{-1})$					$G^E (\text{RT units})$				
	A_0	A_1	A_2	A_3	σ	A_0	A_1	A_2	A_3	σ	A_0	A_1	A_2	A_3	σ	A_0	A_1	A_2	A_3	σ
Benzyl benzoate + o-cresol	-391	354	179	-727	91	568	-2218	-1488	5156	318	421	-263	-127	737	31	1.63	-1.37	1.28	1.60	0.09
Benzyl benzoate + m-cresol	-222	34	-486	741	44	-4693	2594	211	1905	104	-118	101	363	359	16	1.26	-0.56	0.02	1.47	0.06
Benzyl benzoate + p-cresol	-160	189	-501	201	36	-8622	2061	1875	1038	283	-181	461	46	469	14	0.39	-0.69	0.76	1.48	08

TABLE 7 : Redlich – Kister parameters A_0, A_1, A_2 along with standard deviation σ

Name of the system	$\beta^E (10^{11} \text{ N}^{-1} \text{ m}^2)$					$\pi^E (\text{atm})$					$H^E (\text{kJ mole}^{-1})$					$G^E (\text{RT units})$				
	A_0	A_1	A_2	A_3	σ	A_0	A_1	A_2	A_3	σ	A_0	A_1	A_2	A_3	σ	A_0	A_1	A_2	A_3	σ
Benzyl benzoate + 1,4 dioxane	-9	-3	-26	11	8	705	-1614	-153	-473	483	-42	1282	1490	-4865	632	1.49	-0.62	0.15	-0.75	0.26
Benzyl benzoate+ aniline	27	33	9	-5	5	-938	-166	-104	309	166	115	-59	-85	31	17	0.71	-0.36	0.01	0.59	0.09
Benzyl benzoate + pyridine	-4	-5	-20	4	2	-1689	-3169	1233	5072	1307	-63	14	-152	-243	13	1.26	0.15	-0.56	-1.74	0.25

VANDEAL while CFT, NOMOTO and JUNJIE appear to have an edge. The variation of all the thermodynamic and other related parameters (TABLE 3) is as follows. β and π decrease with concentration in dioxane and pyridine systems. L_f increases for aniline system while for the other two it decreases. In all the systems, the other parameters V_m , H and G show increasing trend with the concentration of benzoate. As usual, the excess parameters which reveal the nature of molecular interactions have been computed and are delineated in Figure 15–21. β^E is positive for aniline with maximum at $\sim 0.6\text{m}$ while negative for both pyridine and 1,4 dioxane with a flat minimum. L_f^E is positive for aniline and negative for both pyridine and 1,4 dioxane. From Figure 20, it is seen that π^E is positive for 1, 4 dioxane upto 0.7m and negative afterwards while it is totally negative for both pyridine and aniline with a flat minimum at 0.3 to 0.6m . H^E is negative for pyridine and positive for 1, 4 dioxane and aniline. G^E and η^E are all positive throughout for the three systems.

From the variation of majority parameters, in 1, 4 dioxane, weak interactions and dispersive forces and in the other two system, strong AB interactions besides dipole-dipole type interactions are suggested. The order of the strength of interactions is as follows. Dioxane < pyridine < aniline. Endothermic type of chemical reaction is suggested in all the three systems, being stronger in 1, 4 dioxane system.

The excess parameters have been fitted to Redlich-Kister polynomial of 3rd order are presented in TABLE 6. Jouyban-Acree model is successfully applied to correlate viscosity and surface tension with concentration

and the model parameters are displayed in TABLE 5.

Also an analysis of variation of the parameters relaxation strength, relaxation time and classical absorption as presented in Figure 22–24 shows that relaxation strength increases in aniline system while in the other two mixtures, it decreases. Relaxation time and absorption coefficient- both increase with concentration in all the three system studied. Similar type of interactions as suggested by earlier parameters are indicated from these parameters α , τ and absorption.

At this juncture, the behaviour of cresol systems and azo compounds in other liquids and benzyl benzoate in other liquids is compared. In the mixtures of DMSO + cresols and DMSO + p-chlorophenol, theoretical evaluation of velocities is attempted. CFT and NOMOTO agree well with the experiment. In the binary systems of o-cresol + ethyl acetate and iso amyl acetate, through ultrasonic velocity measurements, interactions are studied besides kinetic rates and free energy. Thirumaran and George^[6] in the binary systems of cresols with NN' dimethyl formamide, have estimated the molecular interactions in the light of excess parameters. In the mixtures of NN' Diethyl acetamide + o-cresol, m-cresol and o-chlorophenol at different temperatures, V^E values are positive, η^E values are positive and K_s^E values are all negative. And no strong specific interactions are suggested. Shahla Praveen et al.^[4] have been shown that molecular interactions in the mixtures of tetra hydrofuran + methanol, o-cresol vary significantly from the behavior of excess parameters. π^E and H^E are negative for benzyl benzoate + dichloro methane and isobutanol^[9], suggesting strong AB interactions.

In the mixtures of alcohols with benzyl benzoate^[10], from negative π^E and H^E strong AB interactions are suggested. Similarly in the mixtures of benzyl benzoate with aromatic alkanes, substituted benzenes^[11] acetones and ketones^[12], DMSO^[13], CS₂ and diethyl ether^[14], acetophenone and DMF^[15], and benzonitrile, acetonitrile^[16], the authors have reported various molecular interactions and the nature of chemical reactions based on the variation of excess parameters. In the binary mixtures of acetonitrile with ethanol and methanol^[17], β^E is observed to be negative. Peculiar behavior in π and V_f is observed in the ternary mixture: 1 butanol + pyridine + benzene^[18]. In the system of β pinene with ethanol and propanol, H^E and V_f^E yield specific interactions^[19]. In the mixtures of NN DMF with toluene and methyl benzoate, V_m^E and η^E behave interestingly^[20].

A comparison of our results and findings with those of the above workers yields good agreement with respect to molecular interactions.

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REFERENCES

- [1] T.Satyanarayana Rao, N.Veeraiah, C.Rambabu; Indian J.Pure.Appl.Phys., **40**, 850 (2002).
- [2] Madhu Rastogi, Ashees Awasthi, Manisha Gupta, J.P.Shukla; Indian J.Pure.Appl.Phys., **40**, 256 (2002).
- [3] R.Usha Rani, J.Siva Pragasam; E.J.Chem., **6**, 1150 (2009).
- [4] Shahla Praveena, Divya Shukla, K.P.Shasi Singh, Manisha Gupta, J.P.Shukla; Applied Acoustics, **70**, 507 (2009).
- [5] V.A.Thabana, Sangeetha Agarwal, Kalidoss; Physics and Chemistry of Liquids, **40**,39 (2002).
- [6] S.Thirumaran, Deepesh George; ARPN Journal of Engineering and Applied Sciences, **4**, 1 (2009).
- [7] V.Ranganayukulu, S.Venkateswarlu, C.Srinivasulu Reddy, D.Linga Reddy; Physics and Chemistry of Liquids, **44**, 269 (2006).
- [8] N.Santhi, P.L.Sabarathinum, M.Emaya Varamban, C.Gopi, C.Manivannan; E.J.Chem., **7**, 648 (2010).
- [9] J.Siva Sankar, M.Geetha Lakshmi, P.S.Naidu, K.Ravindra Prasad; J.Pure Appl. Ultrason., **29**, 82 (2007).
- [10] M.Geetha Lakshmi, P.S.Naidu, K.Ravindra Prasad; J.Pure Appl.Ultrason., **30**, 18 (2008).
- [11] P.Mallikarjuna, N.Jaya Madhuri, K.Ravindra Prasad; J.Pure Appl.Ultrason., **32**, 59 (2010).
- [12] N.Jaya Madhuri, P.S.Naidu, J.Glory, K.Ravindra Prasad; E.J.Chem., **8**, 457 (2011).
- [13] N.Jaya Madhuri, J.Glory, P.S.Naidu, K.Ravindra Prasad; Proceedings of XVIII National Symposium on Ultrasonics (NSU-XVIII) VIT, Vellore, 21-23 Dec. (2009).
- [14] N.Jaya Madhuri, P.S.Naidu, K.Ravindra Prasad; Paper Presented at National seminar on Material science, Vidyanagar, July (2009).
- [15] N.Jaya Madhuri, J.Glory, P.S.Naidu, K.Ravindra Prasad; J.Pure Appl.Ultrason., **33**, 63 (2011).
- [16] P.Ramesh, M.Geetha Lakshmi, N.Jaya Madhuri, P.S.Naidu, K.Ravindra Prasad; Invertis Journal of Science and Technology, **4**, 14 (2011).
- [17] N.Prasad, R.Sinha, O.Prakash; Indian J.Pure & Appl.Phys., **14**, 676 (1976).
- [18] G.Arul, Palaniappan; Indian J.Pure.Appl.Phys., **43**, 755 (2005).
- [19] M.Elisa Langa Anna, I.Mainer, Juon, Pardo, S.Jose; Urieta.J.Chem.Eng.Data, **50**, 2255 (2005).
- [20] S.Pandari Nath, J.Nikam, Sanjeevan, Karat; J.Chem.Eng.Data, **52**,1219 (2004).