Ultrasonic Investigations of Molecular Interaction in Binary Mixtures of Benzyl Benzoate with Acetonitrile and Benzonitrile

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Abstract: Ultrasonic velocity, density and viscosity have been measured in the binary mixtures of benzyl benzoate with acetonitrile, benzonitrile at three temperatures 30, 40 and 50 ^{0}C. From the experimental data, thermodynamic parameters like adiabatic compressibility, internal pressure, enthalpy, activation energy *etc*., were computed and the molecular interactions were predicted based on the variation of excess parameters in the mixture. Also theoretical evaluation of velocities was made employing the standard theories. CFT and NOMOTO were found to have an edge. All the three mixtures have shown out strong intermolecular interactions between the unlike molecules and endothermic type of chemical reaction.

Introduction

The work on medicinally used chemical compounds requires the attention of the society in all aspects including ultrasonic behaviour. Practically, ultrasonic studies are of immense use to study the molecular interactions when these compounds are in binary mixture form with some other liquids - protic /aprotic /polar /nonpolar *etc*. Benzyl benzoate is a carboxylate ester which is used as an insect repellant, a medicine for scabies and also used in oily injections. Behaviour of benzyl benzoate in many liquids such as aliphatic alkanes, aromatic alkanes, aliphatic alcohols, substituted benzenes, acetates, ketones and DMSO (super solvent)[1-4] has been thoroughly studies ultrasonically.

In the present investigation, it is aimed at a detailed study of the binary mixture of benzyl benzoate with two nitriles - acetonitrile and benzonitrile at three temperatures 30, 40 and 50 ^{0}C. From the experimentally measured data of velocity, density and viscosity, thermodynamic and other related parameters like adiabatic compressibility, internal pressure,

activation energy *etc*., are computed and in terms of their excess parameters, the nature of molecular interactions is predicted in the binary mixtures. Also an evaluation of velocities using five theories is attempted. CFT, NOMOTO and JUNJIE have shown an edge.

Experimental

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

Theoretical details

All the thermodynamic and related parameters were computed from the following relations[6-9].

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

$$\text{Internal pressure} \quad \pi = bRT \, [K\eta/U]^{3/2} \, \rho^{2/3} / M_{eff}^{7/6} \tag{2}$$

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

$$\text{Enthalpy} \quad H = \pi \, V_M \tag{4}$$

$$\text{Activation Energy} \quad G = RT \, [\ln \eta V_M] \tag{5}$$

All the excess parameters are computed using the general formula

$$A_{excess} = A_{expt} - A_{ideal} = [A_{expt} - (X_1 A_1 + X_2 A_2)] \tag{6}$$

A is any parameter and X_1 and X_2 are the mole fractions of components 1 and 2 respectively.

Results and Discussion

Ultrasonic velocity, density and viscosity have been measured in the binary systems of benzyl benzoate with the liquids - acetonitrile, benzonitrile at three temperatures 30, 40 and 50 ^{0}C over the entire composition range. Using the standard relations (appended) explained elsewhere, thermodynamic and other allied parameters like adiabatic compressibility, free length, internal pressure, enthalpy, activation energy *etc*., have been computed and in terms of their excess parameters, molecular interactions have been predicted / estimated. Detailed presentation of results, analysis and interpretation are presented for all the three binary mixtures separately and a comparison is made at the end. Also velocities have been evaluated theoretically employing the five theories - FLT, CFT, NOMOTO, VANDAEL & JUNJIE, the details of the theories and method of calculation are given elsewhere[10].

Benzyl benzoate + acetonitrile

Experimentally measured velocity, density and viscosity data as a function of the mole fraction of benzyl benzoate at three different temperatures 30, 40 and 50 ^{0}C in the binary mixture: benzyl benzoate + acetonitrile have been presented in Table 1. It can be observed that

velocity increases from acetonitrile to benzoate and velocity decreases with temperature at all concentrations. Velocities have also been evaluated theoretically employing the five theories - FLT, CFT, NOMOTO, VANDAEL & JUNJIE. On comparing them with the experimental velocities, the maximum % deviations at 30 ^{0}C noticed were -9.02, -3.49, 1.44, -24.60 and 1.04 respectively. From this one infers that CFT, JUNJIE and NOMOTO agree well with the experiment while VANDAEL shows larger deviations with temperature deviations decrease.

Table 1. Ultrasonic velocities, densities and viscosities for the system benzyl benzoate in benzyl benzoate + acetonitrile

Mole fraction of Benzyl benzoate	Velocity, ms^{-1}	Density, k gm^{-3}	Viscosity, milli Pa.s
30 ^{0}C			
0.0000	1261.9	773.01	0.36542
0.0272	1284.0	828.61	0.41306
0.0563	1296.0	855.66	0.49139
0.1438	1335.6	907.40	0.72025
0.2013	1360.8	946.05	0.90228
0.2743	1381.2	976.17	1.16901
0.3702	1404.0	1004.20	1.57945
0.4362	1418.0	1026.15	1.87432
0.5563	1440.8	1044.14	2.41858
0.6939	1456.8	1077.72	3.00453
0.8425	1480.0	1097.43	3.78936
1.0000	1506.0	1119.35	6.53251
40 ^{0}C			
0.0000	1226.4	763.31	0.32902
0.0272	1254.0	821.46	0.40206
0.0563	1272.0	846.14	0.47239
0.1438	1302.0	900.78	0.67779
0.2013	1326.0	944.54	0.85254
0.2743	1344.0	968.07	1.08209
0.3702	1374.0	995.87	1.42204
0.4362	1392.0	1020.20	1.67381
0.5563	1410.3	1031.84	2.10723
0.6939	1428.0	1046.44	2.68134
0.8425	1449.0	1076.94	3.35617
1.0000	1471.4	1109.77	5.02109
50 ^{0}C			
0.0000	1173.4	751.79	0.30662
0.0272	1212.0	832.23	0.38438
0.0563	1236.0	845.22	0.44867
0.1438	1268.0	899.25	0.63785
0.2013	1293.6	939.11	0.79138
0.2743	1312.0	967.02	1.00003
0.3702	1344.0	997.53	1.26843
0.4362	1362.0	1012.76	1.40347
0.5563	1375.9	1031.65	1.81713
0.6939	1392.0	1050.04	2.27957
0.8425	1414.9	1076.32	2.90921
1.0000	1440.0	1070.90	4.29834

The thermodynamic and other related parameters computed are shown in Table 2. Adiabatic compressibility (β), free length (L_f) and internal pressure (π) decrease with concentration of benzyl benzoate while parameters like enthalpy (H) and activation energy (G) increase. All the parameters decrease with temperature. But for a better understanding of the molecular interactions in the mixture, excess parameters computed are delineated from Figures 1(a) - 1(f). As observed from Figures, β^E and L_f^E are negative through out the concentration at all temperatures, with a minimum around 0.3 m. With rise in temperature, they are more negative (slightly positive at higher concentration β^E at 50 ^{0}C).

Table 2. Various parameters adiabatic compressibility, internal pressure, free volume, freelength, enthalpy and activation energy as a function of mole fraction of benzyl benzoate in benzyl benzoate + acetonitrile

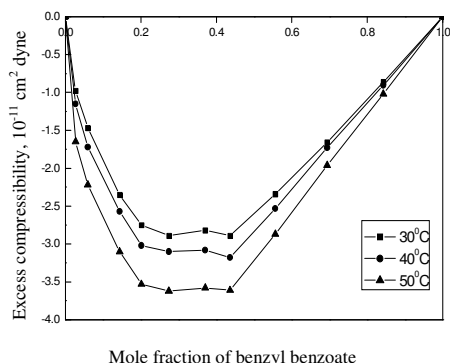| Mole Fraction of BB	Adiabatic Compressibility, 10^{10} N^{-1} m^2	Internal Pressure, atm	Molar Volume, 10^{-3} L.mole^{-1}	Free Length, A^0	Enthalpy, kJ mole^{-1}	Gibb's Energy (RT units)
30 ^{0}C						
0.0000	8.12	5445	53.10	0.5687	289	2.97
0.0272	7.32	5302	55.17	0.5399	293	3.13
0.0563	6.96	5153	59.83	0.5263	308	3.38
0.1438	6.18	4780	72.37	0.4960	346	3.95
0.2013	5.71	4630	79.81	0.4767	369	4.28
0.2743	5.37	4468	90.15	0.4624	403	4.66
0.3702	5.05	4299	104.00	0.4485	447	5.10
0.4362	4.85	4194	112.77	0.4393	473	5.35
0.5563	4.61	3951	130.53	0.4286	516	5.75
0.6939	4.37	3713	148.32	0.4172	551	6.10
0.8425	4.16	3525	168.84	0.4070	0.4070	595
1.0000	3.94	3967	189.62	0.3960	752	752
40 ^{0}C						
0.0000	8.71	5197	53.78	0.5889	280	2.87
0.0272	7.74	2563	55.65	0.5552	292	3.11
0.0563	7.30	5062	60.50	0.5393	306	3.35
0.1438	6.55	4673	72.90	0.5106	341	3.90
0.2013	6.02	4555	79.94	0.4896	364	4.22
0.2743	5.72	4334	90.90	0.4772	394	4.59
0.3702	5.32	4101	104.86	0.4602	430	5.00
0.4362	5.06	3985	113.43	0.4488	452	5.25
0.5563	4.87	3698	132.08	0.4405	488	5.63
0.6939	4.69	3474	152.75	0.4319	531	6.01
0.8425	4.42	3311	172.05	0.4196	570	6.36
1.0000	4.16	3499	191.26	0.4071	669	6.87
50 ^{0}C						
0.0000	9.66	5078	54.60	0.6202	277	2.82
0.0272	8.18	5280	54.93	0.5707	290	3.05
0.0563	7.74	4589	60.57	0.5553	303	3.30
0.1438	6.92	4426	73.02	0.5248	335	3.84
0.2013	6.36	4426	80.40	0.5034	356	4.15
0.2743	6.01	4213	91.00	0.4891	383	4.51
0.3702	5.55	3920	104.69	0.4701	410	4.89
0.4362	5.32	3671	114.27	0.4604	419	5.08
0.5563	5.12	3477	132.11	0.4515	459	5.48
0.6939	4.91	3252	152.23	0.4424	495	5.85
0.8425	4.64	3118	172.14	0.4299	537	6.22
1.0000	4.36	3267	191.72	0.4165	626	6.71

Figure 1a. Variation of excess adiabatic compressibility with mole fraction of benzyl benzoate in the mixture benzyl benzoate + acetonitrile
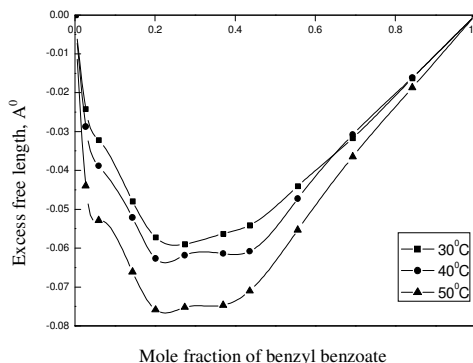

Figure 1b. Variation of excess free length with mole fraction of benzyl benzoate in the mixture benzyl benzoate + acetonitrile
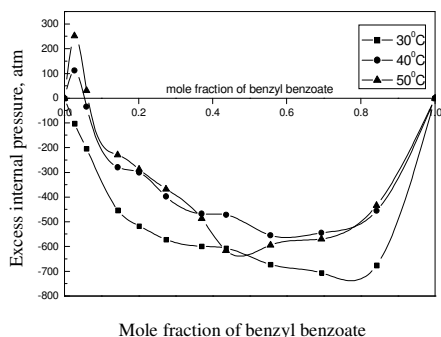

Figure 1c. Variation of excess internal pressure with mole fraction of benzyl benzoate in the mixture benzyl benzoate + acetonitrile
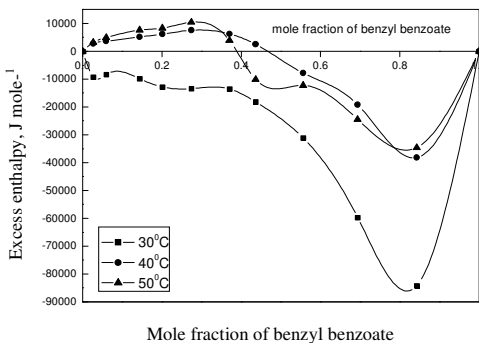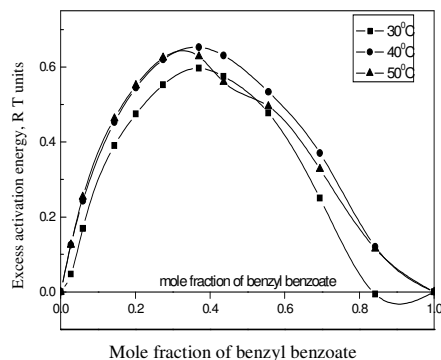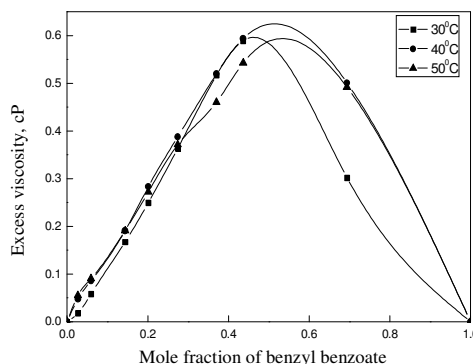

Figure 1d. Variation of excess enthalpy with mole fraction of benzyl benzoate in the mixture benzyl benzoate + acetonitrile

Figure 1e. Variation of excess activation energy with mole fraction of benzyl benzoate in the mixture benzyl benzoate + acetonitrile

Figure 1f. Variation of excess viscosity with mole fraction of benzyl benzoate in the mixture benzyl benzoate + acetonitrile

Systematic and regular variation noticed. π^E is also negative through out at all temperatures (except at 40 & 50 ^{0}C, at very low concentrations slightly positive). Excess enthalpy negative at 30 ^{0}C, at all concentrations but positive up to 0.45 m and thereafter negative at 40 and 50 ^{0}C. Both G^E and η^E show positive variation throughout with maximum at around 0.45 m at all temperature, almost constant at high temperatures.

As most of the excess parameters are negative at all temperatures, it may be suggested that strong AB interactions and dipole-dipole type interactions are predominant. The strength of the interactions increases with temperatures as observed from more negative values of the excess parameters. From the positive G^E and η^E, endothermic type of chemical reaction is predicted through out the concentration range at all temperatures.

Benzyl benzoate + benzonitrile

Ultrasonic velocity, density and viscosity data measured experimentally as a function of mole fraction of benzyl benzoate at at three different temperatures 30, 40 and 50 ^{0}C in the system: benzyl benzoate + benzonitrile is presented in Table 3. In this system, velocity increases from benzonitrile to benzoate, the curve being slightly concave upwards and decreases with temperature. Theoretical evaluation of sound velocity using the already said five theories shows that here also CFT, NOMOTO and JUNJIE appear to have an edge (from the maximum % deviations -3.07,-1.79,-0.37,-6.33,-0.51 in the five theories respectively).

Table 3. Ultrasonic velocities, densities and viscosities for the system benzyl benzoate in Benzyl benzoate + benzonitrile

Mole fraction of Benzyl benzoate	Velocity ms^{-1}	Density kgm^{-3}	Viscosity, milli Pa.s
30 ^{0}C			
0.0000	1402.5	995.00	1.10441
0.0354	1413.6	1009.32	1.27882
0.1099	1422.0	1017.19	1.60421
0.1747	1433.3	1032.81	1.89838
0.2477	1446.0	1051.55	2.24881
0.3306	1454.8	1067.41	2.74163
0.4255	1466.8	1076.61	3.31420
0.5354	1473.8	1083.68	3.82825
0.6670	1485.5	1091.70	4.47007
0.8160	1495.5	1110.45	4.92901
0.9054	1501.8	1115.26	5.64283
1.0000	1506.0	1119.35	6.53251
40 ^{0}C			
0.0000	1376.4	988.47	0.97315
0.0345	1378.8	1003.86	1.18025
0.1099	1398.0	1019.69	1.42016
0.1747	1404.0	1028.17	1.64184
0.2477	1414.8	1042.89	1.95808
0.3306	1425.6	1054.18	2.38980
0.4255	1438.0	1073.00	2.83100
0.5354	1448.0	1078.78	3.16050
0.6667	1453.5	1091.78	3.64468

Contd…

0.5354	4.42	3776	149.75	0.4196	565	6.16
0.6667	4.34	3694	161.09	0.4155	595	6.38
0.8160	4.24	3603	174.24	0.4109	628	6.60
0.9054	4.18	3535	182.46	0.4078	645	6.73
1.0000	4.16	3499	191.26	0.4071	669	6.87
50 ^{0}C						
0.0000	5.81	4302	105.54	0.4809	454	5.07
0.0354	5.53	4585	107.99	0.4692	495	5.30
0.1099	5.38	4605	114.79	0.4626	529	5.54
0.1747	5.28	4712	119.73	0.4562	564	5.75
0.2477	5.11	4554	126.36	0.4509	575	5.87
0.3306	4.91	4592	132.99	0.4419	611	6.09
0.4255	4.76	4440	141.57	0.4354	629	6.25
0.5354	4.69	4163	152.07	0.4326	633	6.37
0.6667	4.58	3885	163.21	0.4272	634	6.49
0.8160	4.49	3534	176.07	0.4229	622	6.56
0.9054	4.42	3429	183.46	0.4196	629	6.65
1.0000	4.36	3267	191.72	0.4165	626	6.71

But as already mentioned, to have a clear picture of the molecular interactions, the excess parameters have been computed and portrayed from Figures 2(a) - 2(f). β^E and L_f^E behave similarly at all concentrations and temperatures. They are negative throughout with a minimum at ~0.4 m and become more negative at all concentrations as the temperature is increased. As seen from Figure 2(c), π^E is positive up to 0.80 m and negative at higher concentrations at 30 ^{0}C and positive throughout at high temperatures. Similar trend is noticed in the variation of excess enthalpy (H^E). G^E is positive through out and becomes more positive at high temperatures with maximum at ~0.4 m. η^E is also similar to that of G^E at all temperatures.
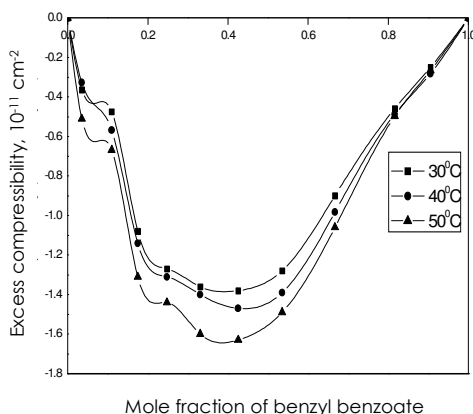

Figure 2a. Variation of excess compressibility with mole fraction of benzyl benzoate in the mixture benzyl benzoate + benzonitrile
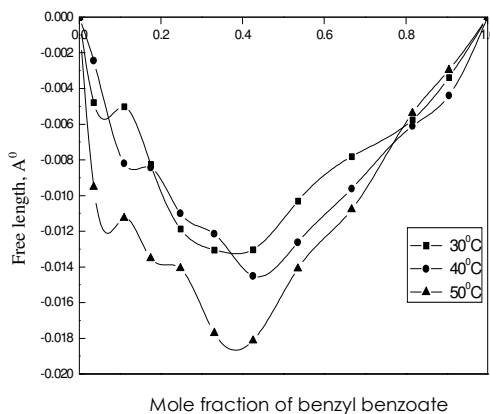

Figure 2b. Variation of excess free length with mole fraction of benzyl benzoate in the mixture benzyl benzoate + benzonitrile
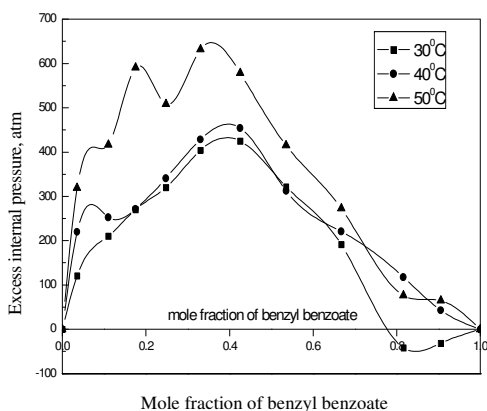
Figure 2c. Variation of excess internal pressure with mole fraction of benzyl benzoate in the mixture benzyl benzoate + benzonitrile
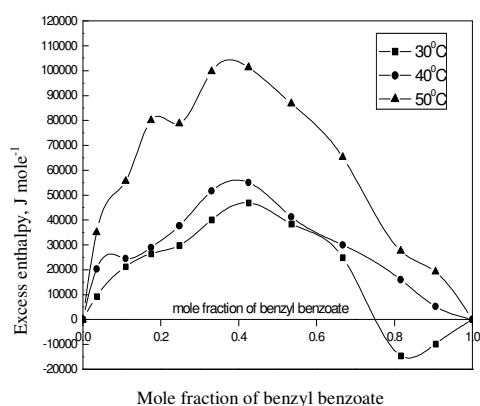

Figure 2d. Variation of excess enthalpy with mole fraction of benzyl benzoate in the mixture benzyl benzoate + benzonitrile
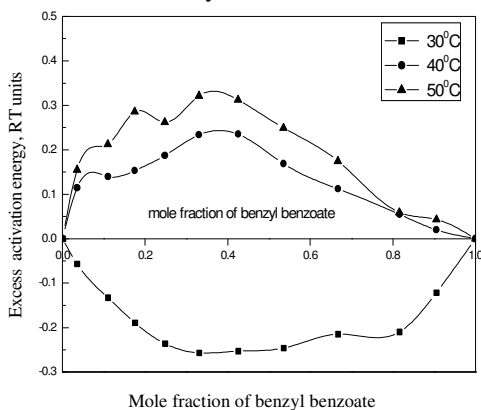

Figure 2e. Variation of excess activation energy with mole fraction of benzyl benzoate in the mixture benzyl benzoate + benzonitrile
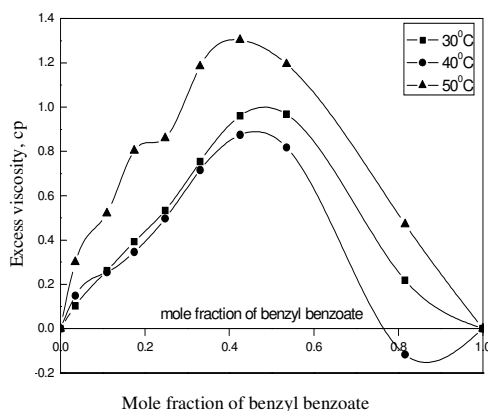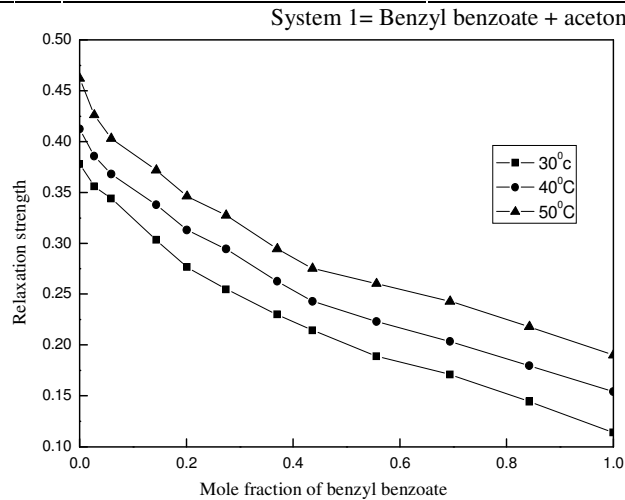

Figure 2f. Variation of excess viscosity with mole fraction of benzyl benzoate in the mixture benzyl benzoate + benzonitrile

Though L_f^E and β^E indicate strong AB interactions, the positive values of π^E and H^E indicate weak interactions and dispersive forces at concentrations below 0.90 m while afterwards *i.e.,* at high concentrations strong AB interactions are indicated at 30 ^{0}C. At 40 and 50 ^{0}C totally weak interactions and dispersive forces result. From the positive values of G^E and η^E mostly endothermic type of reaction is suggested in the mixture. Temperature variation shows the increase of the nature of reaction. The excess parameters are fitted to the Redlich - Kister type of 3rd order polynomial and the coefficients are presented in Table 5.

Table 5. Various parameters- A_0, A_1, A_2, A_3 along with standard deviation σ using Redlich-kister method

System	Temp., °C	β^E, 10^{-10} m² N⁻¹					π^E, atm					H^E, kJ mole⁻¹					G^E, (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_2	σ
1	30	-0.36	-17.44	33.56	-15.83	0.20	-76	-1948	522	1418	103	-14	202	-814	613	16	-0.04	4.22	-8.34	4.14	0.04
	40	-0.45	-18.92	33.89	-17.61	0.24	53	-1791	499	1204	66	-4	167	-534	365	7	0.01	4.05	-7.57	3.49	0.01
	50	-0.71	-21.33	42.64	-20.72	0.35	137	-2235	871	1216	87	-2	163	-568	404	5	0.03	4.04	-7.88	3.82	0.02
2	30	0.01	-8.10	-13.87	-5.77	0.10	-9	2761	-5634	2843	50	-3	302	-605	298	9	0.01	2.18	-3.86	-1.67	0.03
	40	0.02	-8.50	14.32	-5.83	0.08	53	2258	-4278	1963	52	3	261	-446	180	6	0.04	2.04	-3.44	-1.37	0.02
	50	-0.04	-9.42	16.46	-6.98	0.11	532	7046	-16656	9181	285	53	896	-187	937	29	0.28	4.34	-9.13	4.56	0.15

System 1= Benzyl benzoate + acetonitrile   System 2= Benzyl benzoate + benzonitrile

Figure 1(g). Variation of relaxation strength with mole fraction of benzyl benzoate in the mixture of benzyl benzoate+acetonitrile
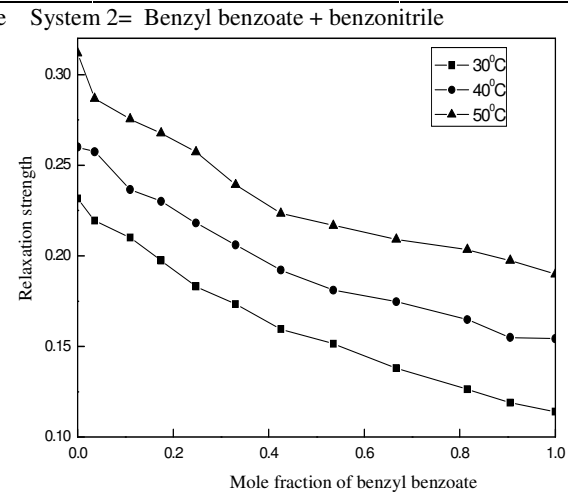
Figure 2(g). Variation of relaxation strength with mole fraction of benzyl benzoate in the mixture of benzyl benzoate+benzonitrile
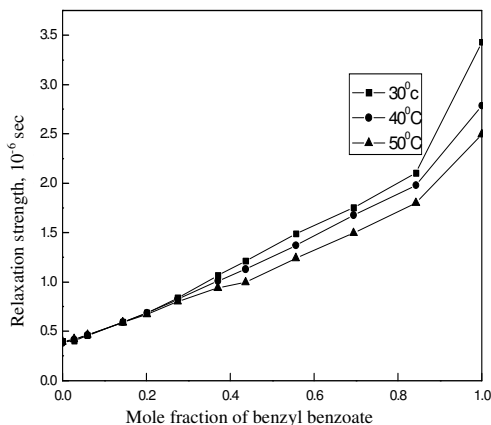
Figure 1(h). Variation of relaxation time with mole fraction of benzyl benzoate in the mixture of benzyl benzoate + acetonitrile
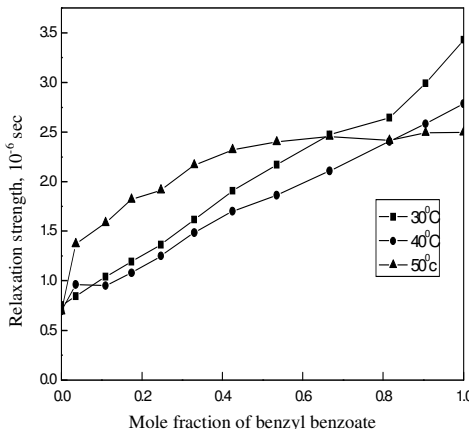
Figure 2(h). Variation of relaxation time with mole fraction of benzyl benzoate in the mixture of benzyl benzoate + benzonitrile
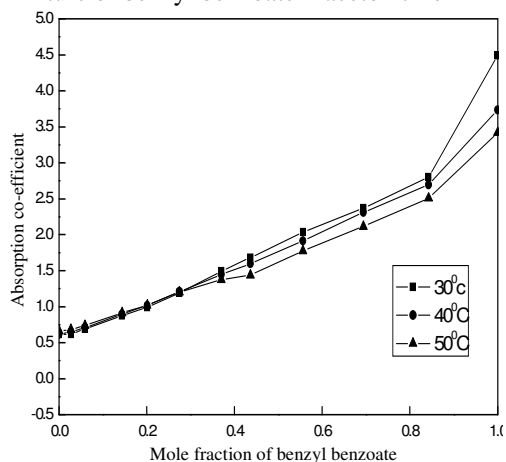
Figure 1(i). Variation of absorption co-efficient with mole fraction of benzyl benzoate in the mixture of benzyl benzoate + acetonitrile
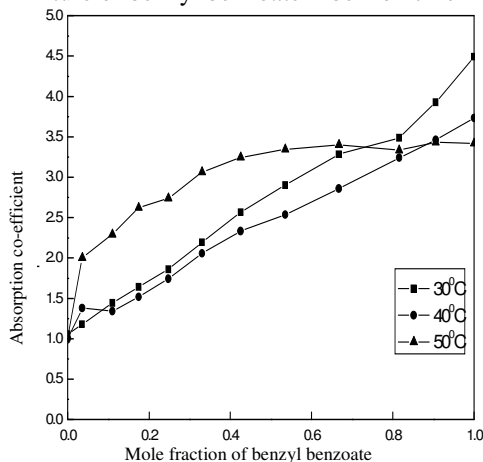
Figure 2(i). Variation of absorption coefficient with mole fraction of benzyl benzoate in the mixture of benzyl benzoate + benzonitrile

At this juncture, a comparison of our results with other results of benzoate is desired. In the solutions of benzyl benzoate in aliphatic alcohols, strong molecular interactions between unlike molecules are predicted besides dipole - dipole interactions. Endothermic reaction is suggested in all the systems. In the mixture of benzoate with aliphatic alkanes also, similar type of interactions are reported. In the mixtures of benzyl benzoate with acetones and ketones also similar interactions are predicted. In the mixtures of benzyl benzoate with acetones and ketones also similar interactions are predicted. In the two acetate systems (MAA and EA), presence of weak interaction besides dispersive forces is suggested and the effect increases from MAA to EA. In the two ketones - MEK and BMK systems also weak interactions are suggested and the strength of bonding further worsens from MEK to BMK

i.e., by increase of molecular weight. Substituted benzenes like chloro, bromo and nitro benzenes yield similar results in benzyl benzoate.

Our results of the present investigation are in conformity with those of the above workers. Relaxation strength $\left(\alpha = 1 - \dfrac{U_{\exp}^2}{U_\infty^2} \right)$, relaxation time $\left(\tau = \dfrac{4\eta}{3\rho U^2} \right)$ and classical absorption coefficient $\left(\left(\dfrac{\alpha}{f^2} \right)_{classical} = \dfrac{8\pi^2 \eta}{3\rho U^3} \right)$ also have been computed using the mentioned standard relations[11] from which the molecular interactions can also be estimated. Relaxation strength (Figures 1(g) and 2(g)) decreases with concentration at all temperatures and increases with temperature at all concentrations of benzyl benzoate in both the systems which indicates the formation of aggregates of solvent molecules around the solute due to which structural arrangement is affected in the systems. Relaxation time (Figures 1(h) and 2(h)) and absorption coefficient (Figures 1(i) and 2(i)) increase with concentration of benzyl benzoate and temperature as well. In acetonitrile system up to ~0.4 m, the temperature variation of relaxation time and absorption is very very small while at higher concentrations, increase with temperature is conspicous and clear. The nature of molecular interactions from the behaviour of the above parameters is similar to the one obtained from the excess parameters.

The opposing tendencies (in various excess parameters) may be due to the fact that strong dipolar interactions and highly directional interaction bonding act simultaneously between the constituent molecules and the relationship between the excess functions is not simple and reflects the properties of the interaction molecules[12]. Also in a system it should be remembered that the effect of interaction between the like and unlike molecules balance each other in varying degrees.

Also for better understanding of the degree of interaction (magnitude *etc*.,) one requires all the theories FLT, CFT, H bond formation, dipole-dipole interactions *etc*. Such a comprehensive expression for intermolecular / atomic potential taking into account all the theories has not yet been worked out[13].

Acknowledgment

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