Available online at **www.joac.info**

ISSN: 2278-1862

Journal of Applicable Chemistry

2019, 8 (3): 1377-1384

(International Peer Reviewed Journal)

Excess Thermodynamic and other Allied Parameters in the Binary Mixtures of p-Xylene with Benzyl benzoate as Common Component

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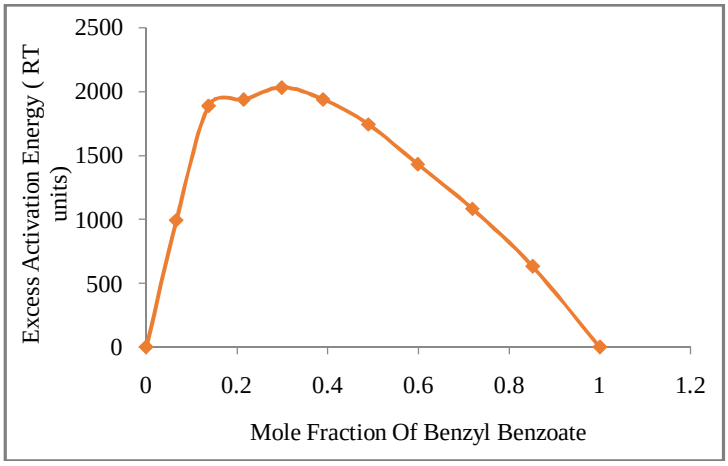
Accepted on 23rd April, 2019

ABSTRACT

Density, viscosity and ultrasonic velocity have been measured in binary mixture of p-Xylene with benzyl benzoate as common component at deferent Temperatures 30℃, 40℃ and 50℃. From the measured data, computed excess thermodynamic parameters like Adiabatic Compressibility, Internal Pressure, Molar Volume, Free length, enthalpy and Gibbs activation energy and the intermolecular interactions are estimated in the light of the excess parameters. In the mixture p-xylene with Benzyl benzoate Strong interactions are suggested.

Graphical Abstract



variation of excess Activation energy with mole fraction of Benzyl benzoate

Keywords: Binary mixtures, p-Xylene, Benzyl benzoate, Relaxation strength, Molecular interactions.

INTRODUCTION

Ultrasonic methods has been accepted as an important tool in predicting the molecular interactions in the binary mixtures and these techniques are comparable to other techniques like Infrared Spectroscopy, NMR spectroscopy and dielectric relaxation studies etc. Though several binary mixtures have been studied, the binary mixtures with at least one component as p-Xylene or Benzyl benzoate have been referred [**1-10**] owing to the nature of the liquids in our present investigation. In the present investigation, the binary mixtures of the p-Xylene 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 additive in artificial flavor, and as a solubilizing agent in the preparation of oily injections and also a good solvent for various chemical reactions. p-Xylene is the principal precursor to teraphtalic acid and dimethyl teraphtalate. Both monomers used in the production of polyethylene teraphtalate (PET) plastic bottles and polyester clothing. Ultrasonic velocity, density and viscosity have been measured in the binary mixtures of benzyl benzoate with p-Xylene at 30°C, 40°C and 50°C. From the thermodynamic and other parameters computed from the measured data, excess parameters have been calculated and inter molecular interactions have been estimated.

MATERIALS AND METHODS

The chemicals used in the present investigation Benzyl benzoate and P-Xylene are extra pure grade from LOBA Chemie Private Limited. The binary mixture was prepared by mixing the weighted quantities of pure liquids. Density of binary mixture has been measured using a double stem capillary type pychnometer with an accuracy of 2 parts in 10^5. Weights are taken using an Digital balance with an accuracy of ±0.001 mg. Viscosity has been measured using Ostwald Viscometer with an accuracy of ±0.1%. Ultrasonic velocity has been measured using a single crystal Interferometer working at frequency 2MHz with an accuracy of ±0.05%. Above all devices Pychnometer, Viscometer and Interferometer are standardized with triply distilled water as reference liquid before carrying out all the measurements in test liquids.

Theoretical Aspects: If the measured ultrasonic velocity (U_{exp}) and density (ρ_{exp}) are known, then adiabatic compressibility of a liquid can be calculated using the relation

$$\beta = \frac{1}{U_{exp}^2 \rho_{exp}} \qquad \text{---1}$$

The difference between the experimentally observed compressibility β^{exp} and that of an ideal solution β^{ideal} is equal to the excess adiabatic compressibility β^E is given by

$$\beta^E = \beta^{exp} - \beta^{ideal} \qquad \text{---2}$$

The internal pressure π and free volume V_f can be calculated using Suryanarayana and Kuppusamy relations [**9**] for pure components at any particular temperature given by

$$\pi = bRT\left[\frac{K\eta}{U}\right]^{1/2} \frac{\rho^{2/3}}{M^{7/6}} \qquad \text{---3}$$

Excess internal pressure

$$\pi^E = \pi^{exp} - \pi^{ideal} \qquad \text{--4}$$

Enthalpy is computed with the help of molar volume and internal pressure. The excess enthalpy is given by

$$H^E = H^{exp} - H^{ideal} \quad \text{---5}$$

$$= \pi V - \left[\pi_A V_A X_A + \pi_B V_B X_B\right] \quad \text{---6}$$

Activation energy [12] of Gibb's is given by

$$G = RT\left[\ln \eta V_M\right] \quad \text{---7}$$

And excess activation energy is given by

$$G^E = RT\left[\ln(\eta V_M) - \left\{X_A \ln\left(\eta^A V_M^A\right) + X_B \ln\left(\eta^B V_M^B\right)\right\}\right] \quad \text{---8}$$

The equation for molar volume of the ideal mixture is given by

$$V^{ideal} = X_A V_A + X_B V_B \quad \text{---9}$$

The excess molar volume of the given binary mixture is given by

$$V^E = V_M^{exp} - V_M^{ideal} \quad \text{---10}$$

The viscosity of a binary liquid mixture can be calculated by employing the measured values of density of a liquid and time of flow of the liquid of the system at any temperature.

$$\text{Viscosity} \qquad \eta = \frac{\rho t}{\rho^1 t^1}\eta^1 \quad \text{---11}$$

The difference between experimental viscosity and ideal viscosity of the liquid is called the excess viscosity and is given by

$$\eta^E = \eta^{exp} - \eta^{ideal} \quad \text{---12}$$

Excess free length can be defined as the difference between experimental free length and ideal free length .and is given by the relation

$$L_f^E = L_f^{exp} - L_f^{ideal} \quad \text{---13}$$

$$= L_f^{exp} - \left(L_f^A X_A + L_f^B X_B\right) \quad \text{---14}$$

Classical absorption (α/f^2), relaxation time (τ) and relaxation strengths (α_R) are computed by using the following relations.

$$\text{Classical absorption} \quad \alpha/f^2 = 8\pi^2\eta/3\rho U^2 \quad \text{---15}$$

$$\text{Relaxation Time} \quad \tau = 4\eta/3\rho U^2 \quad \text{---16}$$

$$\text{Relaxation strength} \quad \alpha_R = 1-(U_{exp}^2/U_\infty^2) \quad \text{---17}$$

RESULTS AND DISCUSSION

Binary Mixtures of Benzyl benzoate with p-Xylene: Ultrasonic velocity, density and viscosity have been measured in the binary mixtures of benzyl benzoate with p-Xylene over the entire compositions range of benzyl benzoate at 30°C, 40°C and 50°C presented in table 1. As observed from table 1 the velocity, Density and Viscosity increases from p-Xylene to Benzyl benzoate at all temperatures 30° C, 40°C and 50°C.

Table. 1. Ultrasonic velocity, density and viscosity in the mixtures of P-Xylene

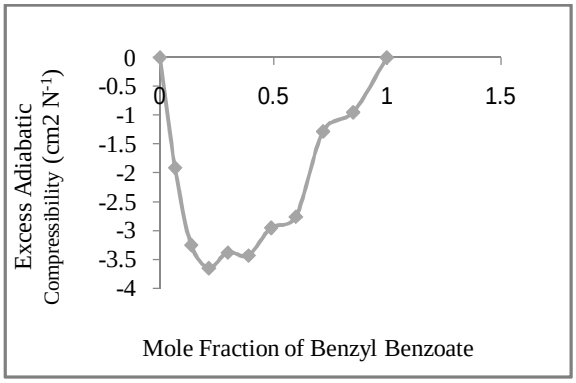
Mole fraction of Benzyl benzoate	Velocity (ms^{-1})	Density (kg/m^3)	Viscosity (m..Pas)	Mole fraction of Benzyl benzoate	Velocity (ms^{-1})	Density (kg/m^3)	Viscosity (mPas)	Mole fraction of Benzyl benzoate	Velocity (ms^{-1})	Density (kg/m^3)	Viscosity (m.Pas)
Benzyl benzoate + p-Xylene at 30°C				**Benzyl benzoate + p-Xylene at 40°C**				**Benzyl benzoate + p-Xylene at 50°C**			
0.00000	1288.1	852.83	0.5782	0.00000	1253.68	846.18	0.5065	0.00000	1205.94	830.39	0.4757
0.06635	1318.5	876.49	0.9980	0.06635	1273.20	869.19	0.8814	0.06635	1234.81	854.41	0.6859
0.13786	1343.8	905.52	1.6902	0.13786	1302.63	897.83	1.4956	0.13786	1256.66	872.04	1.1398
0.21514	1365.6	930.53	2.1665	0.21514	1321.74	923.83	1.8249	0.21514	1279.65	918.67	1.4966
0.29894	1381.9	956.25	2.8182	0.29894	1348.76	948.09	2.4251	0.29894	1301.26	943.73	1.8891
0.39010	1412.7	983.85	3.3436	0.39010	1365.39	977.46	2.9783	0.39010	1330.88	969.75	2.3825
0.48964	1416.9	999.71	3.8614	0.48964	1399.56	997.46	3.4650	0.48964	1350.37	985.22	2.9524
0.59879	1450.3	1033.76	4.5519	0.59879	1411.82	1027.81	3.8770	0.59879	1373.92	1017.82	3.4025
0.71898	1461.3	1056.39	5.1548	0.71898	1430.93	1049.79	4.2518	0.71898	1389.32	1042.88	3.7503
0.85199	1488.6	1079.81	5.7409	0.85199	1452.06	1076.75	4.7837	0.85199	1413.03	1066.40	3.9831
1.00000	1506.90	1119.35	6.5325	1.00000	1471.44	1109.75	5.0210	1.00000	1440.00	1107.09	4.2983

The thermodynamic, acoustic and other related parameters computed from the standard relations are presented in table 2. In binary mixture of benzyl benzoate and p-Xylene adiabatic compressibility, and free length decreases with concentration of benzyl benzoate while internal pressure, molar volume enthalpy and activation energy increases with the increase in concentration of benzyl benzoate at all three temperatures.

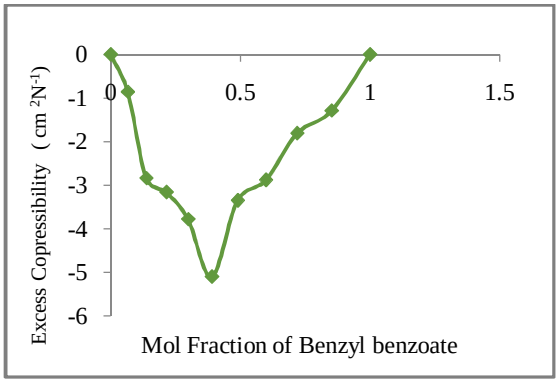
Table .2 Thermodynamic Parameters in the Mixtures of Benzylbenzoate+p-Xylene

Mole fraction of Benzyl benzoate	Adiabatic compressibility (10^{-11} N^{-1} cm^2)	Internal pressure (atms)	Molar volume ($ml.mole^{-1}$)	Free length (A^0)	Enthalpy ($KJ.mole^{-1}$)	Activation energy (RT units)
Benzylbenzoate+p-Xylene at 30°C						
0.00000	7.07	2388.8	124.49	0.5304	297.39	10778.19
0.06635	6.56	2931.2	129.16	0.5111	378.60	12246.75
0.13786	6.12	3580.2	133.39	0.4934	477.58	13656.05
0.21514	5.76	3704.0	138.62	0.4790	513.45	14259.44
0.29894	5.48	3904.7	144.18	0.4669	563.02	14955.04
0.39010	5.16	3997.6	149.97	0.4531	599.54	15515.11
0.48964	4.98	4003.9	158.15	0.4453	633.25	16033.34
0.59879	4.60	4015.9	164.14	0.4278	659.20	16503.84
0.71898	4.43	4026.6	172.69	04201	695.53	17017.47
0.85199	4.18	3994.7	182.02	0.4079	727.12	17521.10
1.00000	3.93	3966.2	189.61	0.3957	752.05	17949.72
Benzylbenzoate+p-Xylene at 40°C						
0.00000	7.52	2254.54	125.46	0.5566	282.87	10464.2
0.06635	7.10	2787.65	130.25	0.5408	363.08	11954.6
0.13786	6.56	3401.15	134.54	0.5201	457.59	13369.1
0.21514	6.20	3521.02	139.62	0.5053	491.63	13964.2
0.29894	5.80	3782.34	145.43	0.4888	550.06	14753.5
0.39010	5.33	3899.85	150.95	0.4687	588.70	15395.3
0.48964	5.27	3940.73	158.56	0.4660	624.87	15900.9
0.59879	4.88	3821.62	165.09	0.4488	630.94	16219.8
0.71898	4.65	3709.29	173.78	0.4378	644.62	16587.6

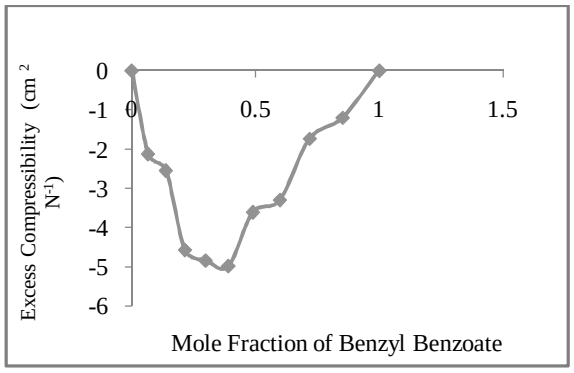
0.85199	4.40	3685.25	182.53	0.4260	672.70	17068.5
1.00000	4.16	3498.69	191.25	0.4141	669.15	17308.2
Benzylbenzoate+p-Xylene at 50°C						
0.00000	8.28	2200.0	127.85	0.5933	281.28	10353.7
0.06635	7.68	2281.8	132.49	0.5712	302.33	10969.0
0.13786	7.26	2238.6	138.51	0.5555	310.09	11341.7
0.21514	6.65	2498.9	140.41	0.5315	350.88	12187.2
0.29894	6.26	2451.7	146.10	0.5155	358.20	12534.8
0.39010	5.82	2696.5	152.15	0.4974	410.29	13480.9
0.48964	5.57	2966.0	160.71	0.4864	475.99	14485.2
0.59879	5.20	3069.6	166.71	0.4703	511.76	15104.2
0.71898	4.97	3264.7	174.93	0.4595	571.12	15908.5
0.85199	4.70	3256.9	184.31	04468	600.29	16433.9
1.00000	4.36	3267.0	191.71	0.4303	626.35	16922.5



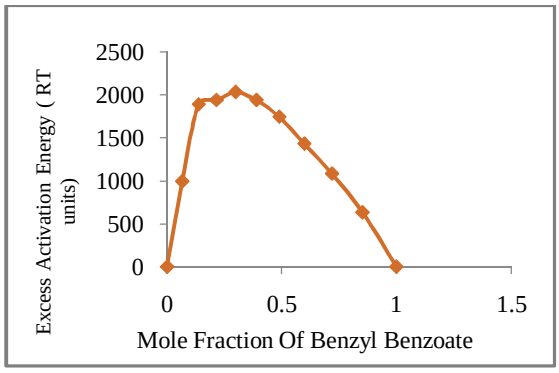
Variation of excess Adiabatic Compressibility with mole fraction at 30°C :Benzylbenzoate+p-Xylene



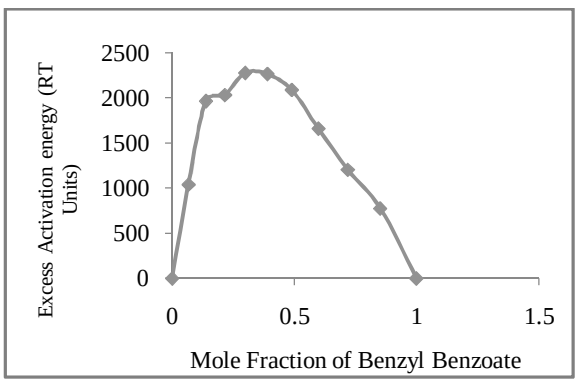
Variation of excess Adiabatic Compressibility with mole fraction at 40°C :Benzylbenzoate+p-Xylene



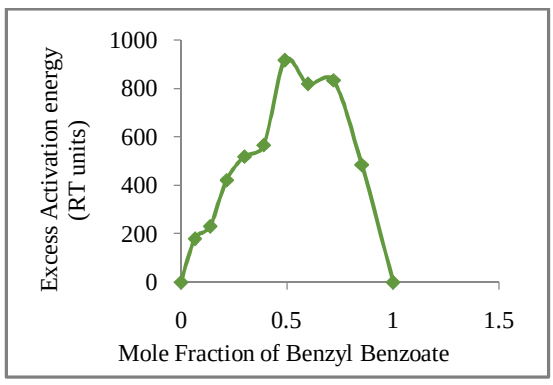
Variation of excess Adiabatic Compressibility with mole fraction at 50°C :Benzylbenzoate+p-Xylene



Variation of excess Activation energy with mole fraction at 30°C : Benzylbenzoate +p-Xylene



Variation of excess Activation energy with mole fraction at



Variation of excess Activation energy with mole fraction

40°C : Benzylbenzoate +p-Xylene at 50°C : Benzylbenzoate +p-Xylene

Figures 1. variation of Thermodynamic parameters at different temperature of Benzylbenzoate +p-Xylene

All the excess parameters are computed at all three temperatures with concentration of benzyl benzoate and are presented in table 3 to estimate the molecular interactions in the binary system. From the table 3 it is noticed that excessive adiabatic compressibility (β^E) is negative at all temperatures 30°C ,40°C and 50°C. Excessive internal pressure is positive at 30°C , 40°C and 50°C. Excessive enthalpy and excessive Gibbs activation energy are positive at all three temperatures. Excessive free length (L^F) is negative at all three temperatures from these excess parameters it may be suggested strong interactions in benzyl benzoate and p-Xylene system.

From the variation of excessive Gibbs activation energy (G^E) which is positive at all three temperatures, it may be that endothermic type of chemical reaction.

Table 3. Excess parameters in the Mixtures of Benzylbenzoate+p-Xylene

Mole fraction of Benzyl benzoate	Adiabatic compressibility (10^{-12} N^{-1} cm^2)	Internal pressure (atms)	Molar volume ($ml.mole^{-1}$)	Free length (A^0)	Enthalpy (K J. $mole^{-1}$)	Activation energy (RT units)
Benzylbenzoate+p-Xylene at 30°C						
0.00000	--	--	--	--	--	--
0.06635	-1.91	437.7	0.35	-0.0103	51.04	992.7
0.13786	-3.25	973.8	-0.07	-0.0184	117.51	1889.1
0.21514	-3.65	975.8	0.12	-0.0224	118.24	1938.3
0.29894	-3.38	1044.4	0.23	-0.0232	129.71	2032.9
0.39010	-3.43	993.5	0.08	-0.0247	124.78	1939.2
0.48964	-2.05	842.7	1.78	-0.0191	113.23	1743.6
0.59879	-2.76	682.6	0.66	-0.0219	89.56	1431.4
0.71898	-1.28	503.6	1.38	-0.0135	71.10	1083.0
0.85199	-6.88	262.0	2.04	-0.0078	42.36	632.7
1.00000	--	--	--	--	--	--
Benzylbenzoate+p-Xylene at 40°C						
0.00000	--	--	--	--	--	--
0.06635	-0.86	450.55	-56.65	-0.0063	54.57	1036.2
0.13786	-2.84	975.09	-47.65	-0.0169	121.46	1961.3
0.21514	-3.16	998.80	-37.48	-0.0206	125.65	2027.5
0.29894	-3.78	1155.87	-26.16	-0.0252	151.71	2273.3
0.39010	-5.10	1159.96	-14.64	-0.0323	155.13	2261.2
0.48964	-2.35	1077.00	-0.48	-0.0208	152.85	2085.5
0.59879	-2.88	822.09	13.23	-0.0228	116.76	1657.5
0.71898	-1.81	560.23	29.83	-0.0163	84.20	1202.7
0.85199	-9.29	370.70	47.33	-0.0091	60.71	773.2
1.00000	--	--	--	--	--	--
Benzylbenzoate+p-Xylene at 50°C						
0.00000	--	--	--	--	--	--
0.06635	-2.12	11.01	0.41	-0.0112	-1.839	179.4
0.13786	-2.34	-108.43	1.86	-0.0152	-18.75	82.43
0.21514	-4.56	69.39	-1.18	-0.0266	-4.63	420.25
0.29894	-4.53	-67.27	-0.84	-0.0288	-26.23	217.39
0.39010	-4.97	-80.32	-0.61	-0.0322	-5.59	564.72
0.48964	-3.60	-243.54	1.36	-0.0270	25.75	915.15
0.59879	-3.29	230.72	0.62	-0.0253	23.86	817.18
0.71898	-1.73	297.55	1.17	-0.0165	41.74	831.97
0.85199	-5.20	147.85	2.04	-0.0076	25.01	483.57
1.00000	--	--	--	--	--	--

Computed other parameters like relaxation strength, relaxation time and classical absorption and presented in table 4. Relaxation strength shows decreasing trend with concentration of benzyl benzoate . The behavior of Relaxation time and classical absorption increases with concentration of benzyl benzoate.

Table 4. Variation of relaxation strength, relaxation time and classical absorption in mixtures of Benzylbenzoate+p-Xylene

Mole fraction of benzyl benzoate	Relaxation strength	Relaxation time (10^{-6}) sec	Classical Absorption (10^{-6})
Benzylbenzoate+p-Xylene at 30°C			
0.00000	0.3518	0.5448	0.1074
0.06635	0.3209	8.732	0.1722
0.13786	0.2945	1.378	0.2717
0.21514	0.2715	1.587	0.3131
0.29894	0.2539	1.911	0.3769
0.39010	0.2302	2.162	0.4263
0.48964	0.2156	2.432	0.4796
0.59879	0.1782	2.607	0.5140
0.71898	0.1658	2.928	0.5774
0.85199	0.1343	3.198	0.6307
1.00000	0.1129	3.426	0.6757
Benzylbenzoate+p-Xylene at 40°C			
0.00000	0.3860	0.5077	0.1001
0.06635	0.3667	0.8340	0.1644
0.13786	0.3371	1.3089	0.2581
0.21514	0.3175	1.5074	0.2972
0.29894	0.2893	1.8748	0.3696
0.39010	0.2502	2.1167	0.4174
0.48964	0.2565	2.4345	0.4800
0.59879	0.2213	2.4581	0.4847
0.71898	0.2001	2.5753	0.5078
0.85199	0.1763	2.8094	0.5540
1.00000	0.1542	2.7862	0.5494
Benzylbenzoate+p-Xylene at 50°C			
0.00000	0.4319	0.5252	0.1035
0.06635	0.4043	0.5997	0.1182
0.13786	0.3831	0.6291	0.1240
0.21514	0.3603	0.7947	0.1567
0.29894	0.3385	08253	0.1627
0.39010	0.3081	1.0731	0.2116
0.48964	0.2876	1.4489	0.2857
0.59879	0.2626	1.6673	0.3287
0.71898	0.2460	2.0866	0.4114
0.85199	0.2200	0.3063	0.4547
1.00000	0.1900	2.4964	0.4922

APPLICATION

Ultrasonic study helps in understanding the molecular interactions in binary liquid mixtures. These properties are extremely useful for the design of process equipment in chemical industries and the data on some of the properties associated with the liquids and liquid mixtures like velocity, viscosity and density find extensive application molecular dynamics.

CONCLUSION

Experimental findings of velocity, viscosity and density in the binary mixtures of benzyl benzoate and p-Xylene at 30°C , 40°C and 50°C are useful in the computation of speeds of sound by various models such as FLT, CFT, Nomoto, VandaeL and Junjie. FLT, CFT, Nomoto and Junjie appear to agree well with the experimental results.

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