DENSITIES, VISCOSITIES, SPEED OF SOUND, AND IR SPECTROSCOPIC STUDIES OF BINARY MIXTURES OF TERT- BUTYL ACETATE WITH FLUOROBENZENE, CHLOROBENZENE AND BROMOBENZENE AT (303·15 AND 313·15) K, AND AT ATMOSPHERIC PRESSURE 0.087 MPa.

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ABSTRACT

Volumetric, Viscometric, speed of sound and IR spectroscopic studies of binary mixtures of tert- butyl acetate (tBAc) with fluorobenzene(FB), chlorobenzene(CB) and bromobenzene(BB) have been measured over the entire range of composition, at (303·15 and 313·15) K and at atmospheric pressure. From the experimental values of density, viscosity , speed of sound and IR spectroscopy the excess molar volumes V^E, deviations in viscosity $\Delta\eta$ and deviation in isentropic compressibility ΔK_s and stretching frequency ν have been calculated. The excess molar volumes, deviations in viscosity and deviations in isentropic compressibility have been fitted to the Redlich-Kister polynomial equation. The interaction parameters of McAllister model is used to correlate the experimental values of density, viscosity and speed of sound.

Key words: Excess molar volumes, deviations in viscosity, excess isentropic compressibility, IR, tert. Butyl Acetate, Benzenes

1. INTRODUCTION

The knowledge of thermodynamic properties of binary liquid mixtures has great relevance in theoretical and applied areas of research. These data are needed for design process in chemical, petrochemical and pharmaceutical industries The tBAc is used as a solvent in the manufacture of many industrially important chemicals such as adhesive, and thinners as well as additive to improve the antiknock properties of motor fuels. Fluorobenzene (FB) is useful solvent for highly reactive species and chlorobenzene (CB) is mainly used as pesticides formulations, degreasing automobile parts. Bromobenzene (BB) is used to introduce a phenyl group via palladium-catalyzed coupling reactions such as the Suzuki reaction and additive to motor oil. Literature survey provides extensive data on density and viscosity of liquid mixtures but combine study of density and viscosity speed of sound, IR is quite scare. The interaction between esters and hydrocarbons were reported [1] for the binary mixtures of butyl acetate with aromatic hydrocarbons.. We have previously reported [2,3] the density, viscosity, speed of sound and IR , studies of binary mixtures of tert-butyl acetate (tBAc) with methanol and hydrocarbons. Quantum mechanical calculations are used to address the interactions responsible for conformer stability [31]. We now present the density, viscosity, speed of sound and IR spectroscopic studies of tBAc with FB, CB and BB at 303·15 and 313·15 K.

2. EXPERIMENTAL :

2.1 Materials

Fluorobenzene, chlorobenzene (Sisco Research Lab Pvt Ltd, purity >99·5%), bromobenzene (s.d.fine chem., purity > 99%) and tert-butyl acetate (Spectrochem Pvt. Ltd, purity > 99%) were used after single distillation. The purity of the solvents, after purification, was ascertained by comparing their densities, viscosities and speed of sound with the corresponding literature values at 303·15 K and 313·15 K (Table 1). Binary mixtures were prepared by mass in air tight stoppered glass bottles. The masses were recorded on an Adairdutt balance to an accuracy of $\pm 1 \cdot 10^{-4}$ g. Care was taken to avoid evaporation and contamination during mixing. The estimated uncertainty in mole fraction was $< 1 \cdot 10^{-4}$.

2.2 Apparatus

Densities were determined by using a 15 cm^3 bicapillary pycnometer as described earlier [4]. The calibration of the pycnometer was done using conductivity water with 0·99705 $g.cm^{-3}$ as its density [5] at 298·15 K. The estimated uncertainty of density measurements of solvent and binary mixtures was 0·0001 $g.cm^{-3}$. At least four measurements were made which had an average deviation of ± 0·0001 $g.cm^{-3}$.

The dynamic viscosities were measured using an Ubbelohde suspended level viscometer [4], calibrated with conductivity water. An electronic digital stop watch with readability of ± 0·01 s was used for the flow time measurements. At least three repetitions of each data reproducible to ± 0·05 s were obtained, and the results were averaged. The uncertainties in dynamic viscosities are of the order ± 0·003 mPa.s.

The speed of sound (u) were measured at a frequency of 2 MHz in these solutions through interferometric method (using Mittal's F-81 model) at (298·15and 308·15) K (± 0·05 K). The uncertainty in speed of sound measurements is ± 0·1 %. The FTIR spectra of the above mixtures were recorded on FTIR spectrometer model SHIMADZU 8400 pc.

3. RESULTS AND DISCUSSION:

Table 2 listed experimental values of densities ρ, viscosities η and speed of sound u of mixtures at (298·15 and 308·15) K as a function of mole fraction. The density values have been used to calculate excess molar volumes V^E using the equation

$$V^E / cm^3 \cdot mol^{-1} = \left(\frac{x_1 M_1 + x_2 M_2}{\rho 12} \right) - \left(\frac{x_1 M_1}{\rho 1} \right) - \left(\frac{x_2 M_2}{\rho 2} \right) \quad (1)$$

where ρ_{12} is the density of the mixture and x_1, M_1, ρ_1, and x_2, M_2, ρ_2 are the mole fraction, the molecular weight, and the density of pure components 1and 2, respectively.

The viscosity deviations $\Delta\eta$ were calculated using the equation

$$\Delta\eta / \text{mPa.s} = \eta_{12} - x_1\eta_1 - x_2\eta_2 \quad (2)$$

where η_{12} is the viscosity of the mixture and x_1 , x_2 and η_1, η_2 are the mole fraction and the viscosity of pure components 1 and 2, respectively.

The isentropic compressibility κ_s was calculated using the Laplace relation,

$$\kappa_s = \left(\frac{1}{u^2 \rho} \right) \quad (3)$$

and the deviation from isentropic compressibility, ($\Delta\kappa_S$), was obtained by the relation,

$$\Delta\kappa_S = \kappa_{S12} - \phi_1\kappa_{S1} - \phi_2\kappa_{S2} \quad (4)$$

where κ_{S12} is the experimental isentropic compressibility of the mixture, ϕ_1, ϕ_2 and κ_{S1}, κ_{S2} are the volume fraction and isentropic compressibility of pure components. The volume fraction ϕ_i, i = 1,2. was calculated using the equation

$$\phi_i = \frac{x_i v_i^o}{x_1 v_1^o + x_2 v_2^o} \quad , i = 1, 2. \quad (5)$$

where, $v_i^0 = x_1 v_1^0 + x_2 v_2^0$, i =1, 2. (6)

and v_i^0 is the molar volume of pure components, 1 and 2.

The excess molar volumes and deviations in viscosity and isentropic compressibility were fitted to Redlich-Kister [6] equation of the type

$$Y = f_1 f_2 \sum_{i=0}^{n} a_i (f_1 - f_2)^i \quad (7)$$

Where Y is either V^E, or $\Delta\eta$, or $\Delta\kappa_S$, and n is the degree of polynomial. f_1, f_2 are mole fractions for V^E and $\Delta\eta$ and volume fraction for $\Delta\kappa_S$. Coefficients a_i were obtained by fitting equation (5) to experimental results using a least-squares regression method. In each case, the optimum number of coefficients is ascertained from an examination of the variation in standard deviation σ. Where σ was calculated using the relation

$$\sigma(Y) = \left[\frac{\sum (Y_{exp\,t} - Y_{calc})^2}{N - n} \right]^{1/2} \quad (8)$$

where 'N' is the number of data points and 'n' is the number of coefficients. The calculated values of the coefficients a_i along with the standard deviations σ are given in Table 3.

The variation of V^E with the mole fraction x_1 of tBAc for (FB),(CB), (BB) is represented in Figure 1 at 298·15K. The values of V^E are negative for all the three binary mixtures studied here. The negative values of V^E are in the order: BB > CB > FB.

The negative values of V^E indicate that there is contraction in volume during the mixing process. It signifies the presence of weak specific interactions and geometrical fitting of one component into the empty space or voids of the other component. The excess molar volumes show dependence on the temperature of measurement.

Figure 2 depicts the variation of $\Delta\eta$ with the mole fraction x_1 of tBAc. The $\Delta\eta$ values are very small and positive for all the three binary mixtures. The $\Delta\eta$ values of many organic liquids with aromatic hydrocarbons are characterised by very low (almost ideal nature) values [7-11]. The positive $\Delta\eta$ values show that there are only weak specific interactions present in the binary mixtures studied. The $\Delta\eta$ values show little or no effect of temperature.

The kinematic viscosities ($\nu = \eta / \rho$) of the binary mixtures of tBAc with FB,CB and BB have been correlated with the help of McAllister's multi body interaction models[12]. The three -body McAllister's model is defined by

$$\ln\nu = x_1^3 \ln\nu_1 + x_2^3 \ln\nu_2 + 3x_1^2 x_2 \ln\nu_{12} + 3x_1 x_2^2 \ln\nu_{21} - \ln\left[x_1 + \frac{x_2 M_2}{M_1}\right] + 3x_1^2 x_2 \ln\left[\frac{2}{3} + \frac{M_2}{3M_1}\right] + 3x_1 x_2^2 \ln\left[\frac{1}{3} + \frac{2M_2}{3M_1}\right] + x_2^3 \ln\left[\frac{M_2}{M_1}\right] \quad (9)$$

where ν_{12}, ν_{21} are interaction parameters and M_1 and M_2 are molecular weights of components 1 and 2.

The correlating ability of equations (9) was tested by calculating the percentage standard deviation (σ %) between the experimental and calculated viscosity as

$$\sigma\ \% = \left[\frac{1}{(n-m)\sum\{(100(\nu_{exptl} - \nu_{calcd})/\nu_{exptl})^2\}^{1/2}}\right] \quad (10)$$

where '*n*' represents the number of experimental points and m represents the number of coefficients.

Table 4 list the parameters for McAllister equation and percentage standard deviations.

The variation of $\Delta\kappa_s$ with mole fraction of tBAc, x_1, is represented in figure 3. The values of Δk_s for mixtures of tBAc with mole fraction, x_1 are represented in figure 3. The values of $\Delta\kappa_s$ for mixtures of tBAc with FB,CB and BB are negative which indicates that the mixtures are less compressible, and observation which is very well supported by the sign of V^E.

The negative values are in the order: BB> CB > FB. Both the components of all the binary mixtures (tBAc and halobenzenes) are polar in nature, therefore dipole-dipole interactions are present in the pure components. When a polar component (tBAc) is added to another polar components (halobenzenes), then there is a possibility that the dipole-dipole interactions between pure components (like molecules) may be disrupted and new dipole-dipole interactions may take place between unlike molecules. If this interaction is strong then $\Delta\kappa_s$ values would be negative. The negative $\Delta\kappa_s$ values indicate that these dipole-dipole interactions between unlike molecules are stronger.

The IR spectroscopic studies of these three binary mixtures were also carried out at room temperature. Instead of tabulating the frequencies of various bounds, we list only the >C=O frequencies of tBAc and C–X (halogen) frequencies in table 5. To explain the IR spectra, we calculate the difference Δν in IR frequencies at x_1= 0·5, as Δν = IR frequencies in the mixture - IR frequencies in pure component.

It is seen that the difference, Δν, in C–X is -2, -6, and -8 for fluorobenzene , chlorobenzene and bromobenzene respectively. It signifies that the strength of specific interaction is more for BB than for CB or FB. Therefore the V^E and $\Delta\kappa_s$ values are more negative for bromobenzene. Thus IR spectroscopy provides supporting evidence to observations and conclusions drawn from density and speed of sound studies.

νC=O increased up to x_1 = 0.6 and then opposite trend is recorded for tBA + FB. νC=C decreased with increases in x_1. The νAr-F decreased upto x_1=0.4 then slightly increases for others. The lone pair of electrons on fluorine atom of fluorobenzene is slightly involved in dipole-induced dipole interaction. Therefore, the magnitude of interaction is very small.

For tBA + CB, νC=O slightly increased as mole fraction of tBA increases. An irregular trend in νC=C is noted. νAr–Cl trend was not systematic. It is concluded that for tBA + chlorobenzene, νC=O is little affected by chlorine of chlorobenzene, because lone pair of electrons of chlorine interact with π- electron cloud of benzene ring.

For tBA + BB, νC=O slight increase up to x_1 = 0.7. Sharp increase in νC=C is noted at x_1 = 0.3 followed by small variations. νAr-Br decreases with increase of x_1 up to x_1= 0.5. It reveals that the lone pair of electrons on bromine atom is involved in dipole-induced dipole interaction.

The IR, spectroscopy provides supporting evidence to observations and conclusion drawn from density and speed of sound studies.

REFERENCES

1. Chandrasekhar G, Venkatesu P, Prabhakara Rao M. V, Excess Volumes and Ultrasonic Studies of n, n-Dimethyl Acetamide with Substituted Benzenes at 303·15 K. *Phys. Chem. Liq.* (2002); **40**: 181-189.
2. Hasan M, Hiray A P, Kadam U B, Shirude D F, Kurhe K J, Sawant A. B, Densities, Sound Speed and IR Studies of (Methenol + 1-Acetoxybutane) and (Methenol +1, 1-Dimethylsters) at (298·15,303·15,308·15,and 313·15) K., *J. Chem. Eng. Data*., (2010); **55**: 535- 538.
3. Hasan M, Sawant A B, Sawant R B, Loke P G, Densities, Viscosities, Speed of Sound and IR Spectroscopic Studies of Binary Mixtures of tert-Butyl Acetate with Benzene, Methylbenzene and Ethylbenzene at T= (298·15 and 308·15) K., *J. Chem.Thermodyn*., (2011);**43**:1389-1394.
4. Kadam U B Hiray A P, Sawant A B, Hasan M, Densities, Viscosities, and Ultrasonic Velocity Studies of Binary Mixtures of Trichloromethane with Methanol, Ethanol, Propan-1-ol, and Butan-1-ol at T = (298·15 and 308·15) K, *J. Chem. Thermodyn*., (2006); **38**: 1675-1683.
5. Marsh K N, Recommended Reference Materials for the Realization of physicochemical Properties, Blackwell Scientific Publication Oxford, U K (1987) . Redlich O , Kister A T, Algebraic Representation of Thermodynamic Properties and the Classification of Solutions., *Ind. Eng. Chem*., (1948); **40**: 345-348.
7. Nikam P S, Kharat S J , Densities, Viscosities, and Thermodynamic Properties of (*N*, *N*-Dimethylformamide + Benzene + Chlorobenzene) Ternary Mixtures at (298·15,303·15, 308·15, and 313·15) K., *J. Chem. Eng. Data*., (2003);**48:** 1202-1207.
8. Viswanathan S, Rao M A, Prasad D H L, Densities and Viscosities of Binary Liquid Mixtures of Anisole or Methyl tert-Butyl Ether with Benzene, Chlorobenzene, Benzonitrile, and Nitrobenzene., *J. Chem. Eng. Data*.,(2000); **45**:764-770.
9. Singh S,Sethi B P S, Katiyal R C, Rattan V K, Viscosities, Densities, and Speeds of Sound of Binary Mixtures of *o*-Xylene, *m*-Xylene, *p*-Xylene, and Isopropyl-benzene with 2-Butanone at 298.15 K., *J. Chem. Eng. Data*., (2005); **50**:125-127.
10. Varshney S., Singh M, Densities, Viscosities, and Excess Molar Volumes of Ternary Liquid Mixtures of Bromobenzene + 1,4-Dioxane + (Benzene or + Toluene or + Carbon Tetrachloride) and Some Associated Binary Liquid Mixtures., *J. Chem. Eng. Data.*,(2006); **51**:1136-1140..
11. Yang C, Xu W,Ma P, Excess Molar Volumes and Viscosities of Binary Mixtures of Dimethyl Carbonate with Chlorobenzene, Hexane, and Heptane from (293.15 to 353.15) K and at Atmospheric Pressure., *J. Chem. Eng. Data*.,(2004); **49:**1802-1808.
12. McAllister R A, The Viscosity of Liquid Mixtures**.** *AIChEJ*. (1960); **6**: 427- 431.
13. Sawant R B, Volumetric, Viscometric, and Speed of Sound Studies of Binary Mixtures of Tert-butyl Acetate with Fluorobenzene, Chlorobenzene and Bromobenzene at T=298.15 and 308.15 K., *J. Soln. Chem*.,(2018);**47**:787-795.
14. Sakurai M, Nakamura K, Nitta K, Partial molar volumes of alkyl acetates in water. *J. Chem. Eng. Data, (1996);**41**: 1171–1175.*
15. Aminabhavi T M, Aminabhavi V A, Balundgi R H, Excess properties of binary mixtures of fluorobenzene with aliphatic liquids in the temperature range 298.15–313.15 K. *Indian J. Technol*., (1991); **29**: 473–477.
16. Chandrasekhar C, Venkatesu P, Rao M V P, Excess Volumes and Ultrasonic Studies of n,n-Dimethyl Acetamide with Substituted Benzenes at 303.15 k., *Phy.Chem. Liq.*, (2002);**40**: 181-189.
17. Neruchev Y A, Bolotnikov M F, Zotov V V, Investigation of ultrasonic velocity in organic liquids on the saturation curve, *High Temperature*, (2005); **43** : 266.-309.
18. Joshi S, Aminabhavi T M, Shukla S S, Densities and Shear Viscosities of Anisole with Nitrobenzene, Chlorobenzene, Carbon tetrachloride, 1,2- Dichloroethane, and Cyclohexane from 40.degree.C,. *J. Chem. Eng. Data*., (1990); **35**: 247-253.
19. Nikam P S, Kapade V M, Hasan M, Molecular Interactions in Binary Mixtures of Chlorobenzene with Normal Alkanols (C_1- C_4) – an Ultrasonic Study, *J. Pure Appl.Ultrason*.,(2000); **22**: 16-20.
20. Venkatesulu D, Rao M V P, Isentropic Compressibilities of Binary Mixtures of Methylcyclohexane with Substitutd Benzenes and Cyclohexane, *Asian J. Chem*,1992), **4 (3):** 452- 456.
21. Krishna K M, Rambhau K, Venkateswarlu, Raman G K, Excess volumes and Speed of Sound of Ternary Mixtures of 2-Methoxyethanol (1)+Butyl Acetate (2)+Aromatic Hydrocarbons (3) at 303.15 K, *J. Chem. & Eng. Data*.,(1995) ;**40(1):**128-131.
22. Ali A,Nain A K, Chand D, Lal B, Molecular interactions in binary mixtures of anisole with benzyl chloride,

chlorobenzene and nitrobenzene at 303.15 K: An ultrasonic, volumetric, viscometric and refractive index study, *IJC-A* (2005); **44 A (03)**: 511-515.
23. Reddy K S, Isentropic compressibilities of binary liquid mixtures at 303.15 and 313.15 K, *J. Chem. Eng. Data*, (1986); **31**: 238-240.
24. Aminabhavi T M , Aminabhavi V A , Joshi S S, Balundgi R H, Excess properties of some binary liquid mixtures in temperature range 298.15–313.15 K. *Indian J. Technol*., (1991); **29**: 545–557.
25. Nigam R K, Singh P P, Viscosity and Molecular Interaction in Binary Mixtures of Benzene and Tolune with Chloro-, and Bromobenzene, *Indian J. Chem*., (1971); **9**: 671- 691.
26. Singh R P, Sinha C P, Viscosities and activation energies of viscous flow of the binary mixtures of n-hexane with toluene, chlorobenzene and 1-hexanol, *J. Chem. Eng. Data*.,(1984); **29**: 132-135.
27. Muhammad G S, Balkrishnan R, Rajsekaran J. F, Ultrasonic Studies on HTPB in Chlorobenzene. *J. Pure Appl. Ultrason*., (1999); 21: 71-74.
28. Nikam P S, Kapade V M, Hasan M, Molecular interactions in binary mixtures of bromobenzene with normal alkanols (C1–C4): an ultrasonic study, *Indian J.Pure Appl. Phys.* (2000); **38**:170–173.
29. Oswal S L, Kotiya A G, Pandya M V, Density and Excess Volumes for Binary Solution of Tetrahydrofuran with Methyl Cyclohexane, Chlorobenzene, Bromo-benzene, Toluene, Ethylbenzene and Acetonitrle., *Indian J. Chem*., (1979);**17**:605-607.
30. Singh R P, Sinha C P, Das J C, Ghosh P, Viscosity and density of ternary mixtures for toluene, ethylbenzene, bromobenzene, and 1-hexanol, *J. Chem. Eng. Data.*, (1989); **34(3)**: 335-338.
31. Miller L, Carman P C, Self-diffusion in mixtures. Part-2 Simple binary mixtures. *Trans. Faraday Soc.*, (1959) **35** :1831–1837.
32. Sastry N V, Thakkor R R, Patel N C, Excess molar volumes, viscosity deviations, excess isentropic compressibilities and deviations in relative permittivities of (alkyl acetates (methyl, ethyl, butyl and isoamyl) + n-hexane, + benzene, + toluene, + (o-, m-, p-) xylenes, + (chloro-, bromo-, nitro-) benzene at temperatures from 298.15 to 313.15 K, *J. Mol. Liq*., (2009); **144**: 13-22.

Table 1. Comparison of experimental density, viscosity and speed of sound of pure liquids with literature values at 303·15 and 313·15K.

Liquid	Tempt	$\rho \times 10^{-3}$ kg.m^{-3}		η (mPa.s)		u (m.s^{-1})	
	K	Expt	Lit	Expt.	Lit	Expt.	Lit.
tert-butyl acetate	303.15	0.8551	-	0.637	-	1080	-
	313.15	0.8386	0.83807 [a]	0.563		1040	-
			1.0123 [b]				1171 [c]
Fluorobenzene	303.15	1.0118	1.013 [c]	0.540	0.5501 [b]	1152	1143.5 [d]
	313.15	0.9992	1.0001 [74]	0.490	0.4910 [b]	1112	1102.9 [d]
			1.0955 [e]				
			1.0949 [f]				
			1.09546 [g]				
Chlorobenzene	303.15	1.0951	1.095 [c]	0.719		1260	1253 [f]
			1.09552 [h]		0.7155 [e]		1253 [n]
			1.0956 [i]		0.716 [l]		1251.7 [i]
			1.09550 [j]		0.7148 [i]		1251 [g]
			1.0951 [k]		0.7184 [m]		1249 [c]
			1.0844 [e]		0.6370 [e]		1206 [j]
	313.15	1.0847	1.08468 [j]	0.639	0.6469 [m]	1216	1222 [n]
			1.0840 [k]				1215 [b]
			1.481569 [h]		0.982 [l]		1137.6 [d]
			1.48150 [j]		0.9850 [q]		1137 [c]
Bromobenzene	303.15	1.4809	1.4817 [o]	0.986	0.985 [r]	1140	1146 [j]
			1.481 [c]		1.0045 [k]		1138.5 [o]
			1.4816 [h]				
			1.4820 [p]				
			1.46803 [40]				1109 [j]
	313.15	1.4672	1.4679 [75]	0.913	0.8883 [75]	1112	1106.4 [d]
			1.467088 [87]				

a Ref 14, b Ref 15, c Ref16,d Ref17, e Ref18,f Ref 19, g Ref 20, h Ref 21, i Ref 22, j Ref 23, k Ref 24, l Ref 25, m Ref 26, n Ref 27, o Ref 28, p Ref 29, q Ref 30,

Table 2 :- Density (ρ), Viscosity (η), Excess Molar Volume (V^E), Deviation in Viscosity (Δη), Speed of Sound (u), Isentropic compressibility (κ_s) and Excess Isentropic ($\Delta\kappa_s$) for (tBAc) (1) FB, + CB, + BB, (2).

x_1	$\rho \cdot 10^{-3}$/ (kg· m^{-3})	$V^E \cdot 10^6$/ ($m^3 \cdot mol^{-1}$)	η / mPa·s	Δη /mPa·s	u /m·s^{-1}	κ_s /TPa^{-1}	$\Delta\kappa_s$ /TPa^{-1}
tBAc (1) + fluorobenzene (2) at 303·15 K							
0.0000	1.0118	0.000	0.540	0.000	1152	745	0
0.0980	0.9918	-0.107	0.560	0.010	1147	766	-14
0.1982	0.9725	-0.153	0.577	0.018	1141	790	-22
0.2990	0.9543	-0.180	0.590	0.021	1134	815	-28
0.3978	0.9375	-0.201	0.601	0.022	1128	838	-30
0.4993	0.9213	-0.202	0.610	0.022	1118	868	-29
0.5995	0.9063	-0.173	0.617	0.019	1109	897	-26
0.6997	0.8922	-0.129	0.623	0.015	1102	923	-20
0.7994	0.8790	-0.090	0.628	0.010	1093	952	-12
0.8977	0.8669	-0.036	0.632	0.005	1086	978	-6
1.0000	0.8551	0.000	0.637	0.000	1080	1003	0
tBAc (1) + fluorobenzene (2) at 313·15 K							
0.0000	0.9992	0.000	0.490	0.000	1112	809	0
0.0980	0.9789	-0.146	0.506	0.009	1109	831	-18
0.1982	0.9591	-0.225	0.519	0.015	1105	854	-32
0.2990	0.9405	-0.279	0.530	0.018	1098	882	-38
0.3978	0.9233	-0.294	0.538	0.019	1091	910	-42
0.4993	0.9066	-0.269	0.544	0.018	1083	940	-42
0.5995	0.8912	-0.233	0.549	0.015	1074	973	-36
0.6997	0.8767	-0.176	0.553	0.012	1065	1006	-29
0.7994	0.8632	-0.116	0.557	0.009	1057	1037	-22
0.8977	0.8504	-0.004	0.560	0.004	1050	1067	-14
1.0000	0.8386	0.000	0.563	0.000	1040	1102	0
tBAc (1) + chlorobenzene (2) at 303·15 K							

0.0000	1.0951	0.000	0.719	0.000	1260	575	0
0.0993	1.0659	-0.132	0.723	0.012	1233	617	-12
0.1990	1.0378	-0.205	0.722	0.019	1211	657	-24
0.2993	1.0108	-0.23	0.719	0.025	1188	701	-28
0.3984	0.9853	-0.251	0.712	0.026	1169	743	-32
0.4982	0.9609	-0.248	0.703	0.025	1151	786	-32
0.5984	0.9375	-0.206	0.692	0.022	1135	828	-31
0.6995	0.9151	-0.185	0.679	0.017	1119	873	-25
0.7989	0.8941	-0.125	0.665	0.012	1105	916	-19
0.8992	0.8742	-0.071	0.652	0.007	1092	959	-11
1.0000	0.8551	0.000	0.637	0.000	1080	1003	0

tBAc (1) + chlorobenzene (2) at 313·15 K

0.0000	1.0847	0.000	0.639	0.000	1216	623	0
0.0993	1.0547	-0.160	0.641	0.010	1193	666	-18
0.1990	1.0258	-0.258	0.641	0.017	1170	712	-30
0.2993	0.9980	-0.305	0.637	0.021	1149	759	-38
0.3984	0.9718	-0.311	0.631	0.022	1130	806	-42
0.4982	0.9467	-0.289	0.622	0.021	1113	853	-43
0.5984	0.9228	-0.252	0.612	0.018	1096	902	-40
0.6995	0.8998	-0.182	0.600	0.014	1081	951	-34
0.7989	0.8785	-0.128	0.588	0.010	1067	1000	-26
0.8992	0.8580	-0.053	0.576	0.005	1053	1051	-14
1.0000	0.8386	0.000	0.563	0.000	1040	1102	0

tBAc (1) + bromobenzene (2) at 303·15 K

0.0000	1.4809	0.000	0.987	0.000	1140	520	0
0.0988	1.4061	-0.176	0.958	0.004	1134	553	-27
0.1987	1.3336	-0.250	0.926	0.007	1127	590	-46

0.2971	1.2649	-0.290	0.894	0.010	1119	631	-59
0.3970	1.1981	-0.310	0.859	0.014	1110	677	-64
0.4986	1.1332	-0.311	0.823	0.011	1102	727	-64
0.5977	1.0728	-0.251	0.786	0.01	1095	777	-60
0.6894	1.0193	-0.222	0.752	0.009	1089	827	-50
0.7970	0.9597	-0.151	0.712	0.005	1085	885	-38
0.8972	0.9067	-0.033	0.674	0.002	1081	944	-19
1.0000	0.8551	0.000	0.637	0.000	1080	1003	0

tBAc (1) + bromobenzene (2) at 313.15K

0.0000	1.4672	0.000	0.913	0.000	1112	551	0.00
0.0988	1.3919	-0.223	0.884	0.006	1105	588	-18.47
0.1987	1.3186	-0.355	0.852	0.009	1095	632	-36.71
0.2971	1.2494	-0.418	0.819	0.010	1085	680	-50.28
0.3970	1.1822	-0.425	0.807	0.033	1075	732	-59.12
0.4986	1.1169	-0.379	0.747	0.009	1066	788	-62.26
0.5977	1.0562	-0.303	0.711	0.007	1059	844	-59.11
0.6894	1.0028	-0.242	0.677	0.005	1052	901	-53.07
0.7970	0.9430	-0.146	0.638	0.004	1047	967	-38.96
0.8972	0.8901	-0.058	0.601	0.002	1043	1033	-21.77
1.0000	0.8386	0.000	0.563	0.000	1040	1102	0.00

Table 3. Parameters and standard deviation σ of equations (7) and (8) for (tBAc) + FB,+ CB, + BB, at 303·15 and 313·15 K and p = 0.089MPa.

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standard deviations	T/K	a_0	a_1	a_2	σ
tBAc + fluorobenzene					
V^E/(cm^3·mol^{-1})	303·15	-0.8059	0.5091	0.0275	0.003
	313·15	-1.1286	0.8142	0.3740	0.018
$\Delta\eta$ /(mPa·.s)	303·15	0·0868	-0·0382	-0.0035	0·0004
	313·15	0·0715	-0·0352	0.0035	0·0004
$\Delta\kappa_s$ /(TPa^{-1})	303·15	-115.3514	56.1404	10.0433	0.903
	313·15	-160.9537	42.2585	-23.9816	1.1262
tBAc + chlorobenzene					
V^E/(cm^3·mol^{-1})	303·15	-1.2531	0.6029	-0.0457	0.005
	313·15	-1.5222	0.7256	-0.0505	0.004
$\Delta\eta$ /(mPa·.s)	303·15	0·0985	-0·0379	0·0076	0·0006
	313·15	0·0835	-0·0037	-0·0161	0·0003
$\Delta\kappa_s$ /(TPa^{-1})	303·15	-129.6961	15.1562	10.33	0.8642
	313·15	-170.5105	26.1287	-11.3656	0.308
tBAc + bromobenzene					
V^E/(cm^3·mol^{-1})	303·15	-1.2531	1.0251	0.0914	0.007
	313·15	-1.5222	1.1497	-0.0771	0.005
$\Delta\eta$ /(mPa·.s)	303·15	0·0409	-0·0322	-0·0028	0·0005
	313·15	0·0566	-0·0368	-0·0282	0·0071
$\Delta\kappa_s$ /(TPa^{-1})	303·15	-258.341	55.8318	2.6555	0.7984
	313·15	-294.769	52.5014	-15.521	0.6551

Standard uncertainties u are u(p) = 4 kPa, u(T) = 0.02 K and combined expanded uncertainties Uc are Uc(ρ) = 1× 10^{-3} g.cm-3 and Uc(V^E) = 0.04 m3.mol^{-1}

Table 4. Interaction parameters of McAllister model and standard deviations σ at 303·15 and 313·15 K.

System	T/K	McAllister		
		v_{12}	v_{21}	σ
tBAc + fluorobenzene	303·15	0·695	0·656	0·12
	313·15	0·629	0·594	0·08
tBAc + chlorobenzene	303·15	0.748	0.739	0.07
	313·15	0.672	0.662	0.05
tBAc + bromobenzene	303·15	0.749	0.724	0.13
	313·15	0.691	0.677	0.63

Table 5 . FTIR stretching frequency (cm^{-1}) of tBAc (x_1) FB, CB and BB, (1-x_1).

tBAc (x_1) + FB (1-x_1)				**tBAc (x_1) + CB (1-x_1)**			**tBAc (x_1) + BB (1-x_1)**		
x_1	**νC=O**	**νC=C**	**νAr-F**	**νC=O**	**νC=C**	**νAr–Cl**	**νC=O**	**νC=C**	**νAr-Br**
0·0	-	1495 (s) 1597 (s)	1223	-	1468 (s) 1580 (s)	1082	-	1462 (s) 1576 (s)	1069
0·3	1734 (s)	1495 (s) 1595 (s)	1221	1728 (s)	1464 (s) 1580 (m)	1084	1732 (s)	1474 (m) 1578 (m)	1069
0·4	1734 (s)	1495 (s) 1456 (s) 1597 (s)	1219	1730 (s)	1466 (s) 1574 (m)	1088	1732 (s)	1462 (m) 1576 (m)	1063
0·5	1736 (s)	1493 (s) 1458 (s) 1595 (s)	1221	1730 (s)	1468 (s) 1580 (m)	1076	1734 (s)	1464 (m) 1576 (m)	1061
0·6	1738 (s)	1493 (s)	1221	1730 (s)	1464 (m)	1080	1734 (s)	1464 (m)	1065

		1458 (s)			1582 (w)			1578 (m)	
		1597 (s)							
0·7	1736 (s)	1491 (m)	1223	1734 (s)	1458 (m)	1074	1734 (s)	1466 (m)	1061
		1458 (m)			1576 (w)			1576 (w)	
		1595 (m)							
1·0	1732 (s)	-	-	1732 (s)	-	-	1732 (s)	-	-

Figures:

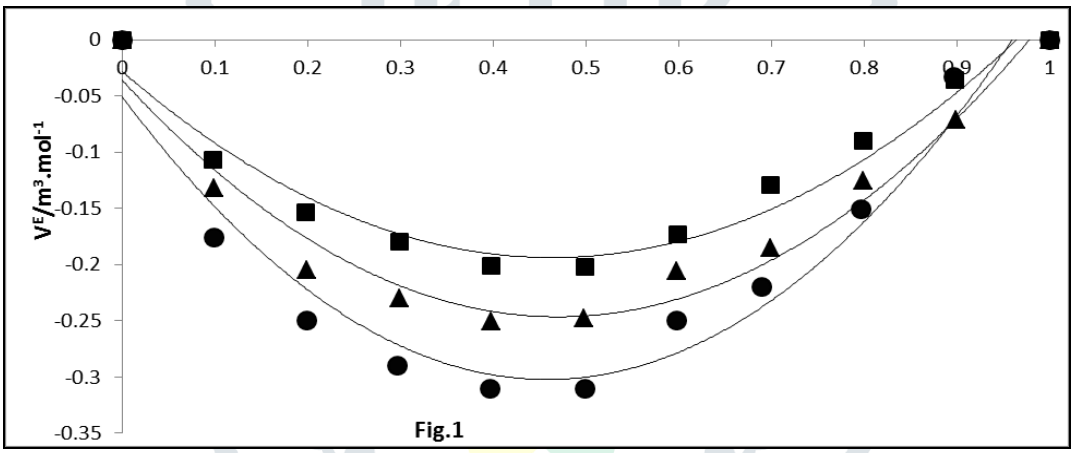

Figure 1. Excess molar volumes V^E at 303·15 K for (x_1) tBAc + (1-x_1) Benzenes:
■ fluorobenzene; ▲ chlorobenzene; ● bromobenzene;.

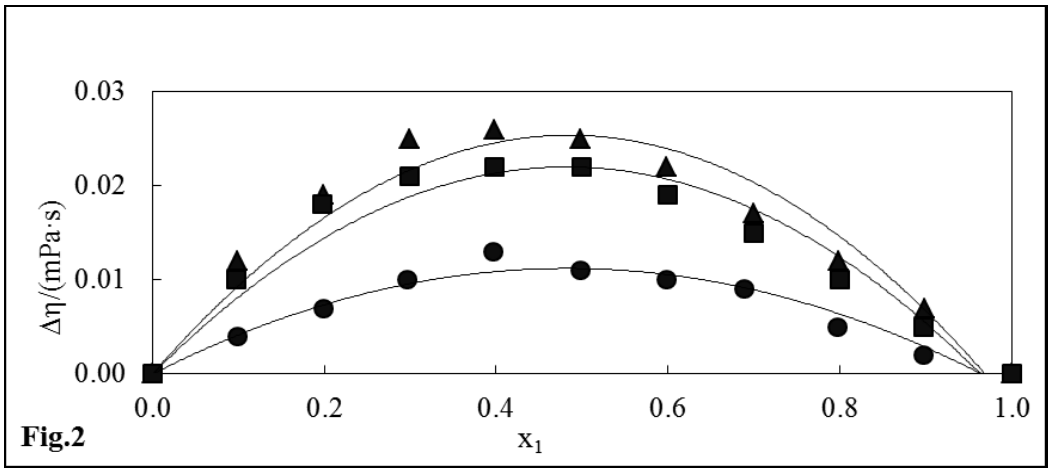

Figure 2. Deviations in viscosity ($\Delta\eta$) at 303·15 K for (x_1) tBAc + (1-x_1) Benzenes:
■ fluorobenzene; ▲ chlorobenzene; ● bromobenzene;.

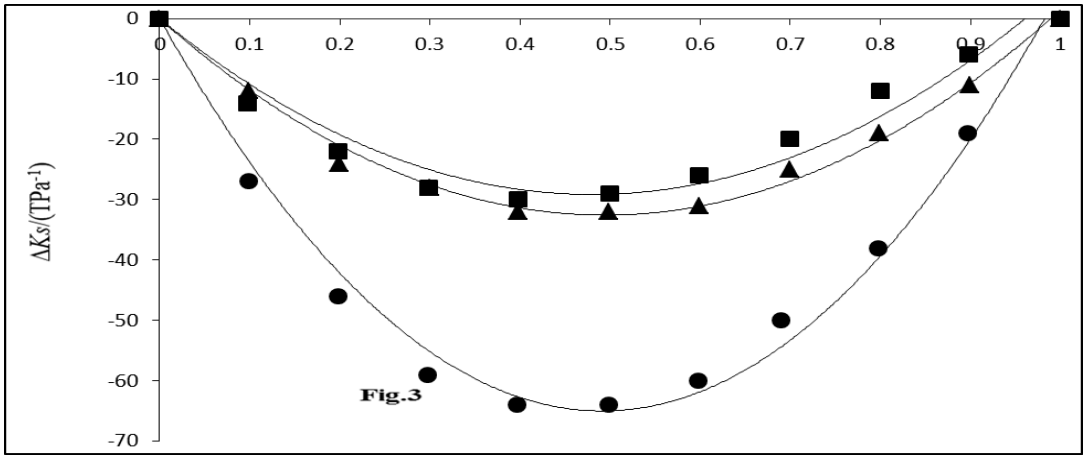

Figure 3. Excess isentropic compressibility (s) at 303·15 K for (ϕ_1) tBAc + (1- ϕ_1) Benzenes: ■ fluorobenzene; ▲ chlorobenzene; ● bromobenzene.