

Physico-chemical properties of binary mixtures of tert-butanol with (nitro-, chloro- and bromo-) benzene at 303.15 K and 308.15 K

Balwinder Saini#, Renu Sharma & Rajinder K Bamezai*

Department of Chemistry, University of Jammu, Jammu 180 006, India

#Department of Chemistry, Lovely Professional University, Jalandhar 144 411, India

*E-mail: rkb10@rediffmail.com

Received 23 August 2014; revised 23 January 2015; accepted 4 August 2015

The density (ρ), viscosity (η) and speed of sound (u) of three binary liquid mixtures of tert-butanol with (nitro-, chloro- and bromo-) benzene have been measured over the entire composition range at 303.15 K, 308.15 K and atmospheric pressure. From the experimental data, excess molar volume (V^E), isentropic compressibility (κ_s), excess Gibbs free energy of activation (ΔG^{*E}), deviation parameters like viscosity ($\Delta\eta$), speed of sound (Δu) and isentropic compressibility ($\Delta\kappa_s$) are obtained. These functions have been fitted to Redlich-Kister polynomial equation to derive the coefficients and standard deviations.

Keywords: Isentropic compressibility, Excess molar volume, Excess Gibbs free energy of activation, Speed of sound

1 Introduction

The ultrasonic behaviour, coupled with the measurement of density and speed of liquids, facilitates the understanding of the physical properties of liquid state. These physical properties form the basis for calculating the excess thermodynamic functions and the data, thus, accumulated may be interpreted in terms of the strength of specific and non-specific interaction¹⁻⁵, amongst the components of selected mixtures.

Although a number of investigations have been conducted on these properties using binary liquids, comprising different alcohols and/or mono substituted benzene⁶⁻¹¹, there seems to have been no report on the physico-chemical properties of binary systems which involve tert-butanol (TB) and (nitro-, chloro- and bromo) benzene, abbreviated as NB, CB and BB, respectively. Therefore, an attempt has been made to investigate the systems involving TB with NB, CB and BB to gather information about the nature of molecular interaction and the effect of substituent on the benzene ring, have been investigated. In view of this, the densities (ρ), viscosities (η) and speeds of solution (u) for the binary solutions TB-NB, TB-CB and TB-BB are measured covering the entire mole fraction range at 303.15 K and 308.15 K.

2 Experimental Details

The materials used in this work, TB, NB, CB and BB, with a stated purity of 99 % were purchased from

Sigma Aldrich Chemicals, India. TB was dried by refluxing with the fused calcium oxide for about ten hours and then distilled. CB, BB and NB were also dried prior to its use. The purity of these liquids was checked by comparing their density (ρ), viscosity (η) and speed (u) values which agreed well with the available literature (Table 1).

The known masses of pure liquids were taken in an airtight stopper bottles which were thoroughly homogenized. Each solution prepared, in this way, was divided into three parts for measuring density, viscosity and speed of sound. The extra precaution was taken during measurements, to prevent losses due to evaporation. The possible error in mole fraction was estimated to be $\pm 10^{-4}$. The densities of solutions were measured using bicapillary pycnometer which was calibrated using triply distilled water. Each reported density data was an average of at least four measurements. The uncertainty during the measurement was $\pm 2 \times 10^{-5} \text{ g cm}^{-3}$.

The viscosity of solvents and the experimental solutions were measured at 303.15 K and 308.15 K at atmospheric pressure using Ubbelohde viscometer calibrated by measuring the flow time (t) with triply distilled water, distilled benzene and cyclohexane. The viscometer was filled with experimental solution and, after attaining the thermal equilibrium, the efflux time of flow of solution was made using an electronic stopwatch with an accuracy of $\pm 0.01 \text{ s}$. The reported

Table 1 — Densities (ρ), viscosities (η) and speeds of sound (u) for pure components at 303.15 K and 308.15 K

Component	T (K)	ρ (g cm ⁻³)		η (mPa s)		u (m s ⁻¹)	
		Exp.	Lit.	Exp.	Lit.	Exp.	Lit.
Tert-butanol	303.15	0.77520	0.77521 ¹²	3.383	3.390 ¹³	1124.0	1124.0 ¹⁴
	308.15	0.76990	0.76997 ¹²	2.588	2.589 ¹³	1108.0	---
Nitrobenzene	303.15	1.19292	1.19340 ¹⁵	1.617	1.619 ¹⁵	1438.0	1438.0 ¹⁷
	308.15	1.18921	1.18830 ¹⁶	1.551	1.554 ²¹	1422.0	1423.0 ¹⁷
Chlorobenzene	303.15	1.09552	1.09500 ⁹	0.720	0.725 ⁹	1249.0	1249.0 ¹⁷
	308.15	1.09100	1.09000 ⁹	0.686	0.683 ⁹	1235.0	1235.0 ¹⁷
Bromobenzene	303.15	1.48110	1.48119 ⁹	1.014	1.013 ⁹	1136.0	1137.0 ¹⁷
	308.15	1.47292	1.47300 ⁹	0.952	0.953 ⁹	1122.0	1121.0 ¹⁷

value was an average of at least three measurements. The uncertainty in the measurement of viscosity was ± 0.003 mPa s.

The speed of sound of solutions was measured with the help of multi-frequency ultrasonic interferometer (M-82, Mittal Enterprises, India) at 4 MHz having an uncertainty of ± 0.5 ms⁻¹ in speed. A thermostatically controlled well-stirred water bath whose temperature was controlled to ± 0.2 K was used for all the measurements.

3 Results and Discussion

The experimentally determined values for density (ρ), viscosity (η) and speed of sound (u) for various binary constituents at 303.15 K and 308.15 K are presented in Table 2. The experimental data was used for calculating various thermodynamic parameters, namely, excess molar volume (V^E), deviation in viscosity ($\Delta\eta$), excess Gibbs free energy of activation (ΔG^{*E}), isentropic compressibility (κ_s), deviation in speed of sound (Δu) and deviation in isentropic compressibility ($\Delta\kappa_s$). The deviation from ideal behaviour of the functions, which depends upon sign and magnitude of the functions, has a bearing on the intermolecular interaction between the components of each mixture. The numeric value of aforementioned excess functions was calculated using various equations discussed below.

3.1 Excess Molar Volume

The excess molar volume (V^E) of each of the two component liquid mixtures, under present investigation, was calculated from experimental determined density of mixture (ρ_m) and density (ρ_i), mole fraction (x_i) and molar masses (M_i) of pure components (i), using Eq. (1).

$$V^E = [(M_1 x_1 + M_2 x_2)/\rho_m] - [(M_1 x_1/\rho_1) + (M_2 x_2/\rho_2)] \quad \dots (1)$$

The V^E value for the binary liquid mixtures of TB + (NB, CB and BB) is shown in Fig. 1 at 303.15 K. The

Table 2 — Densities (ρ), viscosities (η) and speeds of sound (u) for the binary mixture at 303.15 K and 308.15 K

x_1	ρ (g cm ⁻³)	η (mPa s)	u (m s ⁻¹)
Nitrobenzene + tert-butanol			
$T = 303.15$ K			
0.0000	0.77520	3.383	1124.0
0.0931	0.81798	3.120	1161.2
0.2069	0.86981	2.802	1201.8
0.3032	0.91392	2.527	1234.4
0.4011	0.95784	2.284	1267.1
0.5005	1.00136	2.089	1299.4
0.6013	1.04385	1.943	1330.4
0.7039	1.08529	1.838	1361.1
0.8032	1.12397	1.763	1389.8
0.9141	1.16399	1.668	1418.6
1.0000	1.19292	1.617	1438.0
$T = 308.15$ K			
0.0000	0.76990	2.588	1108.0
0.0931	0.81288	2.404	1145.4
0.2069	0.86516	2.167	1186.5
0.3032	0.90964	1.963	1220.8
0.4011	0.95340	1.792	1254.1
0.5005	0.99760	1.669	1285.9
0.6013	1.04063	1.596	1316.4
0.7039	1.08167	1.577	1347.2
0.8032	1.12044	1.567	1375.0
0.9141	1.16016	1.562	1404.2
1.0000	1.18921	1.551	1422.0
Chlorobenzene + tert-butanol			
$T = 303.15$ K			
0.0000	0.77520	3.383	1124.0
0.0940	0.80894	3.046	1139.3
0.2084	0.84893	2.626	1157.2
0.3051	0.88271	2.261	1172.4
0.4033	0.91553	1.928	1186.7
0.5028	0.94783	1.649	1200.0
0.6036	0.97940	1.408	1211.7
0.7059	1.01049	1.215	1221.4
0.8096	1.04133	1.035	1230.5
0.9149	1.07189	0.864	1240.6
1.0000	1.09552	0.720	1249.0
$T = 308.15$ K			
0.0000	0.76990	2.588	1108.0
0.0940	0.80373	2.334	1124.4
0.2084	0.84379	1.995	1142.6
0.3051	0.87754	1.709	1158.8

Contd—

Table 2 — Densities (ρ), viscosities (η) and speeds of sound (u) for the binary mixture at 303.15 K and 308.15 K — *Contd*

x_1	ρ (g cm ⁻³)	η (mPa s)	u (m s ⁻¹)
Chlorobenzene + tert-butanol $T = 308.15$ K			
0.4033	0.91035	1.453	1173.4
0.5028	0.94269	1.251	1186.6
0.6036	0.97445	1.082	1197.8
0.7059	1.00561	0.963	1208.0
0.8096	1.03661	0.865	1225.0
0.9149	1.06730	0.772	1227.9
1.0000	1.09100	0.686	1235.0
Bromobenzene + tert-butanol $T = 303.15$ K			
0.0000	0.77520	3.383	1124.0
0.0912	0.84761	3.065	1131.8
0.2031	0.93425	2.677	1136.7
0.2983	1.00745	2.346	1141.0
0.3955	1.07967	2.041	1143.9
0.4948	1.15122	1.781	1145.8
0.5959	1.22154	1.573	1146.1
0.6992	1.29103	1.354	1145.3
0.8046	1.35981	1.265	1143.2
0.8905	1.41423	1.163	1141.8
1.0000	1.48110	1.014	1136.0
$T = 308.15$ K			
0.0000	0.76990	2.588	1108.0
0.0912	0.84212	2.343	1116.8
0.2031	0.92845	2.042	1122.4
0.2983	1.00168	1.785	1126.7
0.3955	1.07367	1.549	1129.6
0.4948	1.14471	1.363	1131.5
0.5959	1.21461	1.231	1131.8
0.6992	1.28375	1.113	1131.4
0.8046	1.35222	1.069	1129.7
0.8905	1.40636	1.029	1128.3
1.0000	1.47292	0.952	1122.0

observed excess molar volume values in all the mixtures were found to be negative. The V^E values of TB and mono substituted benzene at mole fractions greater than 0.4 follow the negative order as TB + (NB > BB > CB). The nature of V^E curves for the mixtures at both the temperatures is almost identical. However, V^E values show a decrease with rise in temperature.

The observed V^E values, in the present investigation, may be discussed in terms of several effects which may be divided into physical, chemical and geometrical ones¹⁸. The physical interactions between the components of a binary mixture involving mainly dispersion forces, contribute positively to V^E . On the other hand, the chemical interactions between the constituents of the mixture result in the decrease in volume. This implies that the specific interactions between TB and NB molecules which are expected to be of dipole-dipole interactions,

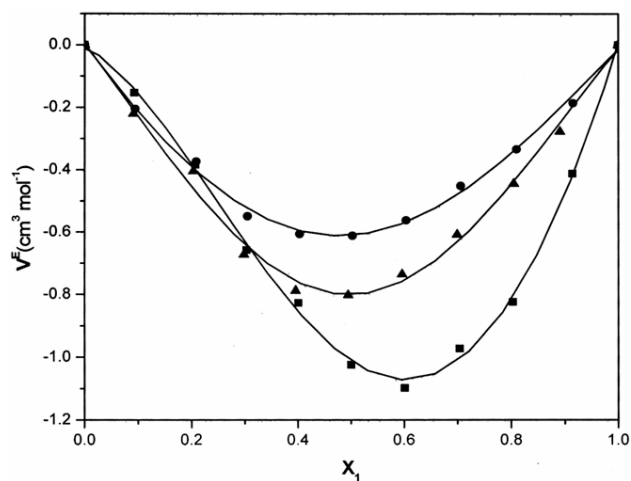


Fig. 1 — Plot of excess molar volume versus mole fraction of tert-butanol with (■) nitrobenzene, (●) chlorobenzene and (▲) bromobenzene at 303.15 K; (—) Redlich Kister equation

involving hydrogen bonds, may be responsible for the negative V^E . However, in case of TB and BB, the negative contribution to V^E may be attributed to the structural contributions arising from the geometrical fitting as a consequence of delocalized Π – orbitals of one component with the polar bond of TB. Also in case of TB and CB, V^E values are less negative probably because of the competitive inductive and mesomeric effects operating in CB, hence weakened Π -polar effects leading to decrease in the geometrical contribution.

3.2 Deviation in Viscosity

The experimental determined values of viscosity (η) for binary liquid mixtures of different compositions are displayed in Table 2. The deviation in viscosity ($\Delta\eta$), calculated by using Eq. (2), and its dependence on the mole fraction for various systems, is graphically shown in Fig. 2.

$$\Delta\eta = \eta_m - (x_1 \eta_1 + x_2 \eta_2) \quad \dots (2)$$

where η_m , η_1 and η_2 represent viscosities of mixture and respective solvents.

It is observed that $\Delta\eta$ values are quite negative for all the binary mixtures over the complete composition range at both temperatures. This may be attributed to the hetero-association between unlike molecules. The most negative values correspond to the system TB + BB and the least negative to the system TB + CB. A similar behaviour for viscosity deviation is seen at higher temperature. Further, $\Delta\eta$ values decrease as the

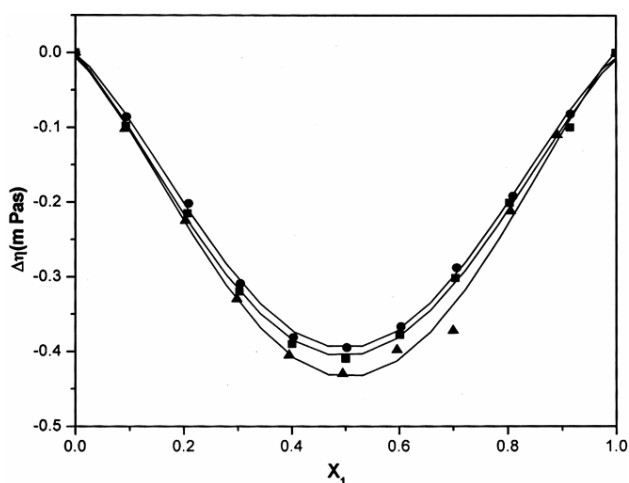


Fig. 2 — Plot of deviation in viscosity versus mole fraction of tert-butanol with (■) nitrobenzene, (●) chlorobenzene and (▲) bromobenzene at 303.15 K; (—) Redlich Kister equation

molecular mass of the variable component (BB > NB > CB) is increased. As expected, the $\Delta\eta$ values decrease, with an increase in temperature, inferring thereby that an increment of temperature diminishes the self association of the pure components.

3.3 Excess Gibbs Free Energy of Activation

The excess Gibbs free energy of activation (ΔG^{*E}) for the components of binary mixture are calculated using Eq. (3).

$$\Delta G^{*E} = RT [\ln(\eta_m V) - x_1 \ln(\eta_1 V_1) - x_2 \ln(\eta_2 V_2)] \quad \dots (3)$$

where V gives molar volume of the mixture; while V_1 and V_2 stand for volume of respective solvents. The values are represented graphically in Fig. 3. The values of ΔG^{*E} have been found to be positive over entire range of mole fraction for all binary mixtures. The positive ΔG^{*E} , with the increase of the mole fraction of one component of the mixture, shows an increasing trend up to a specific concentration, beyond which ΔG^{*E} decreases. The maximum value of ΔG^{*E} has been observed at ~0.5 mole fraction at lower temperatures and at ~0.4 mole fraction at higher temperatures. The specific interactions like hydrogen bonding¹⁴, charge transfer between dissimilar molecules in comparison to the like molecules may be the contributing factors to the positive values of ΔG^{*E} . As the temperature increases, values of ΔG^{*E} decrease for all three binary mixtures.

3.4 Deviation in speed of sound and isentropic compressibility

The deviation in speed of sound, Δu , is calculated with the help of Eq. (4).

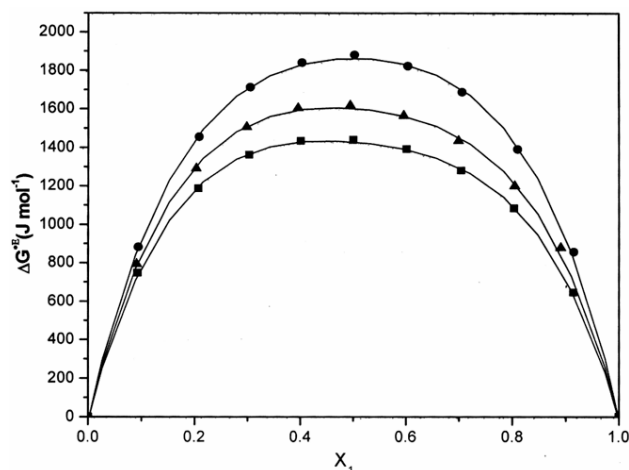


Fig. 3 — Plot of excess Gibbs free energy of activation versus mole fraction of tert-butanol with (■) nitrobenzene, (●) chlorobenzene and (▲) bromobenzene at 303.15 K; (—) Redlich Kister equation

$$\Delta u = u_m - (x_1 u_1 + x_2 u_2) \quad \dots (4)$$

where u_m , u_1 and u_2 denote speed of sound of mixture and two solvents. Once the components are mixed, the variation of speed in solution relies upon changes (increase or decrease) of intermolecular free length. It was proposed by Eyring and Kincaid¹⁹ that, due to mixing of components, the speed should increase if the intermolecular free length decreases. This is observed in the current investigation for all the three binary systems. The data for u is presented in Table 2 and dependence of Δu on the mole fraction for various systems is shown in Fig. 4 at 303.15 K. The magnitude of Δu increases with the increase in temperature from 303.15 K to 308.15 K.

The isentropic compressibility, κ_s , for the systems was obtained using Eq. (5) while its deviation, $\Delta\kappa_s$, was calculated using Eq. (6).

$$\kappa_s = (u^2 \rho)^{-1} \quad \dots (5)$$

$$\Delta\kappa_s = \kappa_s^{\text{mix}} - \sum x_i \kappa_{si} \quad \dots (6)$$

where superscript mix and subscript i in κ_s refer to isentropic compressibility of mixture and i th species ($i = 1$ and 2). Figure 5 shows variation of isentropic compressibility with respect to mole fraction at 303.15 K. As seen from the figure, the negative values at the minimum of these curves vary in the sequence: TB + (NB > BB > CB). The negative value of $\Delta\kappa_s$, over the entire range of mole fractions, in all

the three systems, plays a vital role in assessing the compactness due to molecular interactions leading mixtures to be less compressible than the corresponding ideal mixtures. This accounts for

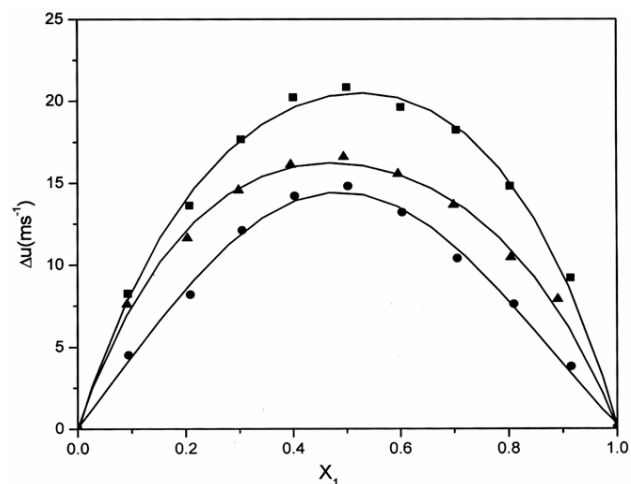


Fig. 4 — Plot of deviation in speed of sound versus mole fraction of tert-butanol with (■) nitrobenzene, (●) chlorobenzene and (▲) bromobenzene at 303.15 K; (—) Redlich Kister equation

the existence of specific molecular interactions and interstitial accommodation due to differences in molar volumes of individual components. As the temperature increases, the value of $\Delta\kappa_s$ decreases in all the binary mixtures.

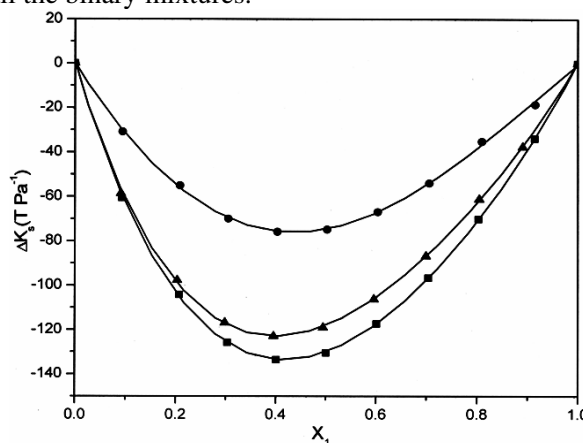


Fig. 5 — Plot of deviation in isentropic compressibility versus mole fraction of tert-butanol with (■) nitrobenzene, (●) chlorobenzene and (▲) bromobenzene at 303.15 K; (—) Redlich Kister equation

Table 3 — Least-square coefficients and standard deviation of Eqs. (7) and (8) at different temperatures

Binary system	Excess function	Temp (K)	A_0	A_1	A_2	A_3	A_4	σ
Nitrobenzene + tert- butanol	V^E ($\text{cm}^3 \text{mol}^{-3}$)	303.15	1.908	0.759	-0.506	-0.165	1.084	0.013
		308.15	-4.064	-2.335	1.175	0.253	-0.619	0.043
	$\Delta\eta$ (m Pas)	303.15	-1.649	0.114	1.288	-0.271	-0.918	0.004
		308.15	-1.605	0.137	1.314	-0.207	-0.642	0.004
	ΔG^{*E} (J mol^{-1})	303.15	5767	-405	3055	-340	1579	2.55
		308.15	5141	-384	3638	109	1705	10.89
	Δu (m s^{-1})	303.15	72.20	9.00	17.39	-14.93	22.05	0.41
		308.15	83.49	0.22	-3.69	18.35	56.01	0.50
	$\Delta\kappa_s$ (T Pa^{-1})	303.15	-485.88	137.26	-31.82	43.94	-67.39	0.82
		308.15	-522.23	160.04	-32.50	19.08	-70.41	0.74
Chlorobenzene + tert-butanol	V^E ($\text{cm}^3 \text{mol}^{-3}$)	303.15	-2.453	0.496	1.305	-0.933	-1.441	0.023
		308.15	-2.477	0.511	1.083	-0.889	-1.342	0.022
	$\Delta\eta$ (m Pas)	303.15	-1.595	0.081	1.164	-0.232	0.474	0.006
		308.15	-1.542	0.065	1.031	-0.224	-0.158	0.005
	ΔG^{*E} (J mol^{-1})	303.15	7522	-744	3087	553	2319	10.03
		308.15	6418	-803	3222	735	2670	8.74
	Δu (m s^{-1})	303.15	53.10	-1.90	-48.15	-10.15	33.03	0.24
		308.15	59.02	-7.88	-42.87	12.08	45.64	0.45
	$\Delta\kappa_s$ (T Pa^{-1})	303.15	-277.89	72.22	49.83	-0.17	-49.39	0.39
		308.15	-301.57	90.11	77.28	-14.03	-104.76	1.28
Bromobenzene + tert-butanol	V^E ($\text{cm}^3 \text{mol}^{-3}$)	303.15	-3.012	0.178	1.949	-0.915	-1.871	0.031
		308.15	-3.251	0.480	2.075	-1.326	-1.942	0.043
	$\Delta\eta$ (m Pas)	303.15	-1.720	-0.177	0.562	0.444	0.594	0.024
		308.15	-1.618	0.204	1.045	-0.312	-0.407	0.019
	ΔG^{*E} (J mol^{-1})	303.15	6478	-533	2854	575	2389	6.85
		308.15	5545	-1095	2906	1152	3160	23.64
	Δu (m s^{-1})	303.15	64.01	-3.20	-26.82	1.50	70.56	0.35
		308.15	66.58	-6.62	-13.67	4.28	67.23	0.33
	$\Delta\kappa_s$ (T Pa^{-1})	303.15	-451.66	160.87	-10.40	24.80	-113.5	0.83
		308.15	-475.20	175.79	-29.55	24.86	114.52	0.88

The excess properties, Y^E (V^E , $\Delta\eta$, ΔG^{*E} , Δu and $\Delta\kappa_s$), for the binary mixtures were fitted to Redlich-Kister polynomial equation²⁰.

$$Y^E = x_1 x_2 \sum_{i=0}^k A_i (x_1 - x_2)^i \quad \dots(7)$$

where x_1 and x_2 are mole fractions of components 1 and 2, respectively. The coefficients A_i were obtained by making use of non linear least square regression method and fitting of Eq. (7) to the experimental results. Using an approximation of variation in the standard deviation, the optimum numbers of coefficients were ascertained. Table 3 displays the estimated values, using Eq. (7), and their standard deviations, using Eq. (8), for all the mixtures.

$$\sigma = \left[\frac{(Y_{\text{Exp}}^E - Y_{\text{cald}}^E)^2}{(n - m)} \right]^{1/2} \quad \dots(8)$$

where n and m represent number of data points and number of coefficients, respectively.

4 Conclusions

The densities, viscosities and speeds of sound for binary mixture comprising tert-butanol (TB) and (nitro-, chloro- and bromo-) benzene have been measured at 303.15 K and 308.15 K over the complete range of composition. Making use of the measured physical properties, the excess molar volume, excess Gibbs free energies of activation, deviation in viscosities, speeds of sound and isentropic compressibilities have been computed and correlated by Redlich-Kister polynomial equation to derive the coefficients and standard deviations. The negative deviations for V^E , $\Delta\eta$, $\Delta\kappa_s$ and positive deviations for ΔG^{*E} and Δu are observed at both the temperatures.

Acknowledgement

The authors are thankful to (Late) Prof T K Razdan for his critical remarks and support during the course of study.

The various calculated values at two temperatures and Figures at 308.15 K are available with the author.

References

- 1 Iloukhani H, Sameti M R, Parsa J B & Azizian S, *J Mol Liq*, 126 (2006) 117.
- 2 Singh J, Mohanty G C & Acharya S, *Indian J Pure & App Phys*, 51 (2013) 542.
- 3 Nadh M L, Mohan M T, Krishna T V & Kumar R S, *Indian J Pure & App Phys*, 51 (2013) 406.
- 4 Kumar R, Mahesh R, Shanmugapriyan B & Kannappan V, *Indian J Pure & App Phys*, 50 (2012) 633.
- 5 Krestor G A, *Thermodynamics of Solutions*, (Ellis Horwood Limited, England) 2001.
- 6 Bhatia S C, Sanghwan J & Bhatia R, *J Mol Liq*, 161 (2011) 95.
- 7 Reddy K S, *J Chem Eng Data*, 31 (1986) 238.
- 8 Sastry N V, Thakor R R & Pal M C, *J Mol Liq*, 144 (2009) 13.
- 9 Nayak J N, Aralaguppi M I & Aminabhavi T M, *J Chem Eng Data*, 48 (2003) 628.
- 10 Djordjevic B D, Radovic I R, Kijevcanin M L J, Tasic A Z & Serbanovic S P, *J Serb Chem Soc*, 74 (2009) 477.
- 11 Thirumaran T S & Karthikeyan N, *Int J Chem Res*, 3 (2011) 83.
- 12 Kim E S & Marsh K N, *J Chem Eng Data*, 33 (1988) 288.
- 13 Nikam P S, Shirsat L N & Hasan M, *J Chem Eng Data*, 43 (1998) 732.
- 14 Kumari P G, Shekhar G C, Ramamohan K & Rao M V P, *Phys Chem Liquids*, 44 (2006) 701.
- 15 Reddick A, Bunger W B & Sakano T K, *Organic Solvents: Physical Properties and Methods of Purification*, (4th ed., Wiley Interscience, New York) 1986.
- 16 Joshi S S, Aminabhavi T M & Balundgi R H, *J Chem Eng Data*, 35 (1990) 185.
- 17 Venkatesu P & Rao M V P, *Phys Chem Liquids*, 34 (1997) 213.
- 18 Treszcanowicz A J, Kiyohara & Benson G C, *J Chem Thermodyn*, 13 (1981) 253.
- 19 Eyring H & Kincaid J E, *J Chem Phys*, 63 (1983) 67.
- 20 Redlich O & Kister A T, *Ind Eng Chem*, 40 (1948) 345.
- 21 Singh S, Rattan V K, Kapoor S, Kumar R & Rampal A, *J Chem Eng Data*, 50 (2005) 288.