



# Transport Properties and Modeling of Viscosity for Binary Mixtures of Butanol Isomers + Hydrocarbons

Sweety Verma<sup>1</sup> · Suman Gahlyan<sup>1</sup> · Manju Rani<sup>2</sup> · Sanjeev Maken<sup>1</sup>

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## Abstract

As butanol would be the potential oxygenates, viscosity of twelve binary systems of butanol isomers with hydrocarbons (cyclohexane or benzene or toluene) was measured with Ubbelohde viscometer over the entire range of composition at 308.15 K. The calculated viscosity deviation values were fitted to Redlich–Kister polynomial. The deviations in viscosity were coupled with previously reported excess molar volume data in order to study the intermolecular interaction in these binary mixtures with one associated component. This approach was proposed for the viscosity of binary mixtures with self-associating component and here applied on butanol + cyclohexane or benzene or toluene mixtures at 308.15 K. It was suggested that depolymerization power of aromatic hydrocarbon toward isomers of butanol as well as strength of intermolecular interactions (electron donor–acceptor type) between monomer of butanol and aromatics depends on  $\pi$ -electron density of aromatic hydrocarbon. The viscosity of these binary mixtures was also correlated by Grunberg–Nissan, Tamura–Kurata, Hind–McLaughlin–Ubbelohde and Katti–Chaudhari correlations. It was found that the viscosity of these binary mixtures was best predicted by Grunberg–Nissan correlation except for *n*-butanol + cyclohexane or toluene and *tert*-butanol + benzene mixtures.

**Keywords** Excess volume · Viscosity · Butanol · Hydrocarbons · Molecular interactions

## 1 Introduction

Thermodynamic and transport properties such as volumetric, acoustical and viscometric properties of oxygenates with hydrocarbon would be of great significance for chemical engineers in chemical designing and for chemist in understanding intermolecular interactions and formulating motor fuel. Viscosity is the fundamental transport property for the process design in petrochemical and petroleum industries involving fluid flow. Many correlations were proposed in the literature based on the equation of state (EOS) and the mixing rule [1–4]. It was reported that the most important factor affecting the estimation is the binary interaction parameter rather than the EOS, and that the mixing rule and the

binary interaction parameters correlated from the densities of mixtures give the most accurate estimations [4]. A group contribution method known as ASOG-VISCO, developed by Tochigi et al, combines the Eyring's model with the ASOG group contribution model [5,6]. The ASOG-VISCO and also UNIFAC-VISCO model were also reported for the viscosity prediction for different kind of mixtures [7–12]. It was shown that excess molar volumes ( $V^E$ ) and deviation in viscosity ( $\Delta\eta$ ) in binary mixtures of nonelectrolytes are related as  $\Delta\eta = K^*V^E$  as both are due to the packing effects [13]. This equation successfully described  $\Delta\eta$  data of many binary mixtures [14,15], but failed in case of binary systems with associated component [16]. It was modified for the associated binary mixtures [16]. It would be interesting to check the applicability of modified approach for the binary mixtures of self-associated butanol isomers with hydrocarbons. As a part of our continuing interest in the study of thermodynamic properties of binary associated mixtures of nonelectrolytes [17–25], we report the viscosities of butanol isomers + hydrocarbons at 308.15 K. The measured viscosity deviation was then combined with the reported  $V^E$  data to get deeper information about the intermolecular interactions [26–28].

✉ Sanjeev Maken  
sanjeevmakin@gmail.com

<sup>1</sup> Department of Chemistry, Deenbandhu Chhotu Ram University of Science and Technology, Murthal 131 039, India

<sup>2</sup> Department of Chemical Engineering, Deenbandhu Chhotu Ram University of Science and Technology, Murthal 131 039, India

## 2 Experimental

The isomers of butanol (Fluka), cyclohexane, benzene or toluene (Merck) were purified by methods described in the following section. Benzene and toluene (Merck) were shaken repeatedly with 15% (v/v) concentrated sulfuric acid in a stoppered separating funnel in order to eliminate thiophene until the acid layer was colorless [29]. After each shaking of a few minutes, the mixtures were allowed to settle, and the acid was drawn off. The remaining acid was neutralized by sodium bicarbonate solution, and the sample was subsequently washed with distilled water and dried over fused calcium chloride for 24 h. It was then fractionally distilled, and the middle fraction of the distillate was collected. The isomers of butanol (Fluka) were fractionally distilled, and the middle fractions of distillate were collected. All the distilled compounds were then dried over type 0.3 nm molecular sieves (Merck) in amber-colored bottles for several days before use.

The density of pure components was measured with a precision of  $\pm 5 \times 10^{-5} \text{ g cm}^{-3}$  by a specially designed densimeter, consisting of a bulb of approximate volume  $35 \text{ cm}^3$  attached to a calibrated capillary through a B-10 standard joint in the manner described by Weissenberger [30]. Air buoyancy correction was also applied to achieve a greater accuracy. Viscosity of pure components as well as binary mixtures was measured with an accuracy of  $\pm 0.003 \text{ mPa s}$  by Ubbelohde viscometer in the manner explained earlier [20]. The temperature of water thermostat was controlled to  $\pm 0.01 \text{ K}$  by a mercury-in-toluene regulator. Average of three independent measurements of viscosity was reported in Tables 1 and 2.

The mixtures were made by weight using a balance (Shimadzu UniBloc 321-62900-64, AUX 120) having an accuracy of  $\pm 0.00001 \text{ g}$ , and mole fraction was reported to  $\pm 0.0001$ .

Experimentally measured densities and viscosities of the purified compounds compared well with their respective literature values shown in Table 1 [31–34]. All samples show  $> 99.6 \text{ wt}\%$  purity by gas chromatography.

## 3 Results and Discussion

The viscosity deviation ( $\Delta\eta$ ) was calculated from the following equation (Table 2)

$$\Delta\eta = \eta_m - x_A\eta_A - x_B\eta_B \quad (1)$$

where  $\eta_m$ ,  $\eta_A$  and  $\eta_B$  represent the viscosity of the binary mixture and pure components A and B, respectively. The  $\Delta\eta$  data were fitted to Redlich–Kister equation [35].

$$\Delta\eta = x_A(1 - x_A) \left[ \sum_{j=0}^n A_j(1 - 2x_A)^j \right] \quad (2)$$

where  $A_j$  are the adjustable parameters, and  $x_A$  is the mole fraction of isomers of butanol in binary mixture. These parameters were reported in Table 3 along with the standard deviations  $\sigma(\Delta\eta)$  of  $\Delta\eta$ .

$$\sigma(\Delta\eta) = \left\{ \left[ \sum_m (\Delta\eta_{\text{exp.}} - \Delta\eta_{\text{calc}})^2 / (m - n) \right]^{1/2} \right\} \quad (3)$$

where  $m$  and  $n$  are the number of experimental data and number of adjustable parameters in Eq. (2). Comparison of experimental  $\Delta\eta$  values with their respective calculated (from Eq. (2)) values for the present systems is shown in Fig. 1. The  $\Delta\eta$  values for *n*-butanol or *tert*-butanol + toluene mixtures at 308.15 K were reported and compared with our data as shown in Fig. 1 [36]. We are unaware of the viscosity data at 308.15 K for other binary systems in literature with which to compare our results. Viscosity deviation ( $\Delta\eta$ ) values are found to be negative at all composition and follow the sequence: *n*-butanol < *sec*-butanol < isobutanol < *tert*-butanol (Fig. 1). Negative  $\Delta\eta$  value indicates the weak interactions among unlike molecules. As expected, the values of  $\Delta\eta$  become more negative with the branching of alkyl group due to weak H-bonding in branched alcohol which make it easily dissociable. Also the branching of butyl group near the carbon atom attached to hydroxyl oxygen offers

**Table 1** Purities (wt%), measured densities ( $\rho$ ) and viscosity ( $\eta$ ) of the pure components and their literature values at 298.15 K

Compound	Purity (GC) (wt%)	$\rho$ ( $\text{kg m}^{-3}$ )		$\eta$ (mPa s)	
		Experimental	Literature	Experimental	Literature
<i>n</i> -butanol	99.8	798.03	798.21 [31]	2.0065	1.9978 [32]
<i>sec</i> -butanol	99.8	793.88	793.8 [31]	2.0938	2.1058 [32]
Isobutanol	99.8	790.56	789.66 [31]	2.5057	2.508 [33]
<i>tert</i> -butanol	99.8	770.13	770.39 [31]	2.6375	2.6448 [32]
Cyclohexane	99.7	762.5	762.96 [34]	0.7310	0.7490 [34]
Benzene	99.8	862.84	862.96 [34]	0.5226	(0.5260) [34]
Toluene	99.9	852.80	852.85 [34]	0.4980	0.4980 [34]

**Table 2** Excess molar volume ( $V^E$ ), measured viscosity ( $\eta_{\text{mix}}$ ) and ( $\Delta\eta$ ) values calculated from Eqs. (1), (4) and (9) at 308.15 K for the (A + B) mixtures

$x_A$	$\eta_{\text{mix}}$ (mPa s)	$V^E$ (cm <sup>3</sup> mol <sup>-1</sup> )	$\Delta\eta_{\text{exptl}}$ (mPa s)	$\Delta\eta^\dagger$ (mPa s)	$\Delta\eta^*$ (mPa s)
<i>n-butanol (A) + cyclohexane (B)</i>					
0.0447	0.7316	0.3454	-0.0396	-0.0123	-0.2022
0.0831	0.7490	0.5985	-0.0777	-0.0683	-0.1251
0.1695	0.7597	1.0358	-0.1491	-0.1677	-0.2165
0.2702	0.7985	1.3392	-0.2208	-0.2417	-0.2799
0.3767	0.8282	1.4584	-0.2752	-0.2793	-0.3048
0.4790	0.9367	1.4158	-0.2959	-0.2836	-0.2959
0.5787	1.0941	1.2601	-0.3118	-0.2647	-0.2634
0.6786	1.1576	1.0213	-0.2679	-0.2291	-0.2134
0.7715	1.3288	0.7493	-0.1961	-0.1858	-0.1566
0.8643	1.5191	0.4500	-0.0557	-0.1370	-0.0941
0.9528	1.8126	0.1556	-0.0296	-0.0887	-0.0325
<i>n-butanol (A) + benzene (B)</i>					
0.03856	0.5226	0.0383	-0.044	0.1278	-0.1018
0.07723	0.5358	0.0728	-0.0883	0.0319	-0.1933
0.14520	0.5489	0.1234	-0.1701	-0.1142	-0.3276
0.24291	0.5680	0.1734	-0.257	-0.2730	-0.4606
0.34136	0.6261	0.1971	-0.3567	-0.3723	-0.5234
0.44056	0.6724	0.1952	-0.4072	-0.4141	-0.5183
0.54053	0.7692	0.1705	-0.4527	-0.4047	-0.4527
0.64126	0.8720	0.1283	-0.4109	-0.3561	-0.3408
0.74277	1.0633	0.0771	-0.3264	-0.2873	-0.2046
0.84506	1.2984	0.0288	-0.2608	-0.2257	-0.0765
0.94815	1.5158	0.0003	-0.1579	-0.2090	-0.0007
<i>n-butanol (A) + toluene (B)</i>					
0.0571	0.4980	0.0032	-0.0803	-0.3072	-0.0141
0.1133	0.5038	0.0052	-0.152	-0.2808	-0.0229
0.1871	0.5169	0.0106	-0.2399	-0.2606	-0.0465
0.2772	0.5404	0.0252	-0.2983	-0.2777	-0.1101
0.3478	0.6179	0.0426	-0.3675	-0.3230	-0.1866
0.3998	0.6552	0.0577	-0.4081	-0.3679	-0.2526
0.5680	0.6930	0.1028	-0.4499	-0.4937	-0.4499
0.6653	0.9049	0.1124	-0.4307	-0.4801	-0.4919
0.7443	1.0709	0.1049	-0.3238	-0.3894	-0.4593
0.8015	1.2970	0.0902	-0.2446	-0.2749	-0.3950
0.9415	1.4625	0.0287	-0.1004	0.1392	-0.1255
<i>sec-butanol (A) + cyclohexane (B)</i>					
0.0562	0.7317	0.7803	-0.0764	0.0450	-0.2102
0.1117	0.7288	1.3500	-0.1549	-0.1107	-0.3636
0.1845	0.7433	1.8537	-0.2397	-0.2603	-0.4992
0.2739	0.7652	2.1834	-0.3394	-0.3789	-0.5880
0.3958	0.8157	2.2868	-0.4550	-0.4627	-0.6159
0.4639	0.8620	2.0512	-0.5015	-0.4933	-0.5524
0.5639	0.9473	1.7906	-0.5524	-0.4832	-0.4822
0.6615	1.1157	1.5164	-0.5170	-0.4610	-0.4084
0.7411	1.2438	1.0249	-0.4973	-0.4045	-0.2760
0.8498	1.5001	0.4664	-0.3891	-0.3239	-0.1256
0.9406	1.7969	0.7803	-0.2160	0.0450	-0.2102

Table 2 continued

$x_A$	$\eta_{\text{mix}}$ (mPa s)	$V^E$ (cm <sup>3</sup> mol <sup>-1</sup> )	$\Delta\eta_{\text{exptl}}$ (mPa s)	$\Delta\eta^\dagger$ (mPa s)	$\Delta\eta^*$ (mPa s)
<i>sec-butanol (A) + benzene (B)</i>					
0.04863	0.5310	0.1325	-0.0681	0.2020	-0.1511
0.09721	0.5394	0.2379	-0.1360	0.0248	-0.2713
0.16236	0.5395	0.3441	-0.2382	-0.1672	-0.3924
0.24417	0.5574	0.4313	-0.3489	-0.3484	-0.4918
0.30992	0.5760	0.4714	-0.4336	-0.4551	-0.5376
0.35941	0.6135	0.4870	-0.4738	-0.5163	-0.5554
0.42565	0.6318	0.4907	-0.5596	-0.5760	-0.5596
0.52552	0.7202	0.4025	-0.6281	-0.6275	-0.4590
0.62602	0.8075	0.3285	-0.6987	-0.6012	-0.3746
0.71026	0.9660	0.1985	-0.6726	-0.5306	-0.2264
0.82893	1.2577	0.0762	-0.5674	-0.4566	-0.0869
<i>sec-butanol (A) + toluene (B)</i>					
0.0375	0.4966	0.0697	-0.0612	0.2749	-0.1491
0.1140	0.5047	0.1870	-0.1753	-0.0042	-0.3998
0.1881	0.5202	0.2693	-0.2779	-0.2178	-0.5758
0.2786	0.5460	0.3315	-0.3966	-0.4091	-0.7089
0.3493	0.5759	0.3540	-0.4796	-0.5113	-0.7571
0.4014	0.6063	0.3579	-0.5323	-0.5637	-0.7654
0.5679	0.7319	0.3144	-0.6724	-0.6292	-0.6724
0.6668	0.8587	0.2603	-0.7033	-0.6169	-0.5567
0.7456	0.9710	0.2080	-0.7168	-0.5903	-0.4449
0.8528	1.2772	0.1277	-0.5817	-0.5377	-0.2731
0.9419	1.6893	0.0534	-0.3118	-0.4802	-0.1142
<i>isobutanol (A) + cyclohexane (B)</i>					
0.0554	0.7520	0.5461	-0.0778	0.0785	-0.2417
0.1101	0.7626	0.9304	-0.1642	-0.1117	-0.4117
0.1910	0.7942	1.2798	-0.2763	-0.3055	-0.5663
0.2969	0.8874	1.4587	-0.3709	-0.4477	-0.6455
0.4005	0.9581	1.4417	-0.4839	-0.5101	-0.6380
0.5887	1.2172	1.1571	-0.5588	-0.5220	-0.5120
0.6861	1.3934	0.9376	-0.5554	-0.4992	-0.4149
0.7932	1.7235	0.6543	-0.4153	-0.4574	-0.2896
0.8863	2.0180	0.3750	-0.2860	-0.4079	-0.1660
0.9549	2.2919	0.1522	-0.1338	-0.3646	-0.0674
<i>isobutanol (A) + benzene (B)</i>					
0.0484	0.5348	0.0931	-0.0837	0.0625	-0.3332
0.0969	0.5471	0.1600	-0.1677	-0.1548	-0.5725
0.1700	0.5728	0.2223	-0.2869	-0.3770	-0.7957
0.2680	0.6080	0.2566	-0.4461	-0.5399	-0.9184
0.3668	0.6647	0.2584	-0.5853	-0.6141	-0.9247
0.4912	0.7695	0.2395	-0.7273	-0.6499	-0.8573
0.5538	0.8121	0.2260	-0.8089	-0.6569	-0.8089
0.6546	1.0370	0.1999	-0.7838	-0.6563	-0.7155
0.7688	1.4020	0.1598	-0.6453	-0.6268	-0.5720
0.8711	1.8186	0.1062	-0.4316	-0.5519	-0.3802
0.9483	2.1354	0.0489	-0.2678	-0.4490	-0.1748



**Table 2** continued

$x_A$	$\eta_{\text{mix}}$ (mPa s)	$V^E$ ( $\text{cm}^3 \text{mol}^{-1}$ )	$\Delta\eta_{\text{exptl}}$ (mPa s)	$\Delta\eta^\dagger$ (mPa s)	$\Delta\eta^*$ (mPa s)
<i>isobutanol (A) + toluene (B)</i>					
0.0572	0.4995	0.0786	-0.1132	0.2229	-0.4404
0.1135	0.5121	0.1313	-0.2138	-0.0729	-0.7360
0.1964	0.5383	0.1765	-0.3540	-0.3702	-0.9896
0.3041	0.6070	0.1978	-0.5017	-0.5967	-1.1090
0.4088	0.6603	0.1948	-0.6584	-0.7158	-1.0923
0.5354	0.7367	0.1731	-0.8362	-0.7827	-0.9705
0.5970	0.8156	0.1572	-0.8811	-0.7923	-0.8811
0.6934	1.0549	0.1258	-0.8354	-0.7802	-0.7054
0.7988	1.3569	0.0838	-0.7448	-0.7334	-0.4695
0.8897	1.7503	0.0438	-0.5340	-0.6774	-0.2453
0.9563	2.1942	0.0157	-0.2239	-0.6419	-0.0882
<i>tert-butanol (A) + cyclohexane (B)</i>					
0.0548	0.7643	0.5767	-0.0717	0.1612	-0.1471
0.1090	0.7705	1.0614	-0.1688	-0.0084	-0.2707
0.1806	0.7767	1.5885	-0.2991	-0.2020	-0.4052
0.2686	0.8098	2.0800	-0.4337	-0.3976	-0.5305
0.3895	0.8899	2.4959	-0.5841	-0.5962	-0.6366
0.4573	0.9403	2.5989	-0.6629	-0.6723	-0.6629
0.5574	1.0415	2.5737	-0.7525	-0.7368	-0.6565
0.6556	1.1670	2.3363	-0.8141	-0.7426	-0.5959
0.7359	1.3300	1.9848	-0.8041	-0.7047	-0.5063
0.8464	1.6606	1.2845	-0.6842	-0.5941	-0.3276
0.9391	2.0980	0.5393	-0.4235	-0.4586	-0.1375
<i>tert-butanol (A) + benzene (B)</i>					
0.0484	0.5416	0.1014	-0.0811	0.2130	-0.1745
0.0969	0.5455	0.1905	-0.1778	0.0210	-0.3276
0.1700	0.5520	0.2902	-0.3064	-0.2032	-0.4993
0.2680	0.5719	0.3864	-0.4568	-0.4353	-0.6647
0.3668	0.6072	0.4740	-0.6626	-0.6814	-0.8154
0.4912	0.6561	0.5030	-0.7531	-0.7868	-0.8653
0.5538	0.7229	0.5215	-0.8971	-0.9032	-0.8971
0.6546	0.8374	0.5111	-0.9961	-0.9714	-0.8792
0.7688	0.9443	0.4764	-1.0689	-0.9848	-0.8196
0.8711	1.2418	0.3696	-1.0259	-0.9056	-0.6359
0.9483	1.8015	0.1904	-0.6871	-0.6897	-0.3275
<i>tert-butanol (A) + toluene (B)</i>					
0.0552	0.5099	0.0942	-0.1062	0.3344	-0.2169
0.1098	0.5181	0.1790	-0.2149	0.0953	-0.4120
0.1817	0.5324	0.2750	-0.3543	-0.1876	-0.6333
0.2701	0.5529	0.3662	-0.523	-0.4800	-0.8432
0.3913	0.5818	0.4410	-0.7533	-0.7774	-1.0153
0.4592	0.6027	0.4583	-0.8778	-0.8936	-1.0552
0.5593	0.6493	0.4540	-1.0452	-1.0035	-1.0452
0.6573	0.7161	0.4173	-1.1881	-1.0445	-0.9608
0.7374	0.8489	0.3637	-1.2269	-1.0295	-0.8374
0.8474	1.2238	0.2521	-1.0871	-0.9306	-0.5805
0.9396	1.8833	0.1164	-0.6249	-0.7610	-0.2679

† represents the viscosity deviation calculated from Eq. (4)

\* represents the viscosity deviation calculated from Eq. (9)

**Table 3** Redlich–Kister equation parameters (mPa s) for deviation in viscosity property of butanol isomers (A) + hydrocarbon (B) system along with standard deviation (mPa s)

System	A <sub>1</sub>	A <sub>2</sub>	A <sub>3</sub>	A <sub>4</sub>	σ
<i>n</i> -butanol (A) + cyclohexane (B)	−1.25E+00	−2.28E−01	7.17E−01	8.61E−01	0.0124
<i>n</i> -butanol (A) + benzene (B)	−1.69E+00	−1.86E−01	−1.30E−02	−7.14E−01	0.0194
<i>n</i> -butanol (A) + toluene (B)	−1.78E+00	−3.88E−01	4.99E−01	6.65E−01	0.0154
<i>sec</i> -butanol (A) + cyclohexane (B)	−2.05E+00	−7.62E−01	−5.35E−01	−6.57E−01	0.0100
<i>sec</i> -butanol (A) + benzene (B)	−2.4682	−1.50E+00	−9.67E−01	−5.72E−01	0.0079
<i>sec</i> -butanol (A) + toluene (B)	−2.4767	−1.6132	−1.4939	−0.8627	0.0048
Isobutanol (A) + cyclohexane (B)	−2.1819	−8.90E−01	−5.17E−02	2.69E−01	0.0115
Isobutanol (A) + benzene (B)	−2.9754	−1.51E+00	−2.31E−02	1.26E−01	0.0238
Isobutanol (A) + toluene (B)	−3.13E+00	−2.17E+00	−8.62E−01	2.98E−01	0.0158
<i>tert</i> -butanol (A) + cyclohexane (B)	−2.80E+00	−1.69E+00	−1.79E+00	−1.81E+00	0.0127
<i>tert</i> -butanol (A) + benzene (B)	−3.4119	−2.40E+00	−3.33E+00	−3.22E+00	0.0159
<i>tert</i> -butanol (A) + toluene (B)	−3.7745	−3.46E+00	−3.33E+00	−2.00E+00	0.0068

steric hindrance to the approaching hydrocarbon molecule. Thus, the branched chain alcohol in hydrocarbon results in reduction in viscosity from ideal values with larger negative  $\Delta\eta$  [37,38].

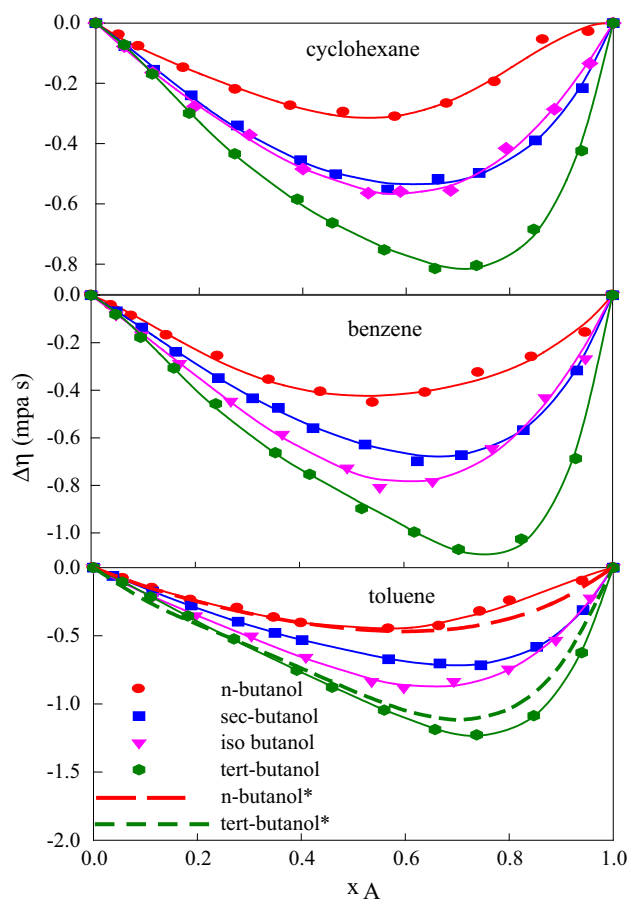
For an equimolar mixtures of butanol isomers + hydrocarbon,  $\Delta\eta$  follow the sequence: toluene < benzene < cyclohexane. This may be due to the extent of disruption of the self-associated butanol molecules due to the  $\pi$ -electron donor–acceptor interactions between aromatic ring and hydroxyl group [39]. Among three hydrocarbons, toluene has maximum  $\pi$ -electron density due to presence of electron donating methyl group and hence causes greater disruption in self-associated butanol.

Next, we predicted the  $\Delta\eta$  values by an approach that relates the  $V^E$  as follow [13]:

$$\Delta\eta = K^* V^E \quad (4)$$

where  $K^*$  parameter is a constant and calculated from the experimental  $\Delta\eta$  and  $V^E$  data for  $x_A = 0.5$  of the respective binary (A+B) mixtures which were subsequently employed to evaluate  $\Delta\eta$  at other compositions using the corresponding  $V^E$  data [41,42]. Such  $\Delta\eta^*$  values are tabulated as  $\Delta\eta^*$  in Table 4. Though  $\Delta\eta^*$  values are of the right order of magnitude, but differ from the experimental  $\Delta\eta_m$  data as evident from corresponding standard deviation ( $\sigma^*$ ) recorded in Table 4. This is quite reasonable as Eq. (4) assumes that  $\Delta\eta$  and  $V^E$  are essentially due to unlike A - B interactions in the molecules of the (A + B) mixtures. But this assumption is a true only when A and B are not self-associated [16].

In order to calculate the viscosity deviation owing to various interactions present in butanol (A) + hydrocarbon (B) mixtures, it is proposed that the process of mixtures formation requires [16]:



**Fig. 1** Deviation in viscosity of binary mixtures of butanol isomers (1) + hydrocarbon (2) mixture as a function of mole fraction of butanol isomers at 308.15 K. The lines represent the value calculated from Eq. (2), and dotted lines represent the values reported in literature (asterisk) [36] at 308.15 K for *n*-butanol or *tert*-butanol with toluene systems



**Table 4** Interactional parameters  $K^*$ ,  $K^\dagger$ ,  $K^o$  of Eqs. (4) and (9), correlation coefficient  $r$  calculated from Eq. (9) and standard deviations of viscosity for isomers of butanol (A) + hydrocarbon (B) system

System	$K^*$	$K^\dagger$	$K^o$	$r$	$\sigma^*$	$\sigma^\dagger$
<i>n</i> -butanol (A) + cyclohexane (B)	−0.209	0.0632	−0.2022	0.9848	0.0677	0.0417
<i>n</i> -butanol (A) + benzene (B)	−2.655	0.2325	−2.2633	0.9923	0.1399	0.0804
<i>n</i> -butanol (A) + toluene (B)	−4.377	−0.3277	−5.2362	0.9662	0.1400	0.1244
<i>sec</i> -butanol (A) + cyclohexane (B)	−0.2693	0.2485	−0.225	0.9933	0.1570	0.0637
<i>sec</i> -butanol (A) + benzene (B)	−1.140	0.4145	−1.2996	0.9898	0.1970	0.1223
<i>sec</i> -butanol (A) + toluene (B)	−2.138	0.4338	−1.8137	0.9779	0.2461	0.1504
Isobutanol (A) + cyclohexane (B)	−0.4425	0.3339	−0.3999	0.9871	0.1811	0.0770
Isobutanol (A) + benzene (B)	−3.578	0.3515	−2.7392	0.9677	0.2827	0.1110
Isobutanol (A) + toluene (B)	−5.605	0.6298	−4.2636	0.9805	0.3803	0.1985
<i>tert</i> -butanol (A) + cyclohexane (B)	−0.255	0.3562	−0.2704	0.9964	0.1985	0.0117
<i>tert</i> -butanol (A) + benzene (B)	−1.7203	0.4258	−1.7011	0.9941	0.2227	0.1336
<i>tert</i> -butanol (A) + toluene (B)	−2.302	0.5935	−2.0556	0.9933	0.3031	0.0454

(a) a mixing of associated butanol ( $A_n$ ) with hydrocarbon ( $B$ ) to establish ( $A_n$ )...( $B$ ) contacts. The increase in viscosity would be directly proportional to the mole fraction of hydrocarbon ( $x_B$ ) and given by

$$(\Delta\eta)_{(A_n)\dots(B)} = K_1 x_B \tag{5}$$

where  $K_1$  is a proportionality constant.

(b) these ( $A_n$ )...( $B$ ) contacts would then cause depolymerization in butanol ( $A_n$ ) to yield monomers of butanol with a decrease in viscosity ( $-(\Delta\eta)_{\text{depolym.}}$ ). This decrease in viscosity would be proportional to stoichiometric mole fraction of butanol ( $x_A$ ). Thus,

$$-(\Delta\eta)_{\text{depolym.}} = K_2 x_A \tag{6}$$

where  $K_1$  and  $K_2$  are the proportionality constants.

(c) the monomers of butanol ( $A$ ) then interact with hydrocarbon ( $B$ ) to give ( $A$ )–( $B$ ) molecular entity. This would result in positive contribution to viscosity ( $(\Delta\eta)_{(A-B)\text{inter}}$ ) and expressed as [13],

$$(\Delta\eta)_{(A-B)\text{inter}} = K^o V^E \tag{7}$$

where  $K^o$  is a constant and is a measure of inter molecular  $A - B$  interactions.

The deviation in viscosity  $\Delta\eta$  due to (a), (b) and (c) would then be expressed by

$$\begin{aligned} \Delta\eta &= (\Delta\eta)_{(A_n)\dots(B)} + (\Delta\eta)_{\text{depolym.}} + (\Delta\eta)_{(A-B)\text{inter}} \\ &= K_1 x_B - K_2 x_A + K^o V^E \end{aligned} \tag{8}$$

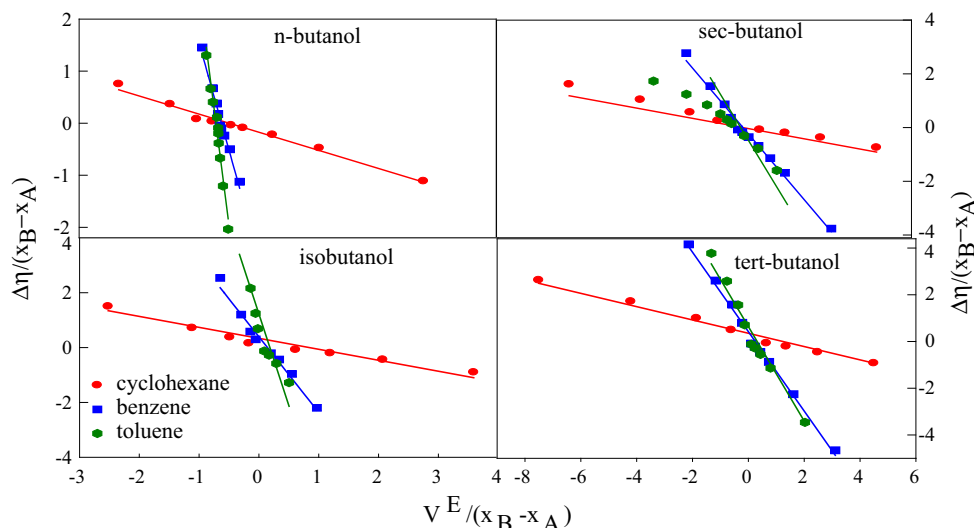
Assuming  $K_1 = K_2 = K^\dagger$  and rearranging Eq. (8), we get

$$\frac{\Delta\eta}{(x_B - x_A)} = K^o \frac{V^E}{(x_B - x_A)} + K^\dagger \tag{9}$$

The plots of  $\Delta\eta/(x_B - x_A)$  versus  $V^E/(x_B - x_A)$  are found to be linear (Fig. 2) as evident from the values of correlation coefficients  $r$  which is very close to unity and tabulated along with slope  $K^o$  and intercept  $K^\dagger$  in Table 4. This gives additional support to the assumptions made in the derivation of Eq. (9) [41,42].

These  $K^o$  and  $K^\dagger$  values were next employed to evaluate  $\Delta\eta$  data for these ( $A + B$ ) mixture. Such data are reported as  $\Delta\eta^\dagger$  in Table 4 evidently agree well with the respective experimental  $\Delta\eta$  values as shown by the standard deviation ( $\sigma^\dagger$ ) in Table 4.

Since  $K^o$  is the intermolecular interactional parameter, greater the magnitude of  $K^o$  greater would be the extent of interaction between unlike molecules. On the other hand,  $K^\dagger$  indicate the extent of depolymerization due to unlike interaction. Change in viscosity is the resultant of contribution of these two parameters  $K^o$  and  $K^\dagger$  (Table 4). Table 4 shows that the  $K^o$  value for studied systems varies in this order: cyclohexane < benzene < toluene for all the butanol isomers + hydrocarbon systems. From the above order it can be concluded that the  $K^o$  value is increasing with increase in  $\pi$ -electron density in the ring. This is as expected because extent of electron donor–acceptor interaction of  $\pi$ -electron with the hydroxyl hydrogen of butanol increases due to increased electron density with the addition of benzene in place of cyclohexane. The  $\pi$ -electron density increases further in case of toluene due to the presence of electron donating methyl groups. As a result of this, toluene has greater electron donor–acceptor interaction with isomers of butanol which results in



**Fig. 2** Plots of  $\Delta\eta/(x_B - x_A)$  versus  $V^E/(x_B - x_A)$  for butanol isomers (1) + hydrocarbon (2) where symbol represents cyclohexane (diamond), benzene (square) and toluene (circle) hydrocarbons

higher  $K^o$  value. In the case of cyclohexane, benzene and toluene, it is indeed true.

The values of  $K^\dagger$  for these systems (Table 4) clearly indicate that extent of depolymerization (resulting in expansion in volume of mixture) varies as: toluene > benzene > cyclohexane. But as  $K^o$  values indicate the extent of interaction between unlike molecules so the net change in volume of mixture is the contribution of these two factors, as  $V^E$  is a packing effect so the  $V^E$  value for these mixtures should vary as cyclohexane > benzene > toluene. The same was observed for excess molar volume of these systems [40–42].

#### Correlations for Viscosity

Viscosity of these systems was also correlated by the following relations and compared with experimental data in terms of percentage standard deviations in Table 5: Grunberg and Nissan [43]

$$\eta = \exp \left[ \sum_{i=A,B} (x_i \ln \eta_i) + G_{AB} \prod_{i=A,B} x_i \right] \quad (10)$$

Tamura and Kurata [44]

$$\eta = \left[ \sum_{i=A,B} x_i \phi_i \eta_i + 2T_{AB} \prod_{i=A,B} (x_i \phi_i)^{1/2} \right] \quad (11)$$

Hind, McLaughlin and Ubbelohde [45]

$$\eta = \left[ \sum_{i=A,B} x_i^2 \eta_i + 2H_{AB} \prod_{i=A,B} x_i \right] \quad (12)$$

Katti and Chaudhari [46,47]

$$\ln \eta V_m = \sum_{i=A,B}^{x_i} \ln (\eta_i V_i) + x_A x_B (W_{vis}/RT) \quad (13)$$

The estimation capabilities of these correlations are expressed in Table 5 as percentage standard deviations  $\sigma$ .

$$\sigma (\%) = \left[ \frac{\sum \{ (\eta_{\text{exptl.}} - \eta_{\text{theo.}}) / \eta_{\text{exptl.}} \times 100 \}^2}{(n-1)} \right]^{1/2} \quad (14)$$

where all the terms in these Eqs. (6)–(10) have their usual meanings and defined earlier [20].

Grunberg–Nissan correlation gave the best prediction of viscosity deviation among the four correlations applied as it has least percentage standard deviation (Table 5).

## 4 Conclusions

The viscosity deviations as function of composition were calculated from the measured viscosity of binary mixtures of isomers of butanol + hydrocarbons at 308.15 K. An approach was applied in which viscosity deviations for binary mixtures with one self-associated components were coupled with corresponding excess molar volume data. This approach yields two interactional parameters  $K^\dagger$  and  $K^o$  which signify the extent of depolymerization of associated component and unlike  $A - B$  interaction, respectively. It was suggested



**Table 5** Percentage standard deviation of viscosity of various correlations like Gruenberg–Nissan (G–N), Tamura–Kurata (T–K), Hind–McLaughlin–Ubbelohde (H–Mc–U) and Katti–Chaudhari (K–C) correlation and their interactional parameters

System	G–N		T–K		H–Mc–U		$W_{vis}/RT$	
	$\sigma$ (%)	$G_{AB}$	$\sigma$ (%)	$T_{AB}$	$\sigma$ (%)	$H_{AB}$	$\sigma$ (%)	$W_{vis}/RT$
<i>n</i> -butanol (A) + cyclohexane (B)	4.5187	−0.4335	3.6658	0.8831	3.4388	0.8239	5.7217	−2.9784
<i>n</i> -butanol (A) + benzene (B)	3.2127	−0.7695	5.8585	0.4122	5.6546	0.4207	5.8323	−3.3277
<i>n</i> -butanol (A) + toluene (B)	5.4693	−0.7953	3.0482	0.4709	4.0177	0.4138	5.5849	−3.3326
<i>sec</i> -butanol (A) + cyclohexane (B)	1.4963	−1.2836	7.3385	0.3976	8.9733	0.3393	5.3749	−3.8348
<i>sec</i> -butanol (A) + benzene (B)	4.1184	−1.6253	19.9838	0.0371	19.5353	0.0469	5.8324	−4.1985
<i>sec</i> -butanol (A) + toluene (B)	5.2003	−1.7474	21.2956	−0.0145	24.5697	−0.0708	7.2866	−4.2843
Isobutanol (A) + cyclohexane (B)	2.3380	−0.9152	5.2644	0.5963	6.7252	0.5198	5.2045	−3.4361
Isobutanol (A) + benzene (B)	4.0789	−1.4184	17.4042	0.0157	16.8538	0.0316	7.750	−3.9775
Isobutanol (A) + toluene (B)	4.4107	−1.6976	21.1639	−0.0913	23.9802	−0.1655	8.0312	−4.2498
<i>tert</i> -butanol (A) + cyclohexane (B)	6.3862	−1.4540	17.1958	0.1954	18.9751	0.1304	8.6211	−4.0082
<i>tert</i> -butanol (A) + benzene (B)	11.5588	−2.1179	38.8173	−0.4003	37.5404	−0.3722	10.5934	−4.6861
<i>tert</i> -butanol (A) + toluene (B)	16.7315	−2.5684	47.1479	−0.5541	50.2737	−0.6140	18.4205	−5.1252

that depolymerization power of hydrocarbon toward isomers of butanol and strength of intermolecular interactions (electron donor–acceptor type) between monomer of isomers of butanol and aromatics depend on  $\pi$ -electron density of the aromatic hydrocarbon. The viscosities of these binary mixtures were also theoretically predicted from various correlations, and Gruenberg–Nissan correlation gave the best prediction of viscosity deviation.

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