Viscometric Properties of Binary Mixtures of 1,4-Butanediol + Cresols at Different Temperatures

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The viscosities of binary mixtures of 1,4-butanediol with _o_-cresol, _m_-cresol and _p_-cresol were determined at 303.15, 308.15, 313.15 and 318.15 K over the entire mole fraction range. The deviation in viscosity, $\Delta\eta$ and excess Gibbs energy of activation (ΔG^{*E}) of viscous flow were examined in terms of structural changes and interactions. The deviation/excess values were fitted to the Redlich-Kister equation to determine the fitting parameters and the root-mean square deviations. The results obtained for viscosity of binary mixtures were used to test the semi-empirical relations of Bingham, Frenkel, Kendall, HindUbbelhode, Refutas, Sutherland Wassiljiewa, Gambill, McAllister, Hind, Grunberg, Wijk, McAllister 4-body, Tamura Kurata, Katti-Chaudhri and Nhaesi.

INTRODUCTION

Systematic studies have been made on thermodynamic, acoustic and optical properties of binary liquid mixtures of 1,4-butanediol with picolines [1], cresols [2] and alkoxyalkanols [3]. The speeds of sound, isentropic compressibilities, molar isentropic compressibilities and excess molar volumes have been studied previously. In the present investigation, the analysis was extended to study viscometric behavior of binary mixtures of 1,4-butanediol (BD) with _o_-cresol, _m_-cresol and _p_-cresol to get a better understanding of the intermolecular interactions. The information pertaining to the viscometric behavior of liquid mixtures is of major significance to multifarious chemical industry related applications [4-6], _viz_., heat and mass-transfer operations, surface facilities, pipeline flows, _etc_. The results obtained for viscosities of binary mixtures were used to test the semi-empirical relations of Bingham,

Frenkel, Kendall, HindUbbelhode, Refutas, Sutherland Wassiljiewa, Gambill, McAllister, Hind, Grunberg, Wijk, McAllister 4-body, Tamura Kurata, Katti-Chaudhri and Nhaesi.

1,4-Butanediol is a viscous, transparent liquid, miscible in water and many polar organic solvents. It has two hydroxyl groups at the vicinal positions (at positions 1 and 4) which makes it an ideal candidate for acting as a chemical intermediate in multifarious manufacturing processes of several products [7-9].

Cresols can be used as the second generation of bio-oils/fuels. Bio fuels have slowly emerged as a viable fossil fuel alternative. The investigation is aimed at providing a deeper insight to the H-bonds association, extent of intermolecular interactions and the nature of the structures formed in these mixtures at different temperatures. Secondly, an attempt has been made to explore the effect of -OH groups in the 1,4-BD molecules, and their influence on the physicochemical properties of the systems under study.

Literature survey reveals that inter and intramolecular

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investigations of 1,4-butanediol with *o*-cresol, *m*-cresol and *p*-cresol based on viscometric studies have not been attempted so far. In this investigation, viscosity (η) values of 1,4-butanediol with *o*-, *m*- and *p*-cresols have been measured at 303.15, 308.15, 313.15 and 318.15 K over the entire composition range. Viscosity deviations ($\Delta\eta$) have also been evaluated employing experimental viscosity values. Furthermore, evaluation of excess Gibbs energy of activation of viscous flow (ΔG^{*E}) has been performed and the findings have been made to fit the Redlich-Kister polynomial equation. Absolute Average Percentage Deviation values have been used as an approach to obtain extent of deviation from the experimental values.

EXPERIMENTAL

The chemicals namely 1,4-butanediol and cresols were supplied by Sigma-Aldrich, USA, with mass fraction purity 0.99. These liquids were purified by vacuum distillation over calcium oxide [10,11]. Before use, to remove the water content, if any, the chemicals were stored over the 0.4 nm molecular sieves for 72 h and low pressure degassing was carried out. The mixtures were prepared by mass, and to avoid evaporation, they were kept in airtight stoppered glass bottles. An electronic balance with a precision of $\pm$ 0.1 mg was used for weighing the chemicals.

An Ostwald's viscometer was used to measure viscosities of pure liquids and their binary mixtures. The calibration of viscometer was done with tripled distilled water at T = (303.15, 308.15, 313.15 and 318.15) K. To minimize the possibility of thermal fluctuations, the viscometer containing the sample under investigation was allowed to stand for 30 min in a thermostatic water bath. A digital stop-watch with an accuracy of ±0.01 s was used to record the time of flow in triplicate. The temperatures of the liquids under investigation were maintained at an accuracy of ±0.02 K in an electronically controlled thermostatic water bath. The following relationship [12] was used to calculate the viscosity, η.

$$\eta/\eta_w = \rho t/\rho_w t_w$$

where η, ρ, t and η_w, ρ_w, t_w are the viscosities, densities and flow times of mixture and water respectively. The viscosity

and density values of pure water are taken from Lange's Handbook of Chemistry [13].

The reliability of experimentally determined viscosity values were validated by comparison of the data of pure liquids to that of the corresponding literature values [14-19] at the temperatures under investigation.

Theory

The viscosities measured with the instruments described above are reported in Table 1.
The deviation in viscosity was calculated from

$$\Delta\eta = \eta_{mix} - (x_1\eta_1 + x_2\eta_2) \tag{1}$$

where x and η represent mole fractions and viscosities, of 1st and 2nd components respectively and η_{mix} is the viscosity of the mixture.
The excess Gibbs energy of activation ΔG^{*E} of viscous flow [20] has been evaluated through

$$\Delta G^{*E} = RT[ln\eta_m V_m - (x_1 ln\eta_1 V_1 + x_2 ln\eta_2 V_2)] \tag{2}$$

where all the symbols have their own usual meaning. Densities and molar volumes of *o*-, *m*- and *p*-cresols were taken from our previous study [2] and are presented in supplementary data: Tables S1 and S2.

The values of viscosity deviation and ΔG^{*E} for the mixtures have been fitted to Redlich-Kister polynomial equation [21].

$$\Delta\eta \ or \ \Delta G^{*E} = x_1(1-x_1)\sum_{i=0}^{m} A_i(2x_1-1)^i \tag{3}$$

Correlating Equations

Several semi-empirical and correlative approaches have also been employed to estimate the absolute viscosity η of liquid mixtures in terms of pure component data [22,23]. Various approaches proposed by Bingham [24], Kendall [24], Hind Ubbelhode [24], Refutas [25], Sutherland Wassiljiewa [24], Gambill [26], Frenkel [27], Grunberg-Nissan [28], Tamura Kurata [29], Katti-Chaudhri [30], McAllister [31], Hind [32], Wijk [33], McAllister 4-body [34] and Nhaesi[24] were tested.
Bingham relation is given as:

Table 1. Experimental Viscosities, η, of the Binary Mixtures of 1,4-Butanediol (1) with Cresols (2) at Different temperatures

x_1	η ($\times 10^{-3}$ Nm^{-2} s)			
	303.15 K	308.15 K	313.15 K	318.15 K
1,4-Butanediol + *o*-cresol				
0.0000	7.503	6.066	4.241	2.179
0.1001	9.677	8.131	6.174	3.929
0.2001	12.472	10.481	8.090	5.493
0.3002	16.089	13.618	10.524	7.525
0.4002	20.594	17.163	13.509	9.876
0.5002	25.523	21.504	17.097	12.815
0.6002	30.947	26.009	20.911	15.980
0.7002	36.699	30.701	24.871	19.422
0.8001	42.713	35.391	28.821	22.818
0.9001	48.827	40.328	33.063	26.439
1.0000	55.473	45.657	37.535	30.034
1,4-Butanediol + *m*-cresol				
0.0000	8.929	7.524	6.129	5.174
0.0992	11.093	9.625	8.048	6.814
0.1986	13.950	11.954	9.980	8.476
0.2982	17.469	15.008	12.420	10.236
0.3979	21.635	18.576	15.465	12.577
0.4979	26.752	22.825	19.028	15.489
0.5979	32.289	27.391	22.784	18.549
0.6982	38.099	31.918	26.676	21.527
0.7986	43.970	36.618	30.447	24.520
0.8992	49.737	41.197	34.088	27.368
1.0000	55.473	45.657	37.535	30.034
1,4-Butanediol + *p*-cresol				
0.0000	9.618	8.168	6.719	5.548
0.0961	11.728	10.199	8.617	7.181
0.1931	14.581	12.586	10.576	8.755
0.2909	18.177	15.651	13.005	10.705
0.3895	22.382	19.193	15.911	12.961
0.4890	27.483	23.420	19.416	15.801
0.5894	32.989	27.844	23.157	18.778
0.6907	38.686	32.452	26.964	21.799
0.7929	44.414	36.996	30.694	24.716
0.8960	50.026	41.390	34.182	27.480
1.0000	55.473	45.657	37.535	30.034

Standard uncertainties, *u*, are $u(T) = \pm 0.02$ K, $u(\eta) = \pm 0.002$ Nm^{-2} s and $u(x) = \pm 1 \times 10^{-3}$.

$$\eta = x_1\eta_1 + x_2\eta_2 \tag{4}$$

where x_1 and x_2 represent the mole fractions of two components and η_1 and η_2 represent their viscosities in the pure state.

Frenkel relation is represented by:

$$\ln\eta = x_1{}^2\ln\eta_1 + x_2{}^2\ln\eta_2 + 2x_1x_2\ln\eta_{12} \tag{5}$$

where η_{12} is a constant. Its value is obtained by,

$$\eta_{12} = (\eta_1 + \eta_2)/2$$

Dey *et al.* [35] have recently proposed a modified form of the above mentioned interaction parameter, which is expressed as:

$$\eta_{12} = 2(\eta_1\eta_2/[\eta_1 + \eta_2]) \tag{6}$$

The viscosity of multicomponent systems, according to the Kendall-Munroe equation is given by,

$$\ln\eta = x_1\ln\eta_1 + x_2\ln\eta_2 \tag{7}$$

The Hind and Ubbelhode approach for binary mixtures is,

$$\eta = x_1{}^2\eta_1 + x_2{}^2\eta_2 + 2x_1x_2\eta_{12} \tag{8}$$

Refutas equation is:

$$\eta_{12} = \exp\left[\exp\left(\frac{A_{12} - 10.975}{14.534}\right)\right] - 0.8 \tag{9}$$

where A_{12} is the average viscosity blending index,

$$A_{12} = x_1A_1 + x_2A_2$$

The Sutherland-Wassiljewa relation is given as

$$\eta = \Sigma\left[\frac{\eta_i\, x_i}{\Sigma A_{ij}\, x_j}\right] \tag{10}$$

where all the symbols have their own usual meaning.

Gambill method is given by:

$$\eta_{mix}^{1/3} = x_1\eta_1^{1/3} + x_2\eta_2^{1/3} \tag{11}$$

Hind relation is expressed as:

$$\eta = x_1{}^2\eta_1 + x_2{}^2\eta_2 + 2x_1x_2H_{12}$$

The Grunberg-Nissan equation is:

$$\eta = \exp(x_1\ln\eta_1 + x_2\ln\eta_2 + x_1x_2\, G_{12}) \tag{13}$$

where G_{12} is a parameter proportional to the interchange energy.

The Tamura Kurata relation is:

$$\eta = x_1\phi_1\eta_1 + x_2\phi_2\eta_2 + 2(x_1x_2\phi_1\phi_2)^{1/2}T_{12}$$

Katti-Chaudhri equation is:

$$\ln\eta V = x_1\ln V_1\eta_1 + x_2\ln V_2\eta_2 + x_1x_2K_{12} \tag{15}$$

The McAllister correlative equation is:

$$\begin{aligned}
\ln\eta = {}& x_1^4\ln\eta_1 + 4x_1^3x_2\ln\eta_{1112} + 6x_1^2x_2^2\ln\mu_{1122} + 4x_1x_2^3\ln\eta_{2221} \\
& + x_2^4\ln\eta_2\ln[x_1 + x_2M_2/M_1] + 4x_1^3x_2\ln[(3 + M_2/M_1)/4] \\
& + 6x_1^2x_2^2\ln[(1 + M_2/M_1)/2] + 4x_2^3x_1\ln[(1 + 3M_2/M_1)/4] \\
& + x_2^4\ln(M_2/M_1)
\end{aligned} \tag{16}$$

where η_{1112}, η_{1122} and η_{2221} are interaction parameters and M_i and η_i are the molecular mass and kinematic viscosity of pure component i.

Wijk relation is given by:

$$\log(\eta) = x_1{}^2\log(\eta_1) + x_2{}^2\log(\eta_2) + 2x_1x_2\log(\eta_{12}) \tag{17}$$

Nhaesi-Asfourequation equation is:

$$\frac{\eta_{12}}{(\eta_1^2\eta_2)^{1/3}} = 0.8735 + 0.0715\frac{(N_2 - N_1)^2}{(N_1^2 N_2)^{1/3}} \tag{18}$$

where N, the effective carbon number, is obtained from:

$$\ln\eta = -1.943 + 0.193N$$

The absolute average percentage deviation (AAPD) has

Table 2. Values of $\Delta\eta$ and ΔG^{*E} for all the Studied Systems at Different Temperatures

x_1	$\Delta\eta$ ($\times 10^{-3}$ Nm^{-2} s)				ΔG^{*E} (kJ mol^{-1})			
	303.15K	308.15K	313.15K	318.15K	303.15K	308.15K	313.15K	318.15K
1,4-Butanediol + *o*-cresol								
0.0000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
0.1001	-2.627	-1.898	-1.399	-1.037	-0.951	-0.800	-0.656	-0.564
0.2001	-4.631	-3.509	-2.814	-2.260	-1.591	-1.324	-1.087	-0.901
0.3002	-5.814	-4.332	-3.711	-3.015	-1.976	-1.630	-1.318	-1.073
0.4002	-6.107	-4.747	-4.057	-3.450	-2.160	-1.771	-1.417	-1.137
0.5002	-5.975	-4.366	-3.799	-3.297	-2.195	-1.801	-1.438	-1.150
0.6002	-5.348	-3.819	-3.313	-2.917	-2.119	-1.758	-1.421	-1.150
0.7002	-4.401	-3.086	-2.682	-2.261	-1.894	-1.601	-1.320	-1.094
0.8001	-3.173	-2.353	-2.060	-1.648	-1.507	-1.311	-1.115	-0.956
0.9001	-1.853	-1.373	-1.146	-0.811	-0.901	-0.812	-0.720	-0.642
1.0000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
1,4-Butanediol + *m*-cresol								
0.0000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
0.0992	-2.454	-1.682	-1.196	-0.826	-0.606	-0.470	-0.360	-0.295
0.1986	-4.224	-3.144	-2.387	-1.635	-1.091	-0.867	-0.688	-0.579
0.2982	-5.339	-3.887	-3.074	-2.351	-1.399	-1.148	-0.871	-0.756
0.3979	-5.816	-4.122	-3.162	-2.489	-1.547	-1.273	-0.992	-0.870
0.4979	-5.350	-3.683	-2.736	-2.060	-1.558	-1.272	-1.026	-0.909
0.5979	-4.470	-2.934	-2.124	-1.489	-1.503	-1.205	-0.940	-0.833
0.6982	-3.327	-2.230	-1.381	-1.004	-1.336	-1.061	-0.813	-0.718
0.7986	-2.130	-1.359	-0.764	-0.507	-1.022	-0.846	-0.657	-0.570
0.8992	-1.046	-0.616	-0.282	-0.160	-0.573	-0.480	-0.406	-0.349
1.0000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
1,4-Butanediol + *p*-cresol								
0.0000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
0.0961	-2.297	-1.581	-1.063	-0.720	-0.504	-0.331	-0.213	-0.133
0.1931	-3.892	-2.821	-2.093	-1.521	-0.979	-0.652	-0.428	-0.287
0.2909	-4.781	-3.423	-2.678	-1.966	-1.361	-0.965	-0.681	-0.478
0.3895	-5.097	-3.577	-2.811	-2.124	-1.602	-1.206	-0.930	-0.687
0.4890	-4.559	-3.080	-2.372	-1.721	-1.710	-1.350	-1.062	-0.846
0.5894	-3.655	-2.420	-1.725	-1.201	-1.638	-1.292	-1.004	-0.785
0.6907	-2.604	-1.610	-1.040	-0.660	-1.411	-1.056	-0.780	-0.579
0.7929	-1.562	-0.897	-0.459	-0.246	-1.030	-0.737	-0.516	-0.367
0.8960	-0.678	-0.368	-0.149	-0.007	-0.550	-0.369	-0.243	-0.165
1.0000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000

been employed as a tool [36] to get an assessment of the deviation of a particular approach from the experimental values for a system. It is given by:

$$AAPD = \frac{1}{n} \sum \left| \frac{\eta_{\text{exp erimental}} - \eta_{\text{theoretical}}}{\eta_{\text{exp erimental}}} \right| \times 100 \qquad (19)$$

RESULTS AND DISCUSSION

The measured values of viscosity, η, for the three binary mixtures at T = 303.15, 308.15, 313.15 and 318.15 K are shown in Table 1. The deviations in viscosity, $\Delta\eta$ and the excess Gibbs free energy of activation of viscous flow, ΔG^{*E} for the three binary mixtures are shown in Table 2. The coefficients, A_i, of Eq. (3) and standard deviations, σ, for $\Delta\eta$ and ΔG^{*E} for the three mixtures at all the four temperatures are given in Table 3.

Figures 1 and 2 depict the plots of $\Delta\eta$ and ΔG^{*E} for the binary mixtures under investigation with mole fractions of 1,4-BD at 303.15 K. The $\Delta\eta$ values (Fig. 1) for all the three binary mixtures were found to be negative over the entire mole fraction range of the mixtures with a minimum value at $x_1 = 0.4002$. Further, it was observed that the negative $\Delta\eta$ values exhibit a decreasing trend with a rise in temperature for all mixtures. The increase in temperature causes a reduction in the self-association of pure components and generates hetero association between unlike components in the mixtures. This results in less negative values of $\Delta\eta$ with temperature increase as observed in this investigation. Marigliano [32] reported similar trend in dependence on temperature. The $\Delta\eta$ values are found to be negative due to presence of dipolar interactions and dispersion, whereas positive values of $\Delta\eta$ emanate from hydrogen bonding interactions, charge transfer and some other chemical forces resulting in complex formation between unlike molecules.

A scrutiny of Table 1 shows that all the studied mixtures exhibit similar trends with temperature variation. The viscosity values show a sharp rise in the values after the equimolar region due to the dominant play of the more viscous liquid, 1,4-butanediol. A glance at Table 1 and Fig. 2 shows that ΔG^{*E} values are negative at all the temperatures over the entire range of mole fraction. According to Meyer *et al.* [37], the negative values of ΔG^{*E}

correspond to the existence of solute-solute association. These values indicate that intermolecular interactions are on the larger side for the *p*-cresol system at two temperatures as compared to the corresponding isomers. This observation is in conjunction with literature wherein it has been reported that reactivity is highest for the *p*-cresol amongst the isomeric cresols when oxidative ammonolysis is carried out on vanadium oxide catalyst. This behavior can be attributed to the predominance of structural effects over those resulting from interactions generated due to mixing. Furthermore, literature survey indicates that positive values of ΔG^{*E} represent stronger and specific interactions.

Various viscosity relations have been tested and a comparative study has been carried out based on their predictive capability. In the present investigation, viscosity values have been evaluated using different approaches including Frenkel, Bingham, Sutherland-Wassiljewa, modified Nheasi as four models based on the effective carbon number [24,37], *etc.* Use has been also made of 7 correlative approaches including McAllister 3- and 4-body models along with Tamura Kurata, Katti-Chaudhri, Grunberg Nissan, *etc.*

A comparative study has then been carried out based on the AAPD values obtained thereof to get an understanding of the predictive capability. A perusal of Fig. 3 shows that Frenkel approach gives better AAPD values compared to the other predictive approaches. A scrutiny of the figure also shows that the AAPD values given by the SW approach is highest amongst all the predictive models. The McAllister 4-body model is seen to give best results in comparison to the experimental findings with the lowest AAPD values in all the correlative models under consideration.

As seen in Fig. 4, the highest AAPD values amongst the predictive approaches are seen to be given by the Sutherland Wassiljewa approach. Among all the predictive equations taken for consideration, Frenkel approach is seen to give the lowest AAPD values. Most of the correlative models except the McAllister 3-body and 4-body models are seen to give AAPDs on the higher side compared to the other two cresol isomers.

A perusal of the AAPD values (Fig. 5) shows that the least values are recorded for this binary system. As seen in the other two systems, the lowest AAPD values are given by the Frenkel relation, and highest values for the predictive

Table 3. Values of A_i and σ of Eq. (3) for all the Studied Systems at Different Temperatures

Property	Temperature	A_0	A_1	A_2	A_3	A_4	σ
1,4-BD + *o*-cresol							
$\Delta\eta$	303.15K	-23.9000	9.1000	-2.2900	-5.2700	1.2800	0.0454
	308.15K	-17.6000	9.1600	-1.9400	-8.7900	1.3600	0.0515
	313.15K	-15.2000	7.6400	-1.3100	-9.6100	4.5700	0.0302
	318.15K	-13.2000	5.5400	2.3400	-6.3600	3.2200	0.0407
$\Delta G*^E$	303.15K	-8.7978	0.5047	-2.6808	-0.2379	0.5730	0.0035
	308.15K	-7.2212	0.2181	-3.0174	-0.4619	0.5010	0.0036
	313.15K	-5.7666	0.0987	-3.3395	-0.7931	0.6456	0.0048
	318.15K	-4.6173	-0.0233	-3.4224	-0.7800	0.2854	0.0040
1,4-BD + *m*-cresol							
$\Delta\eta$	303.15K	-21.5000	13.4000	6.0900	-5.8100	-4.5400	0.0437
	308.15K	-14.7000	11.6000	0.0311	-6.4000	4.4800	0.0435
	313.15K	-11.0000	11.3000	1.5900	-7.6700	4.1700	0.0134
	318.15K	-8.3400	9.5700	2.8000	-8.4800	2.9700	0.0625
$\Delta G*^E$	303.15K	-6.2661	0.4967	-1.7925	-0.2992	2.1566	0.0059
	308.15K	-5.1000	0.7172	-1.2700	-1.2860	1.5427	0.0078
	313.15K	-4.0413	0.6422	-0.0175	-1.3868	-0.6383	0.0126
	318.15K	-3.5808	0.4845	0.3423	-1.2448	-0.6274	0.0094
1,4-BD + *p*-cresol							
$\Delta\eta$	303.15K	-18.0000	15.0000	3.4000	-5.1500	-2.3800	0.0436
	308.15K	-12.2000	12.5000	1.2400	-5.5300	0.7820	0.0303
	313.15K	-9.3100	11.8000	3.0400	-7.8800	1.0700	0.0198
	318.15K	-6.7700	9.5700	2.7100	-7.0000	1.9700	0.0330
$\Delta G*^E$	303.15K	-6.8269	0.0610	1.4759	-0.1091	0.0792	0.0042
	308.15K	-5.3807	-0.3630	3.8651	0.4767	-2.4358	0.0077
	313.15K	-4.2392	-0.3904	5.1649	0.4346	-3.9674	0.0072
	318.15K	-3.3233	-0.4998	5.4831	0.5865	-4.6359	0.0151

models are given by the SW relation. Here also, McAllister 4 body model gives the best results amongst all the approaches taken for the comparative study.

It is pertinent to note that both Frenkel and Kendall Munroe show an increasing trend in the AAPD values with an increase in the temperature from 298.15 to 318.15 K,
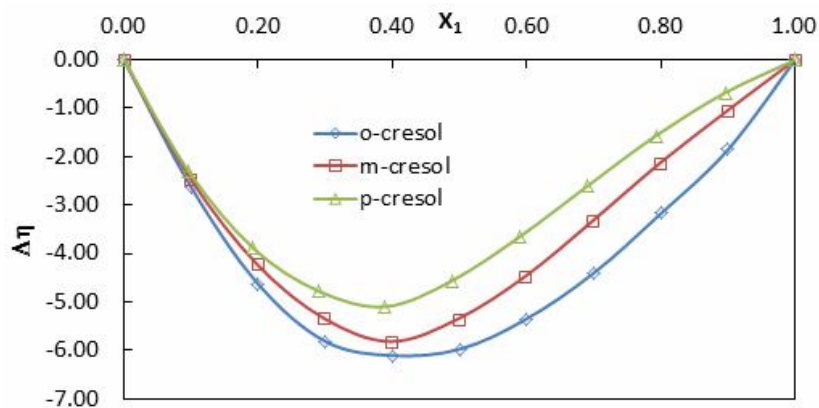
Fig. 1. Deviation in viscosity ($\Delta\eta$) for 1,4-butanediol + *o*-cresol (◊), + *m*-cresol (□) and + *p*-cresol (Δ) at 303.15 K. Solid lines have been drawn from Eq. (3) using the coefficients given in Table 3.
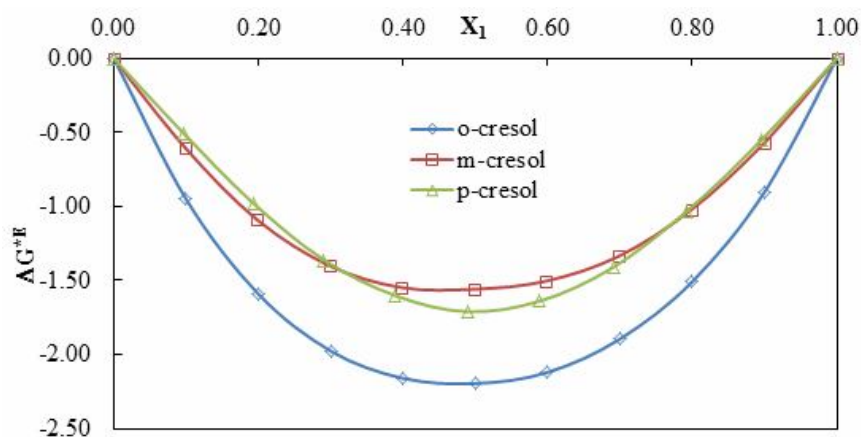
**Fig. 2.** Excess Gibbs energy of activation of viscous flow (ΔG^{*E}) for 1,4-butanediol + *o*-cresol (◊), + *m*-cresol (□), and + *p*-cresol (Δ) at 303.15 K. Solid lines have been drawn from Eq. (3) using the coefficients given in Table 3.

while the other predictive models do not show such behavior. This may be attributed to the logarithmic behavior of these two models. The McAllister 3- and 4-body models are seen to give the best results for all the three systems under consideration over the entire range of temperature. The McAllister 4-body approach gives very accurate results with the AAPD values being less than 0.5 for all the systems under consideration. This may be resulting from the fact that the 4-body model closely resembles [31] the actual three dimensional picture present in the system compared to the 2-parameter 3-body model that takes into account only

three molecules interacting at a time. All the systems under investigation fit well with the McAllister three-parameter 4-body model.

CONCLUSIONS

The present investigation reports the viscosity deviation and excess Gibbs free energy of activation of viscous flow for the three systems 1,4-BD + *o*-cresol/*m*-cresol/*p*-cresol in the temperature range of T = 303.15 K to 318.15 K. Considering the pattern of $\Delta\eta$ against mole fraction
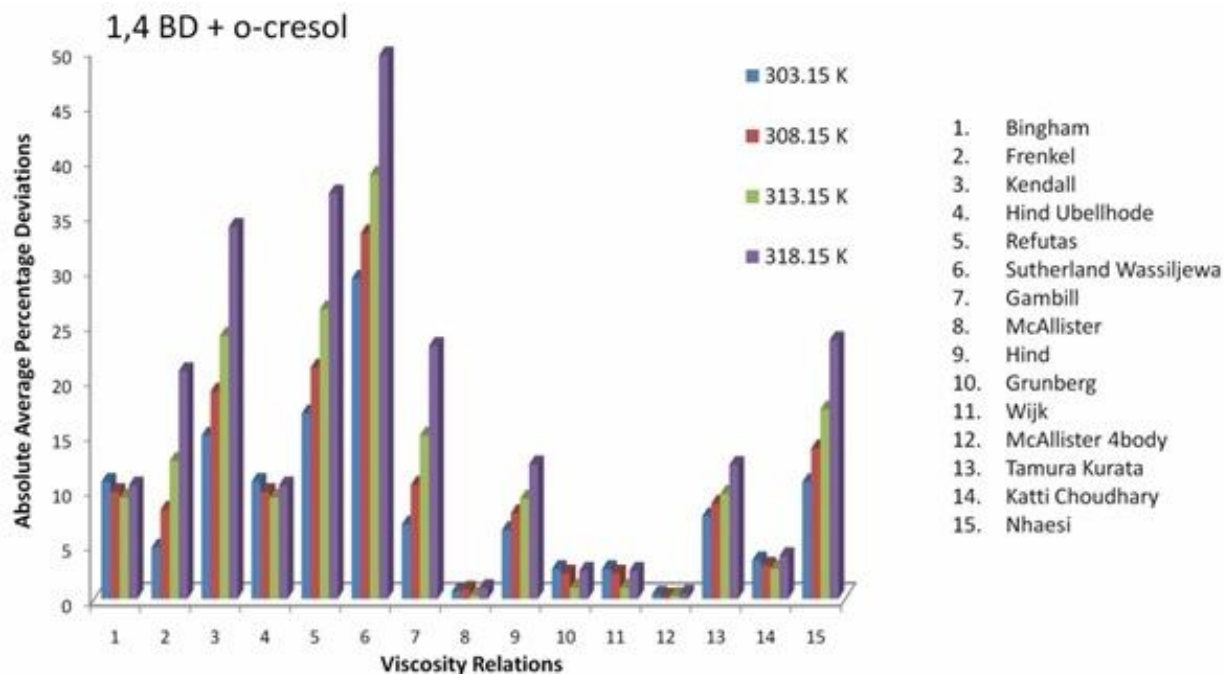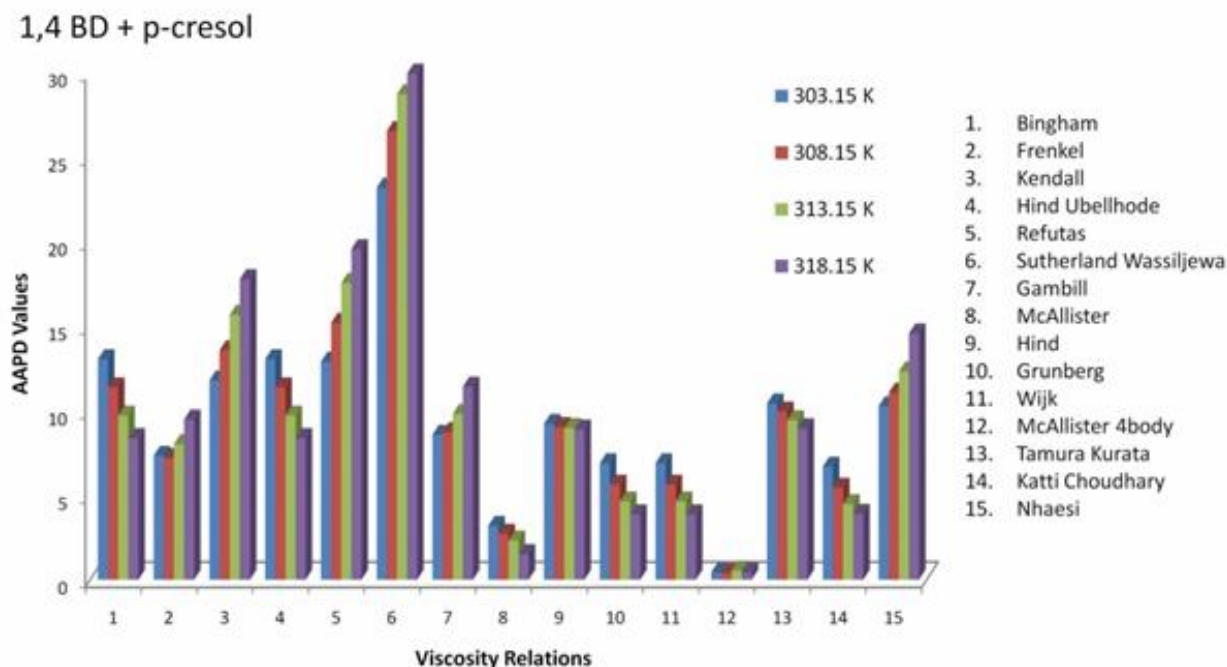
Fig. 3. Plots of AAPD *vs.* viscosity relations of binary mixtures of 1,4-butanediol with o-cresol at different temperatures.
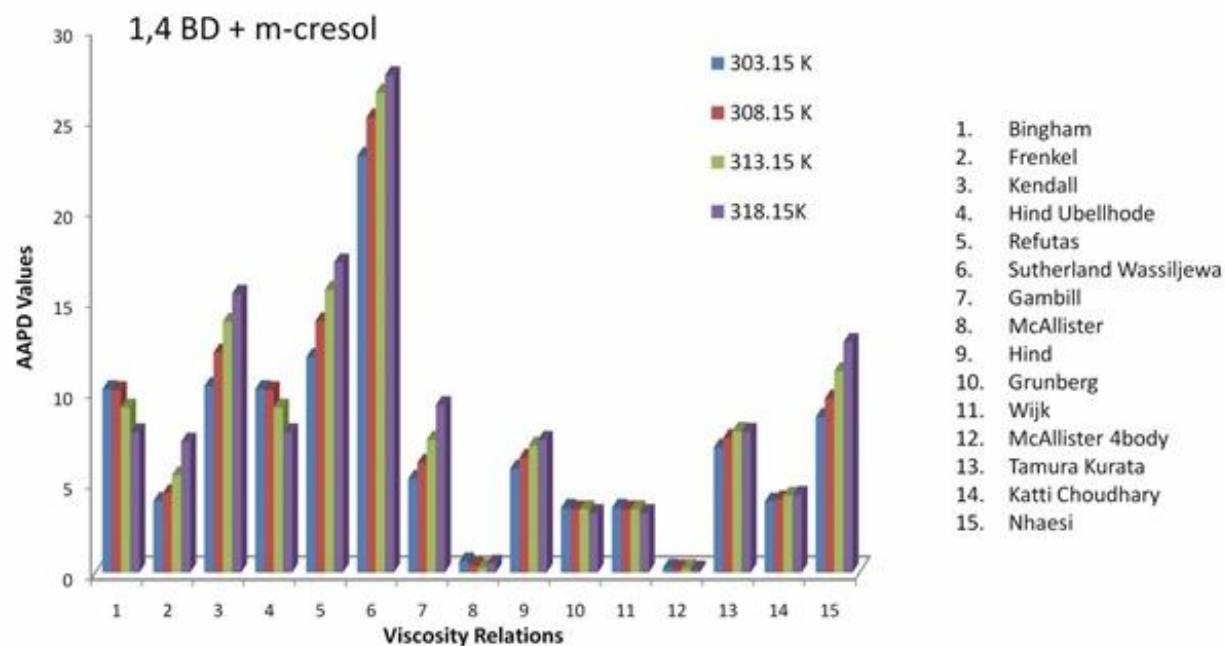
Fig. 4. Plots of AAPD *vs.* viscosity relations of binary mixtures of 1,4-butanediol with m-cresol at different temperatures.

1,4 BD + p-cresol

Fig. 5. Plots of AAPD *vs.* viscosity relations of binary mixtures of 1,4-butanediol with p-cresol at different temperatures.

composition, a deep minimum is detected at all the temperatures investigated. This minimum is observed at $x_1 = 0.4002$. The negative values of the aforementioned parameters, $\Delta\eta$ and ΔG^{*E} point towards presence of very specific interactions between unlike molecules with the highest degree of interactions being present in the 1,4-BD + p-cresol system as compared to its o- and m- counterpart systems. The McAllister 4-body approach gives very accurate results with the AAPD values being less than 0.5 for all the systems under consideration.

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