Viscometric and FTIR studies of molecular interactions in 2-propanol+hydrocarbons mixtures at 298.15 and 308.15 K

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Abstract–The deviation in viscosity was coupled with respective excess molar volume data to study the molecular interaction in binary mixtures with one associated component. This approach was applied to the experimentally measured viscosity and excess molar volume data of the 2-propanol+hydrocarbons at 298.15 K and 308.15 K. It was suggested that depolymerization power of aromatic hydrocarbon toward 2-propanol as well as strength of intermolecular interactions (electron-donor-acceptor type) between monomer of 2-propanol and aromatics depend on π-electron density of the aromatic hydrocarbon. These interactions were further confirmed by FTIR spectroscopy. The viscosity of these binary mixtures was best predicted by Gruenberg-Nissan correlation among the four correlations applied.

Keywords: Excess Volume, Viscosity, 2-Propanol, Hydrocarbons, FT-IR, Molecular Interactions

INTRODUCTION

Thermodynamic and transport properties such as volumetric, acoustical, and viscometric properties of oxygenates with hydrocarbon would be of great significance in understanding intermolecular interactions and formulating motor fuel. Viscosity is the fundamental transport property for process design in petrochemical and petroleum industries involving fluid flow. Many correlations have been 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, ASOG-VISCO, developed by Tochigi et al., combines Eyring's model with the ASOG group contribution model [5,6]. It was shown that excess molar volumes (V^E) and deviation in viscosity ($\Delta\eta$) in binary mixtures of non-electrolytes are related as $\Delta\eta = K^* V^E$ as both are due to the packing effects [7]. This equation successfully describes $\Delta\eta$ data of many binary mixtures [8,9] but fails in case of binary systems with associated component. It was modified for the associated binary mixtures [10]. It would be interesting to check the applicability of this approach for the binary mixtures of 2-propanol with hydrocarbons. As a part of our continuing interest in the study of thermodynamic properties of binary associated mixtures of non-electrolytes [11-19], we report the viscosities of 2-propanol+hydrocarbons at 298.15 K and 308.15 K. The measured viscosity deviation was then combined with the relevant V^E data to know deeper information about the intermolecular interactions [20-22].

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EXPERIMENTAL

1. Chemicals

The chemicals cyclohexane, 2-propanol, benzene, toluene and xylenes were purified by standard methods [19,23]. Experimentally measured densities, refractive indices and viscosities of the purified compounds compared well with their respective literature values shown in Table 1 [24-35]. All samples show ≥99.6 wt% purity by gas chromatography (Table 1).

2. Apparatus and Procedure

Refractive indices (±0.001) and density (±5×10^{-5} g cm^{-3}) of pure components were measured by a thermostatically controlled Abbe refractometer (OSAW, India) and dilatometric technique, respectively, as described elsewhere [36,37]. The temperature of water thermostat was controlled to ±0.01 K by a mercury-in-toluene regulator.

The binary mixtures were prepared by weight using a weighing balance (Shimadzu UniBloc 321-62900-64, AUX 120) which can be measured with an accuracy of ±0.00001 g and accuracy in mole fraction is ±0.0001. Viscosities in the pure liquids and their binary mixtures were measured by using a modified suspended level Ubbelohde viscometer. The viscometer was calibrated at working temperatures beforehand. A freshly distilled liquid was filled in the reservoir of the viscometer through the side tube. Then it was clamped gently at the top in a vertical position after immersing it to an appropriate depth in the water thermostat to maintain the required temperature. To avoid a change in the effective length of capillary from one reading to another, the viscometer was hung exactly vertical. After remaining in bath for about 30 minutes, the liquid was drawn up through the capillary tube into bulb. The time of flow of each liquid was measured at least 3-4 times until reproducible timing was attained. The characteristic constants A and B of viscometer were then determined from the measured times of flow of two liquids of known viscosities at desired temperatures using following equation

Table 1. Purities (wt%), measured densities (r), refractive indices (n_D) and viscosity (η) of the pure components

Compound	GC results	T/K	ρ/(kg m^{-3})		n_D		η	
			This work	Literature	This work	Literature	This work	Literature
2-Propanol	99.8	298.15	781.16	781.28[a]	1.375	1.375[b]	2.035	2.0763[j]
		308.15	771.31	772.27[a]	1.371	1.3716[d]	1.535	1.5317[j]
Cyclohexane	99.6	298.15	774.2	773.5[f]	1.498	1.49792[f]	0.896	0.898[f]
		308.15	762.4	762.96[h]	1.491	1.4917[i]	0.732	0.749[h]
Benzene	99.7	298.15	871.54	873.60[f]	1.498	1.49792[f]	0.292	0.291[f]
		308.15	864.92	862.96[h]	1.491	1.4917[i]	0.280	0.271[k]
Toluene	99.8	298.15	861.21	862.19[f]	1.494	1.49413[f]	0.612	0.6028[f]
		308.15	853.84	852.85[h]	1.489	1.4887[i]	0.523	0.526[h]
o-Xylene	99.7	298.15	874.92	875.94[f]	1.503	1.50295[f]	0.551	0.5525[f]
		308.15	867.15	867.38[h]	1.503	1.50295[f]	0.498	0.499[h]
m-Xylene	99.8	298.15	861.06	860.09[f]	1.495	1.49464[f]	0.746	0.756[f]
		308.15	850.53	851.57[h]	1.468	1.488[l]	0.620	0.658[h]
p-Xylene	99.9	298.15	856.65	856.61[f]	1.493	1.49325[f]	0.590	0.581[f]
		308.15	848.83	847.87[h]	1.489	1.4881[i]	0.471	0.499[h]

[a][24]; [b][25]; [c][26]; [d][27]; [e][28]; [f][29]; [g][30]; [h][31]; [i][32]; [j][33]; [k][34]; [l][35]

$$\upsilon_i = \eta_i/\rho_i = At_i - B/t_i$$

where υ_i, η_i and ρ_i are the kinematic viscosity, absolute viscosity and density of pure liquids respectively and t_i is the time of flow in seconds. The dynamic viscosity, η, is deduced with an uncertainty of $\pm 0.003 \times 10^{-3}$ Ns m^{-2}. For viscometer, the values of constants at 298.15 K, A=4.2673×10^{-9} m^{2}s^{-2}, B=1.984×10^{-6} m^2 and at 308.15 K are A=4.32×10^{-9} m^{2}s^{-2}, B=8.6×10^{-8} m^2, respectively.

RESULTS AND DISCUSSION

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

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

where η_m and η_i represent the respective viscosity of the mixture and pure components. The $\Delta\eta$ data were fitted to Redlich-Kister equation [38]:

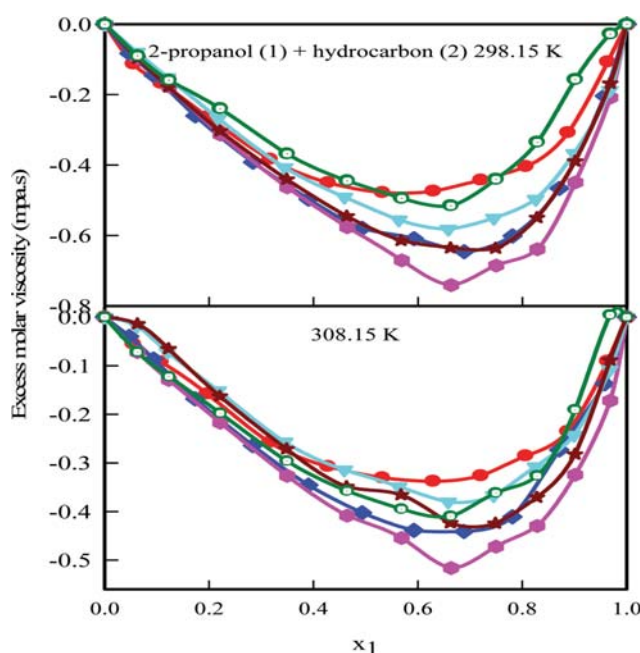$$\Delta\eta = x_A(1-x_A)\left[\sum_{j=0}^{n}A_j(1-2x_A)^j\right] \qquad (2)$$

where A_j are the adjustable parameters, and x_A is the mole fraction of 2-propanol in binary mixture. These parameters were reported in Table 3 along with the standard deviations $\sigma(\Delta\eta)$ of $\Delta\eta$.

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

Comparison of experimental $\Delta\eta$ values with their respective calculated (from Eq. (2)) values for the present systems is shown in Fig. 1.

Viscosity deviation ($\Delta\eta$) values were found to be negative at all compositions (Fig. 1). Negative $\Delta\eta$ value indicates the specific interactions among unlike molecules. The $\Delta\eta$ values at x_A=0.5 follow the sequence: cyclohexane>p-xylene>o-xylene>m-xylene>benzene>toluene.

Greater $\Delta\eta$ for 2-propanol (A)+cyclohexane (B) system is due

Fig. 1. Excess molar viscosity of binary mixture of 2-propanol (1)+ hydrocarbon (2) mixture as a function of mole fraction of 2-propanol at 298.15 and 308.15 K: ● cyclohexane, ◆ benzene, toluene, ⬢ o-xylene, ▼ m-xylene, ★ p-xylene.

to rupture of hydrogen bonding as well as dipole-dipole interaction of monomer and polymer of 2-propanol and rupture of cohesive forces in cyclohexane [39]. In 2-propanol+aromatic hydrocarbon, π-electron donor-acceptor interactions exist, which makes the $\Delta\eta$ values lower than that for 2-propanol+cyclohexane mixtures [40]. The absolute value of $\Delta\eta$ increases with decrease in temperature due to weakening of intermolecular interactions at higher temperature.

Next, we predicted the viscosity deviation values by an approach

given by Singh, that employs the excess molar volume in the following relation [7]:

$$\Delta\eta = K^* V^E \tag{4}$$

We utilized experimental $\Delta\eta$ and V^E data for an equimolar composition binary mixtures to evaluate its K^* parameters, which were subsequently employed to evaluate $\Delta\eta$ at other compositions using

Table 2. Comparison of experimental and calculated ($\Delta\eta$) values from the Eqs. (1), (4) and (5) at 298.15 K and 308.15 K for the various (A+B) mixtures

x_1	η_m (mPa s)	V^E (cm^3 mol^{-1})	$\Delta\eta_{exp.}$ (mPa s)	$\Delta\eta^*$ (mPa s)	$\Delta\eta^\dagger$ (mPa s)
2-Propanol (A)+Cyclohexane (B); T=298.15 K					
0.1055	0.851	0.269	−0.168	−0.270	−0.106
0.1931	0.856	0.432	−0.263	−0.387	−0.225
0.3114	0.873	0.559	−0.384	−0.458	−0.314
0.4221	0.933	0.593	−0.450	−0.473	−0.358
0.5260	1.024	0.573	−0.478	−0.459	−0.376
0.6238	1.138	0.523	−0.474	−0.423	−0.374
0.7158	1.274	0.457	−0.443	−0.365	−0.353
0.8027	1.410	0.374	−0.404	−0.284	−0.313
0.8849	1.598	0.261	−0.308	−0.182	−0.254
T=308.15 K					
0.1055	0.726	0.445	−0.092	−0.150	−0.106
0.1931	0.732	0.667	−0.158	−0.224	−0.190
0.3114	0.728	0.841	−0.258	−0.283	−0.262
0.4221	0.768	0.931	−0.307	−0.313	−0.305
0.5260	0.828	0.971	−0.331	−0.326	−0.330
0.6238	0.899	0.966	−0.338	−0.325	−0.339
0.7158	0.984	0.903	−0.327	−0.303	−0.328
0.8027	1.093	0.766	−0.286	−0.258	−0.292
0.8849	1.209	0.539	−0.236	−0.181	−0.225
2-Propanol (A)+Benzene (B); T=298.15 K					
0.0937	0.600	0.181	−0.145	−0.386	−0.008
0.1735	0.599	0.261	−0.260	−0.558	−0.257
0.2839	0.624	0.303	−0.392	−0.649	−0.451
0.3904	0.671	0.299	−0.497	−0.640	−0.542
0.4932	0.735	0.272	−0.579	−0.580	−0.579
0.5925	0.846	0.230	−0.609	−0.492	−0.584
0.6884	0.946	0.180	−0.646	−0.385	−0.565
0.7811	1.123	0.124	−0.601	−0.265	−0.532
0.8708	1.385	0.067	−0.466	−0.144	−0.494
T=308.15 K					
0.0937	0.531	0.292	−0.086	−0.239	−0.007
0.1735	0.530	0.437	−0.168	−0.356	−0.168
0.2839	0.546	0.529	−0.264	−0.431	−0.304
0.3904	0.572	0.540	−0.346	−0.440	−0.372
0.4932	0.619	0.505	−0.402	−0.412	−0.402
0.5925	0.684	0.443	−0.439	−0.362	−0.408
0.6884	0.778	0.364	−0.441	−0.297	−0.398
0.7811	0.902	0.271	−0.411	−0.221	−0.376
0.8708	1.131	0.167	−0.273	−0.136	−0.343

Table 2. Continued

x_1	η_m (mPa s)	V^E (cm^3 mol^{-1})	$\Delta\eta_{exp.}$ (mPa s)	$\Delta\eta^*$ (mPa s)	$\Delta\eta^\dagger$ (mPa s)
2-Propanol (A)+Toluene (B); T=298.15 K					
0.1230	0.556	0.157	−0.177	−0.639	0.039
0.2215	0.566	0.199	−0.314	−0.812	−0.304
0.3496	0.607	0.196	−0.463	−0.800	−0.518
0.4648	0.664	0.164	−0.577	−0.669	−0.593
0.5689	0.725	0.121	−0.671	−0.494	−0.606
0.6634	0.795	0.075	−0.741	−0.307	−0.590
0.7497	0.978	0.032	−0.685	−0.132	−0.571
0.8287	1.142	−0.001	−0.639	0.005	−0.576
0.9014	1.440	−0.019	−0.449	0.076	−0.634
T=308.15 K					
0.1230	0.496	0.233	−0.129	−0.409	−0.057
0.2215	0.510	0.296	−0.217	−0.520	−0.257
0.3496	0.534	0.295	−0.327	−0.517	−0.373
0.4648	0.571	0.257	−0.408	−0.451	−0.414
0.5689	0.633	0.211	−0.455	−0.370	−0.430
0.6634	0.669	0.164	−0.516	−0.288	−0.436
0.7497	0.803	0.119	−0.472	−0.208	−0.437
0.8287	0.927	0.076	−0.430	−0.133	−0.436
0.9014	1.108	0.039	−0.324	−0.068	−0.438
2-Propanol (A)+o-Xylene (B); T=298.15 K					
0.1205	0.750	0.157	−0.152	−0.596	0.028
0.2173	0.759	0.204	−0.268	−0.774	−0.301
0.3443	0.783	0.198	−0.407	−0.753	−0.484
0.4589	0.847	0.156	−0.491	−0.592	−0.510
0.5631	0.917	0.105	−0.556	−0.397	−0.488
0.6581	1.013	0.058	−0.582	−0.219	−0.467
0.7452	1.156	0.021	−0.551	−0.081	−0.471
0.8253	1.313	−0.002	−0.497	0.009	−0.512
0.8993	1.539	−0.012	−0.367	0.046	−0.595
T=308.15 K					
0.1205	0.658	0.223	−0.072	−0.329	0.021
0.2173	0.668	0.305	−0.151	−0.448	−0.180
0.3443	0.678	0.311	−0.257	−0.458	−0.302
0.4589	0.726	0.255	−0.314	−0.375	−0.324
0.5631	0.786	0.183	−0.349	−0.269	−0.314
0.6581	0.842	0.117	−0.380	−0.172	−0.306
0.7452	0.935	0.068	−0.367	−0.100	−0.314
0.8253	1.067	0.037	−0.308	−0.054	−0.341
0.8993	1.200	0.018	−0.243	−0.026	−0.380
2-Propanol (A)+m-Xylene (B); T=298.15 K					
0.1224	0.588	0.182	−0.179	−0.382	0.079
0.2206	0.605	0.274	−0.303	−0.577	−0.236
0.3484	0.653	0.317	−0.440	−0.667	−0.481
0.4635	0.714	0.290	−0.545	−0.609	−0.563
0.5676	0.796	0.227	−0.614	−0.478	−0.558
0.6622	0.912	0.155	−0.635	−0.327	−0.523
0.7487	1.036	0.091	−0.636	−0.191	−0.492
0.8280	1.237	0.042	−0.550	−0.087	−0.486
0.9009	1.503	0.011	−0.389	−0.024	−0.511

Table 2. Continued

x_1	η_m (mPa s)	V^E (cm^3 mol^{-1})	$\Delta\eta_{exp.}$ (mPa s)	$\Delta\eta^*$ (mPa s)	$\Delta\eta^\dagger$ (mPa s)
		T=308.15 K			
0.1224	0.536	0.247	−0.065	−0.283	−0.029
0.2206	0.543	0.333	−0.163	−0.381	−0.191
0.3484	0.571	0.357	−0.271	−0.409	−0.303
0.4635	0.615	0.330	−0.349	−0.378	−0.349
0.5676	0.709	0.283	−0.366	−0.324	−0.365
0.6622	0.752	0.227	−0.423	−0.260	−0.365
0.7487	0.843	0.169	−0.424	−0.194	−0.356
0.8280	0.981	0.112	−0.371	−0.128	−0.345
0.9009	1.147	0.060	−0.282	−0.069	−0.334
	2-Propanol (A)+p-Xylene (B); T=298.15 K				
0.1228	0.611	0.173	−0.159	−0.473	−0.097
0.2213	0.658	0.223	−0.240	−0.610	−0.317
0.3492	0.695	0.222	−0.368	−0.608	−0.433
0.4644	0.767	0.189	−0.445	−0.517	−0.454
0.5685	0.852	0.147	−0.495	−0.404	−0.443
0.6631	0.953	0.107	−0.516	−0.292	−0.425
0.7494	1.139	0.070	−0.441	−0.191	−0.410
0.8285	1.346	0.039	−0.335	−0.106	−0.403
0.9012	1.618	0.016	−0.157	−0.043	−0.411
		T=308.15 K			
0.1228	0.549	0.256	−0.122	−0.346	−0.098
0.2213	0.571	0.324	−0.198	−0.437	−0.248
0.3492	0.598	0.327	−0.296	−0.442	−0.333
0.4644	0.650	0.295	−0.358	−0.398	−0.362
0.5685	0.715	0.250	−0.395	−0.338	−0.370
0.6631	0.793	0.199	−0.410	−0.269	−0.362
0.7494	0.926	0.143	−0.362	−0.194	−0.344
0.8285	1.039	0.088	−0.327	−0.119	−0.320
0.9012	1.247	0.040	−0.191	−0.053	−0.303

the corresponding V^E data [20-22]. Such $\Delta\eta$ values are recorded as $\Delta\eta^*$ in Table 2. Though $\Delta\eta^*$ values are of the right order of magni-

tude, they differ from the experimental $\Delta\eta$ data as evident from corresponding standard deviation (σ^*) given in Table 4. This is understandable because Eq. (4) implicitly assumes that $\Delta\eta$ and V^E are due essentially to unlike A−B interactions in the molecules of the (A+B) mixtures. But this is a reasonable assumption only when A and B are not self-associated.

However, if A or B is associated, unlike A−B interaction takes place only after the depolymerization of the associated 2-propanol or hydrocarbon entity to monomeric moieties. Since 2-propanol is known to be associated through H-bonding, the viscosity change $\Delta\eta$ of the present (A+B) mixtures would thus involve contributions from (i) depolymerization of 2-propanol (A_n) to give monomers (($\Delta\eta$)$_{depolym.}$) and then (ii) these monomers interact with hydrocarbon to form unlike (A−B) interactions (($\Delta\eta$)$_{A-B\ int.}$).

While the formation of A_n····B contacts will increase the viscosity, the associated depolymerization process will decrease the viscosity of the (A+B) mixture. Evidently, the increase in viscosity due to A_n····B contact formation, would be directly proportional to the mole fraction x_B of hydrocarbon. Hence, ($\Delta\eta$)$_{An···B}$=K′x_B where K′ is a constant of proportionality. On the other hand, the decrease in viscosity ($-\Delta\eta$) due to depolymerization of (A_n) would be dependent on the stoichiometric mole fraction of associated 2-butanol (A_n), i.e., $-(\Delta\eta)_{depolym.}$=K″x_A. If it be assumed that K′=K″=K†, then ($\Delta\eta$)$_{depolym.}$ would be given by K†(x_B-x_A).

As after depolymerisation both the component are monomer, thus, viscosity changes due to A−B interaction would be given as [7]

$$(\Delta\eta)_{A-B\ int.}=K^o V^E,$$

Thus net viscosity deviation, ($\Delta\eta$) of the present (A_n+B) mixture would be given by:

$$\Delta\eta=(\Delta\eta)_{depolym.}+(\Delta\eta)_{A-B\ int.}=K^\dagger(x_B-x_A)+K^o V^E, \qquad (5)$$

Rearranging above equation, we get

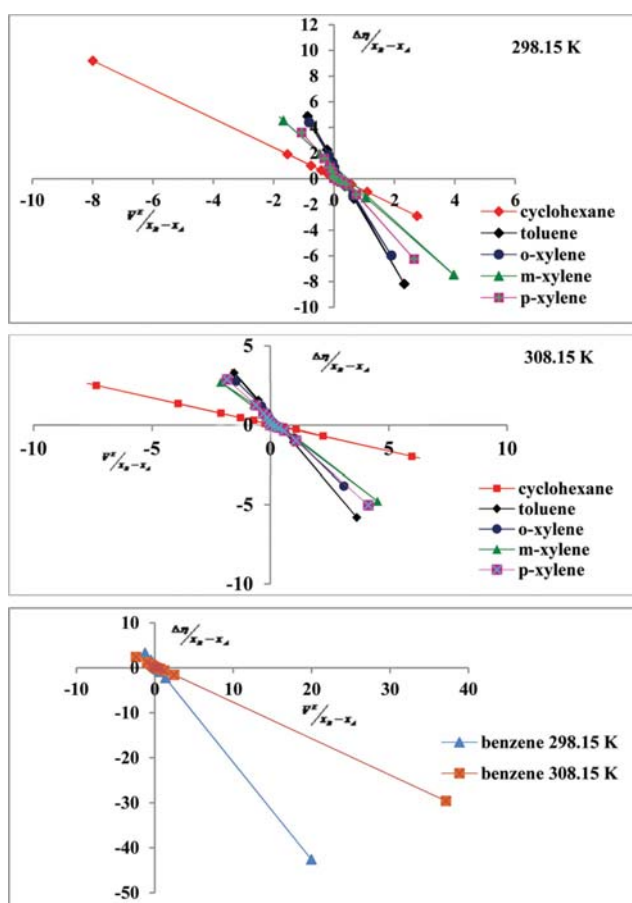$$\frac{\Delta\eta}{(x_B-x_A)}=K^o\frac{V^E}{(x_B-x_A)}+K^\dagger$$

If the basic arguments in deriving Eq. (5) are valid, then the plot of $\Delta\eta/(x_B-x_A)$ versus $V^E/(x_B-x_A)$ should be linear with slope K^o and intercept $K^\dagger$. This has indeed been observed in Fig. 2. Such K^o and

Table 3. Redlich-Kister equation parameters (in mpa s) for deviation in viscosity, $\Delta\eta$, of (A+B) mixtures along with standard deviation

System	T/K	A_1	A_2	A_3	A_4	σ
2-Propanol (A)+Cyclohexane (B)	298.15	−1.9E+00	−4.8E−01	−8.2E−01	−4.7E−01	1.4E−02
	308.15	−1.3E+00	−4.1E−01	−5.0E−01	−7.0E−01	9.0E−03
2-Propanol (A)+Benzene (B)	298.15	−2.3E+00	−1.2E+00	−1.2E+00	−6.6E−01	7.4E-03
	308.15	−1.6E+00	−9.2E−01	−4.0E−01	−2.0E−01	1.2E−02
2-Propanol (A)+Toluene (B)	298.15	−2.5E+00	−1.8E+00	−1.5E+00	−6.8E−01	1.7E−02
	308.15	−1.7E+00	−1.1E+00	−1.1E+00	−7.5E−01	2.0E−02
2-Propanol (A)+o-Xylene (B)	298.15	−2.1E+00	−1.1E+00	−1.0E+00	−1.0E+00	1.6E−02
	308.15	−1.3E+00	−7.4E−01	−4.2E−01	−8.8E−01	9.3E−03
2-Propanol (A)+m-Xylene (B)	298.15	−2.3E+00	−1.4E+00	−1.2E+00	−5.3E−01	7.3E−03
	308.15	−1.4E+00	−9.6E−01	−5.8E−01	−1.0E+00	1.5E−02
2-Propanol (A)+p-Xylene (B)	298.15	−1.9E+00	−1.3E+00	2.5E−01	1.7E+00	1.7E−02
	308.15	−1.5E+00	−1.0E+00	−1.9E−01	7.4E−01	2.9E−02

Table 4. Standard deviation σ^* and $\sigma^\dagger$ of viscosity for (A+B) mixtures using Eqs. (4) and (5), respectively, along with parameters $K^\dagger$, K^o and the correlation coefficient r calculated from Eq. (5)

System	T/K	$K^\dagger$	K^o	r	σ^*	$\sigma^\dagger$
2-Propanol (A)+Cyclohexane (B)	298.15	0.140	−0.886	0.999	0.0868	0.0922
	308.15	0.056	−0.337	0.999	0.0400	0.0142
2-Propanol (A)+Benzene (B)	298.15	0.470	−2.157	0.999	0.2579	0.0729
	308.15	0.281	−0.804	0.999	0.1489	0.0499
2-Propanol (A)+Toluene (B)	298.15	0.883	−4.001	0.986	0.4744	0.1356
	308.15	0.462	−1.737	0.993	0.2476	0.0657
2-Propanol (A)+o-Xylene (B)	298.15	0.801	−3.695	0.979	0.4163	0.1288
	308.15	0.444	−1.413	0.984	0.2319	0.0764
2-Propanol (A)+m-Xylene (B)	298.15	0.608	−2.096	0.988	0.1292	0.0461
	308.15	0.332	−1.131	0.995	0.1940	0.0457
2-Propanol (A)+p-Xylene (B)	298.15	0.461	−2.576	0.988	0.2459	0.1161
	308.15	0.313	−1.306	0.993	0.1745	0.0539

Fig. 2. Plot of $\Delta\eta/(x_B−x_A)$ versus $V^E/(x_B−x_A)$ for 2-propanol (A)+ hydrocarbons (B) at 298.15 K and 308.15 K.

$K^\dagger$ data along with the correlation coefficient r and the relevant V^E data [20-22] for present systems are recorded in Table 4. It is interesting that, r, for all the present (A+B) mixtures is very close to unity. This lends credence to the assumption that for these mixtures $K''=K'=K^\dagger$ $K'=K''=K^\dagger$. These K^o and $K^\dagger$ values were next employed to evaluate $\Delta\eta$ data for the (A+B) mixture. Such data

reported as $\Delta\eta^\dagger$ in Table 2 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, the greater the value of K^o the greater is the extent of interaction between unlike molecules. On other hand, $K^\dagger$ indicates 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<xylene<toluene. From the above order it can be concluded that the K^o value is increasing with increase in π-electron density in the ring. This is as expected because the extent of electron donor-acceptor interaction of π-electron with the hydroxyl hydrogen of 2-propanol increases due to increased electron density with the addition of benzene in place of cyclohexane. The π-electron density increases further in case of toluene and xylenes due to the presence of electron donating methyl groups. As a result of this, toluene or xylenes have greater electron donor-acceptor interaction with 2-propanol, which results in higher K^o value. In the case of cyclohexane, benzene and toluene, it is indeed true. In case of mixtures with xylenes, this interaction should increase further. But the presence of two CH3 groups offers stearic hindrance, which decreases these specific interactions of 2-propanol toward the ring. Thus K^o values for xylenes mixtures lie between benzene and toluene.

A perusal of $K^\dagger$ for these systems (Table 4) clearly indicates that extent of deploymerization (resulting in expansion in volume of mixture) varies as: toluene>o-xylene>m-xylene>p-xylene≈benzene>cyclohexane. But as K^o values indicate the extent of interaction between unlike molecules, so the resultant 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 cyclohexane should be larger positive than benzene, and benzene should have larger value than toluene and xylene mixture. The same was observed for excess molar volume of these systems [20-22].

1. Correlations for Viscosity

Viscosity of these systems was also correlated by the following relations and compared with experimental data in terms of per-

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 as well as their interactional parameters

System	T/K	G-N		T-K		H-Mc-U		K-C	
		σ(%)	G_{AB}	σ(%)	T_{AB}	σ(%)	H_{AB}	σ(%)	W_{vis}/RT
2-Propanol (A)+Cyclohexane (B)	298.15	2.295	−1.301	3.746	0.550	5.958	0.434	4.284	−3.831
	308.15	2.472	−1.131	4.577	0.506	6.863	0.422	6.986	−3.660
2-Propanol (A)+Benzene (B)	298.15	3.152	−1.710	14.089	0.094	16.090	0.039	4.962	−4.253
	308.15	3.616	−1.430	11.066	0.206	12.727	0.167	7.131	−3.982
2-Propanol (A)+Toluene (B)	298.15	7.057	−1.921	19.457	−0.015	24.969	−0.155	11.126	−4.451
	308.15	6.790	−1.742	15.560	−0.099	15.559	8.52E-05	10.514	−4.276
2-Propanol (A)+o-Xylene (B)	298.15	4.573	−1.480	9.193	0.377	13.983	0.199	10.166	−3.990
	308.15	5.970	−1.103	8.287	0.466	11.837	0.338	11.901	−3.613
2-Propanol (A)+m-Xylene (B)	298.15	4.163	−1.673	11.768	0.201	18.411	−0.002	9.918	−4.182
	308.15	8.665	−1.123	12.654	0.342	17.442	0.191	14.609	−3.634
2-Propanol (A)+p-Xylene (B)	298.15	3.492	−1.171	4.661	0.500	38.811	−0.313	8.599	−3.681
	308.15	3.027	−1.262	5.208	0.400	9.406	0.256	8.855	−3.770

centage standard deviations in Table 5:

Grunberg and Nissan [41]

$$\eta = \exp\left[\sum_{i=A,B}(x_i \ln \eta_i) + G_{AB}\prod_{i=A,B}x_i\right] \quad (6)$$

Tamura and Kurata [42]

$$\eta = \left[\sum_{i=A,B}x_i\phi_i\eta_i + 2T_{AB}\prod_{i=A,B}(x_i\phi_i)^{1/2}\right] \quad (7)$$

Hind, McLaughlin and Ubbelohde [43]

$$\eta = \left[\sum_{i=A,B}x_i^2\eta_i + 2H_{AB}\prod_{i=A,B}x_i\right] \quad (8)$$

Katti and Chaudhari [44,45]

$$\ln \eta V_m = \sum_{i=A,B}x_i\ln(\eta_i V_i) + x_A x_B(W_{vis}/RT) \quad (9)$$

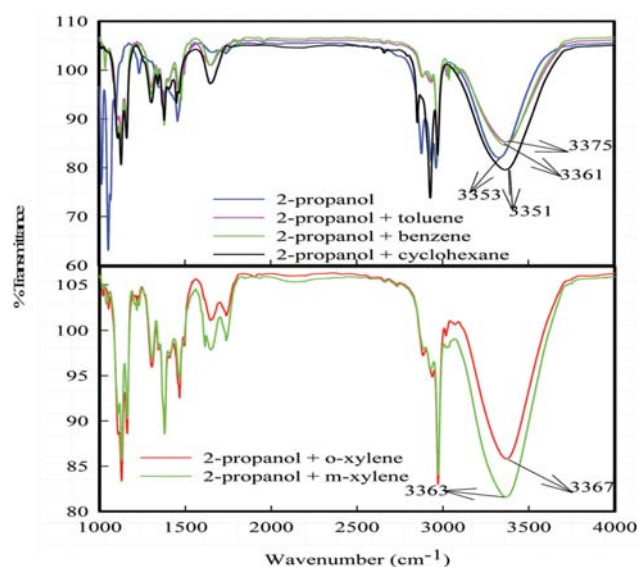The estimation capabilities of these correlations are expressed in Table 5 as percentage standard deviations σ:

$$\sigma(\%) = \left[\frac{\sum\{(\eta_{exptl.}-\eta_{theo.})/\eta_{exptl.}\times 100\}^2}{(n-1)}\right]^{1/2} \quad (10)$$

where all the terms in Eqs. (6)-(10) have their usual meanings and were defined earlier [14].

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

2. FT-IR Studies

The strength of intermolecular hydrogen bonding and specific interaction (π--OH) in these mixtures was also confirmed by FTIR spectroscopy. IR spectral data of the 2-propanol and hydrocarbon and their equimolar binary mixtures are recorded in Fig. 3. From Fig. 3, 2-propanol shows a characteristic absorption peak at around 3,353 cm^{-1} (OH stretch), 2,962 cm^{-1} (sym. CH stretch), and 1,070 cm^{-1} (C-O) due to free -OH group. The characteristic absorption peaks for other hydrocarbons were reported earlier [4]. Due to specific interactions between 2-propanol and hydrocarbon, the characteristic peak of free OH group 3,353 cm^{-1} (OH stretch) in

Fig. 3. Normalized FT-IR spectra of equimolar mixtures of 2-propanol+hydrocarbons over the range 4,000 to 1,000 cm^{-1}.

2-propanol was shifted to 3,351 cm^{-1}, 3,361 cm^{-1}, 3,375 cm^{-1}, 3,363 cm^{-1} and 3,367 cm^{-1} in binary mixtures of cyclohexane, benzene, toluene, o-xylene, m-xylene with 2-propanol, respectively.

Thus, FTIR study further confirms the extent of specific interactions yielded by viscosity data as the absorption band shifted toward higher wave number owing to increased π-electron density at benzene ring. This was also observed by other workers [48,49].

CONCLUSION

The viscosity deviations as function of composition were calculated from the measured viscosity of binary mixtures of 2-propanol+hydrocarbons at 298.15 K and 308.15 K. An approach was applied in which viscosity deviations for binary mixtures with one self-associated component was coupled with corresponding excess

molar volume data. This approach yielded two constants $K^{\dagger}$ and K^{o} which signify the extent of depolymerization of associated component and unlike A-B interaction, respectively. It was suggested that the depolymerization power of aromatic hydrocarbon toward 2-propanol as well as strength of intermolecular interactions (electron-donor-acceptor type) between monomer of 2-propanol and aromatics depend on π-electron density of the aromatic hydrocarbon. It was confirmed that the modified approach [10] for associating mixtures describes well the viscosity deviation as shown in terms of standard deviation σ^{*} and $\sigma^{\dagger}$ of viscosity for the present binary mixtures in Table 4.

These interactions were also supplemented by FTIR spectroscopy. The viscosities of these binary mixtures were also theoretically predicted from various correlations. The viscosity of these binary mixtures was best predicted by Gruenberg-Nissan correlation among the four correlations applied.

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