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Estimation of Excess molar volume and Viscosity of associated polymeric solutions at 298.15-318.15K

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Abstract

Density and Viscosity is an important thermodynamic property of liquids, used in various industrial and pharmaceutical applications. The present investigation deals with the theoretical estimation of viscosity of two binary liquid mixtures of 2-Propenol and 2-Phenylehanol or Benzyl alcohol over the entire range of mole fractions at elevated temperatures from 298.15-318.15K and atmospheric pressure by six empirical relations such as Eyring, Bingham, Kendall-Munroe, Frenkel, Dey and Hind. Computed values of viscosities obtained by the aforementioned relations were compared with the experimental findings. Deviation in viscosity ($\Delta\eta$) was derived from measured data and fitted to redlich-kister polynomial to estimate the binary coefficient and standard deviation. Excess molar volume (V^E) was also computed to analyze the extent of molecular interactions and Furthermore, Joubyan Acree model is used to correlate the experimental findings. Eyring, Hind, and Frenkel models show the best agreement with experimental data.

Keywords: Density, Viscosity, Excess molar volume, Interactions, Hind, Frenkel.

Introduction

Density, viscosity and excess molar volume are key parameters for understanding the molecular interactions and structural behavior in liquid mixtures. These properties are essential for industrial applications, such as in chemical engineering and materials science. The study of their thermodynamic and transport properties, like excess molar volume and viscosity, is crucial in understanding the interactions between the molecules in the mixture. Various researchers[1-6] investigated the excess molar volumes and viscosities at different temperature in binary mixtures of alcohols with other polar and non polar solvents. Liquids used in the present investigation have its industrial and pharmaceutical applications. Benzyl alcohol is primarily known for its function as a preservative in injectable drugs[7] and intravenous solutions, ensuring sterility and stability. Additionally, it is employed as a local anaesthetic[8] and solvent in pharmaceutical formulations. Its presence in the cosmetic and food industry as a fragrance enhancer and flavouring agent further highlights its versatility. Phenyl ethanol is another significant compound known for its antiseptic and fragrance properties. It is widely used in eye drops[9], nasal sprays[10], and acting as an antibacterial agent. Beyond pharmaceuticals[11], its floral scent makes it a valuable ingredient in perfumes, cosmetics and food flavouring. Its role in pesticide formulations and ink production also demonstrates its broad industrial relevance whereas Propenol is widely recognized for its disinfectant and antiseptic properties. In the continuation of our previously published work[12-15], this paper is concerned with the theoretical estimation of viscosity by six empirical relations such as Eyring[16], Bingham[17], Kendall-Munroe[18-19], Frenkel[20], Dey[21] and Hind[22] to evaluate the theoretical values of viscosity and compared with the literature value[23]. Deviation in viscosity ($\Delta\eta$) was derived from measured data and fitted to redlich-kister[24] polynomial to estimate the binary coefficient and standard deviation. Excess molar volume (V^E) was also computed to analyze the extent of molecular interactions Jouyban Acree[25-27] model was used to correlate the experimental findings. The main purpose of this work is to understand the effect of carbon chain length of benzyl alcohol and 2- phenyl ethanol with 2-Propenol in molecular interactions at different temperatures as well as test the validity and applicability of these aforesaid models at different temperatures for associated polymeric solutions. Absolute average % deviation (AAPD) was the criteria of success of result.

Theoretical Modeling

Eyring relation: $\ln\eta = x_1^2 + x_2^2 + 2x_1x_2\ln(0.5\eta_1 + 0.5\eta_2)$ (1)

Bingham relation: $\eta = x_1\eta_1 + x_2\eta_2$ (2)

Kendall-Munroe: $\ln\eta = x_1\ln\eta_1 + x_2\ln\eta_2$ (3)

Frenkel relation: $\ln\eta = x_1^2\ln\eta_1 + x_1^2\ln\eta_2 + 2x_1x_2\ln\eta_{12}$ (4)

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

Dey et al (modified Frenkel relation): $\eta_{12} = \frac{2(\eta_1\eta_2)}{|\eta_1+\eta_2|}$ (5)

Hind et al: $\eta = x_1^2\eta_1 + x_2^2\eta_2 + 2x_1x_2H_{12}$ (6)

Where η_1 and η_2 are viscosity of pure liquids and η is the viscosity of binary liquid mixture.

Results and Discussion

The experimental values of density (ρ), viscosity (η), and excess volume (V^E) of the binary liquid mixtures involving 2-Propenol, Benzyl alcohol, and 2-Phenyl ethanol were determined at different mole fractions and temperatures. The obtained data were analyzed to understand the molecular interactions and structural effects in given binary systems. Table-1 represents the coefficient of Redlich-Kister equation and standard deviation (δ) for dynamic viscosity for binary liquid mixtures at different temperature. For 2-Propenol and Benzyl alcohol binary system the standard deviation varies from 0.005-0.007. The small standard deviation (δ) values (0.005-0.007) confirm that the redlich-kister equation provides a good fit for the experimental data. In case of 2-Propenol and 2-Phenyl ethanol system value varies from 0.008-0.011. The slightly higher standard in this system compared to the 2-Propenol + Benzyl Alcohol system suggests a more complex interaction mechanism. Correlation of experimental data was carried out by Joubyan Acree model in terms of correlation coefficient and standard deviation (δ) for the binary mixtures at different temperatures calculated by equation 9 is reported in Table-2. The results indicate significant variations in the interaction parameters across temperature ranges. The 2-Propenol + 2-Phenylethanol system shows consistently higher J_0 values than the 2-Propenol + Benzyl Alcohol system**,** indicating stronger intermolecular interactions. The low standard deviation values (δ) indicate that the Jouyban-Acree model provides an accurate representation of the experimental data for both systems.

$$\Delta\eta = X_I(1-X_1)\sum_{i=0}^{n} A_i(1-X_1)^i \quad (7)$$

In above equation $\Delta\eta$ refers to deviation in viscosity. A_i is coefficient of Redlich-kister polynomial evaluated by multiple regression technique.

The standard deviation (δ) is defined by;

$$\delta = \left[\left(\sum_{i=1}^{n} \frac{\left(\eta_{exp} - \eta_{tho}\right)^2}{(n-p)}\right)^{1/2}\right] \quad (8)$$

Table-3 and 4 represents the experimental and theoretical values of viscosity computed by the aforementioned six empirical relations at different temperatures and their absolute average percent deviation. A very close observation of Table-3 reveals that the density values for both the binary mixtures show a systematic variation with the composition. In most cases, the density decreases with an increasing mole fraction of 2-Propenol due to its lower molecular weight and weaker intermolecular interactions compared to Benzyl alcohol and 2-Phenyl ethanol. The observed trends suggest a non-ideal mixing behaviour influenced by molecular size, shape, and polarity. The binary mixtures show non-ideal behaviour, as indicated by negative V^E. The values of V^E are consistently negative as shown in Figure-1, indicating that the actual volume of the mixture is lower than the ideal volume calculated from the pure liquids. The trends in both graphs are similar, showing negative excess molar volumes, indicating strong intermolecular interactions.

$$\ln\eta = X_1\ln\eta_1 + X_2\ln\eta_2 + J_0\left[\frac{X_1X_2}{T}\right] + J_1\left[\frac{X_1X_2(X_1-X_2)}{T}\right] + J_2\left[\frac{X_1X_2(X_1-X_2)^2}{T}\right] \quad (9)$$

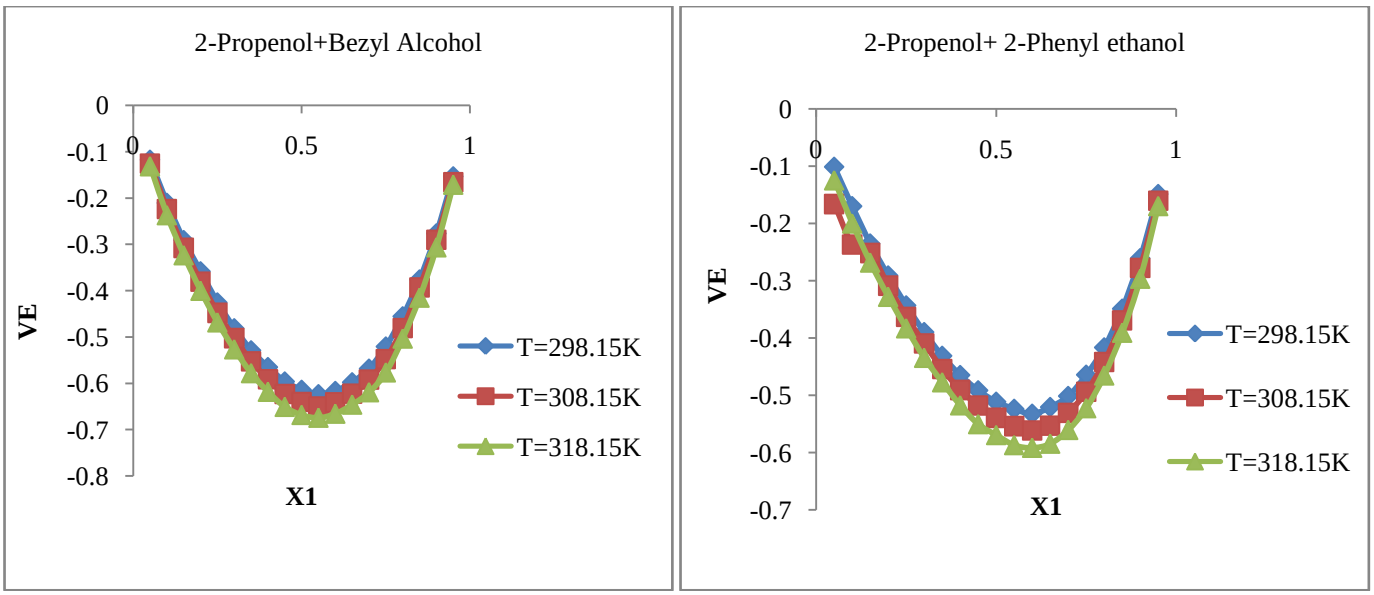

Figure-1: Plot of excess molar volume with mole fraction at different temperatures.

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This suggests strong intermolecular interactions, likely due to hydrogen bonding between 2-propenol and benzyl alcohol as well as 2-propenol and 2-phenyl ethanol. Since 2-propenol has an –OH group capable of forming hydrogen bonds with the –OH of benzyl alcohol and 2-phenyl ethanol. The molecular packing in the mixture is more efficient than in the pure components, leading to a volume contraction. With increase in temperature, the magnitude of negative V^E decreases. This indicates that higher temperatures weaken the intermolecular interactions, possibly due to thermal expansion and reduced hydrogen bonding strength. Benzyl alcohol has a benzyl group that slightly affects the polarity, influencing dipole-dipole interactions. The benzyl group in benzyl alcohol may slightly restrict hydrogen bond formation at higher concentrations. Both systems exhibit a symmetric curve with a minimum around X_1=0.50. This suggests that maximum molecular packing efficiency and strongest interactions occur at equimolar composition in both cases. However, the minimum V^E in the Benzyl Alcohol system is lower; indicating greater volume contraction. 2-Propenol and Benzyl alcohol system shows a slightly more negative V^E than the 2-Propenol and 2-Phenyl ethanol system. This suggests that intermolecular interactions (such as hydrogen bonding and dipole-dipole forces) are stronger in the first system. Benzyl alcohol has a smaller steric hindrance compared to 2-Phenyl ethanol, allowing for stronger hydrogen bonding. The viscosity decreases with increasing temperature, consistent with reduced intermolecular interactions. Eyring and Frenkel models exhibit good predictive accuracy for both systems, particularly at higher temperatures**.** Bingham model consistently shows the highest AAPD values, indicating that it may not be suitable for predicting viscosities in these systems. Kendall-Munroe model remains relatively stable for the 2-Propenol + Benzyl Alcohol system but shows fluctuations for the 2-Propanol + 2-Phenylethanol system. Dey model show significant deviations, particularly at higher temperatures. The Hind model provides the lowest AAPD values at high temperatures, making it a reliable choice for viscosity modeling under these conditions. Eyring, Hind, and Frenkel models show the best agreement with experimental data, while Bingham model exhibits the highest deviations.

Table-1: Coefficient of Redlich-Kister equation and standard deviation (δ).

2-Propenol+Benzyl alcohol					
T/K	A_0	A_1	A_2	A_3	δ
298.15	-1.909	0.014	-0.040	-0.337	0.005
308.15	-1.262	-0.011	-0.086	-0.233	0.007
318.15	-0.736	-0.159	-0.115	-0.005	0.006
2-Propenol+2-Phenyl ethanol					
T/K	A_0	A_1	A_2	A_3	δ
298.15	-5.350	0.814	-0.444	-0.809	0.008
308.15	-3.488	0.344	0.017	-0.192	0.009
318.15	-2.002	0.089	0.170	-0.188	0.011

Table-2: Coefficient of correlation and standard deviation (δ) computed by Joubyan Acree model.

2-Propenol+Benzyl alcohol						2-Propanol+2-Phenylethnol				
T/K	J0	J1	J2	δ		T/K	J0	J1	J2	δ
298.15	-21.193	-45.511	-20.006	0.006		298.15	125.814	6.372	-42.131	0.025
308.15	-8.592	-40.288	-13.115	0.006		308.15	89.296	-11.115	-26.406	0.010
318.15	27.704	-39.225	-20.007	0.071		318.15	112.895	-2.764	-18.964	0.010

Table-3: Experimental and theoretical values of density, viscosity and excess volume of binary liquid mixtures at different temperatures.

TK	X_1	ρ_{mix}	η_{exp}	V^E	$\eta_{Eyring(eq.1)}$	$\eta_{Kndm(eq.2)}$	$\eta_{Bingham(eq.3)}$	$\eta_{Frenkel(eq.4)}$	$\eta_{Dey(eq.5)}$	$\eta_{Hind(eq.6)}$
2-Propenol+Benzyl alcohol										
298.15	0.05	1.033	5.299	-0.118	5.348	5.289	5.381	5.348	5.231	5.306
	0.1	1.024	5.053	-0.211	5.142	5.036	5.208	5.142	4.932	5.066
	0.15	1.014	4.799	-0.291	4.938	4.795	5.034	4.938	4.655	4.833
	0.2	1.004	4.559	-0.358	4.737	4.565	4.860	4.737	4.399	4.608
	0.25	0.994	4.332	-0.426	4.539	4.346	4.687	4.539	4.162	4.391
	0.3	0.984	4.116	-0.481	4.345	4.138	4.513	4.345	3.942	4.181
	0.35	0.973	3.911	-0.529	4.153	3.940	4.339	4.153	3.738	3.980
	0.4	0.961	3.714	-0.565	3.966	3.751	4.166	3.966	3.549	3.787
	0.45	0.949	3.523	-0.596	3.783	3.572	3.992	3.783	3.373	3.601
	0.5	0.937	3.335	-0.614	3.604	3.401	3.819	3.604	3.209	3.424
	0.55	0.924	3.169	-0.623	3.429	3.238	3.645	3.429	3.058	3.254
	0.6	0.911	3.01	-0.616	3.259	3.083	3.471	3.259	2.916	3.092
	0.65	0.897	2.858	-0.598	3.094	2.935	3.298	3.094	2.785	2.938
	0.7	0.882	2.715	-0.568	2.934	2.795	3.124	2.934	2.662	2.792
	0.75	0.867	2.58	-0.521	2.779	2.661	2.950	2.779	2.548	2.654
	0.8	0.852	2.46	-0.455	2.629	2.534	2.777	2.629	2.441	2.524
	0.85	0.835	2.346	-0.376	2.485	2.412	2.603	2.485	2.342	2.402
	0.9	0.818	2.251	-0.277	2.345	2.297	2.429	2.345	2.249	2.287
	0.95	0.800	2.148	-0.154	2.211	2.187	2.256	2.211	2.163	2.181
308.15	0.05	1.025	3.91	-0.126	3.941	3.899	3.966	3.941	3.857	3.911
	0.1	1.016	3.73	-0.224	3.791	3.714	3.839	3.791	3.639	3.736
	0.15	1.006	3.558	-0.308	3.642	3.538	3.712	3.642	3.437	3.565
	0.2	0.997	3.389	-0.381	3.495	3.371	3.584	3.495	3.250	3.401
	0.25	0.986	3.23	-0.448	3.350	3.211	3.457	3.350	3.077	3.242
	0.3	0.976	3.076	-0.503	3.208	3.059	3.330	3.208	2.916	3.089
	0.35	0.965	2.921	-0.553	3.068	2.914	3.203	3.068	2.767	2.942

	0.4	0.953	2.772	-0.591	2.931	2.776	3.076	2.931	2.628	2.801
	0.45	0.941	2.631	-0.623	2.797	2.644	2.949	2.797	2.500	2.665
	0.5	0.929	2.49	-0.641	2.666	2.519	2.822	2.666	2.380	2.535
	0.55	0.916	2.37	-0.650	2.538	2.399	2.694	2.538	2.268	2.411
	0.6	0.902	2.256	-0.641	2.414	2.286	2.567	2.414	2.164	2.292
	0.65	0.889	2.145	-0.623	2.293	2.177	2.440	2.293	2.068	2.179
	0.7	0.874	2.042	-0.592	2.175	2.074	2.313	2.175	1.978	2.072
	0.75	0.859	1.946	-0.548	2.062	1.976	2.186	2.062	1.894	1.971
	0.8	0.843	1.851	-0.481	1.952	1.882	2.059	1.952	1.815	1.875
	0.85	0.827	1.761	-0.393	1.846	1.793	1.931	1.846	1.742	1.785
	0.9	0.809	1.675	-0.290	1.743	1.708	1.804	1.743	1.674	1.701
	0.95	0.791	1.602	-0.166	1.645	1.627	1.677	1.645	1.610	1.623
318.15	0.05	1.017	2.989	-0.131	3.004	2.972	3.023	3.004	2.940	2.982
	0.1	1.008	2.864	-0.237	2.890	2.831	2.926	2.890	2.774	2.847
	0.15	0.998	2.745	-0.323	2.776	2.697	2.829	2.776	2.620	2.718
	0.2	0.988	2.628	-0.400	2.664	2.569	2.732	2.664	2.477	2.592
	0.25	0.978	2.513	-0.468	2.554	2.447	2.635	2.554	2.345	2.471
	0.3	0.967	2.4	-0.526	2.445	2.331	2.538	2.445	2.223	2.355
	0.35	0.956	2.285	-0.578	2.338	2.221	2.441	2.338	2.109	2.242
	0.4	0.945	2.172	-0.618	2.234	2.115	2.344	2.234	2.003	2.135
	0.45	0.933	2.059	-0.651	2.132	2.015	2.247	2.132	1.905	2.031
	0.5	0.920	1.953	-0.668	2.032	1.920	2.151	2.032	1.814	1.932
	0.55	0.907	1.858	-0.674	1.934	1.829	2.054	1.934	1.729	1.837
	0.6	0.894	1.769	-0.665	1.839	1.742	1.957	1.839	1.649	1.747
	0.65	0.880	1.68	-0.646	1.747	1.659	1.860	1.747	1.576	1.661
	0.7	0.865	1.594	-0.619	1.658	1.581	1.763	1.658	1.507	1.579
	0.75	0.850	1.511	-0.576	1.571	1.506	1.666	1.571	1.443	1.502
	0.8	0.834	1.434	-0.503	1.487	1.434	1.569	1.487	1.383	1.429
	0.85	0.818	1.359	-0.415	1.406	1.366	1.472	1.406	1.327	1.360

	0.9	0.801	1.295	-0.306	1.328	1.301	1.375	1.328	1.275	1.296
	0.95	0.782	1.228	-0.171	1.253	1.240	1.278	1.253	1.226	1.236
2-propanol+2-phenylethnol										
298.15	0.05	1.0094	10.665	-0.102	10.804	10.475	10.939	10.804	10.157	10.633
	0.1	1.0021	9.933	-0.170	10.201	9.621	10.473	10.201	9.075	9.893
	0.15	0.9944	9.256	-0.236	9.600	8.837	10.007	9.600	8.134	9.185
	0.2	0.9864	8.618	-0.291	9.006	8.117	9.540	9.006	7.315	8.509
	0.25	0.9780	8.000	-0.344	8.421	7.455	9.074	8.421	6.600	7.866
	0.3	0.9691	7.407	-0.390	7.848	6.847	8.608	7.848	5.974	7.255
	0.35	0.9599	6.858	-0.432	7.291	6.289	8.142	7.291	5.425	6.676
	0.4	0.9502	6.350	-0.465	6.751	5.776	7.676	6.751	4.942	6.129
	0.45	0.9400	5.862	-0.492	6.231	5.305	7.210	6.231	4.517	5.615
	0.5	0.9293	5.412	-0.512	5.732	4.873	6.744	5.732	4.142	5.132
	0.55	0.9180	4.978	-0.524	5.257	4.476	6.277	5.257	3.811	4.682
	0.6	0.9062	4.571	-0.533	4.805	4.111	5.811	4.805	3.517	4.264
	0.65	0.8936	4.173	-0.521	4.377	3.776	5.345	4.377	3.257	3.879
	0.7	0.8804	3.793	-0.502	3.975	3.468	4.879	3.975	3.026	3.526
	0.75	0.8663	3.438	-0.465	3.598	3.185	4.413	3.598	2.820	3.204
	0.8	0.8513	3.101	-0.417	3.246	2.926	3.947	3.246	2.637	2.915
	0.85	0.8355	2.808	-0.349	2.919	2.687	3.480	2.919	2.473	2.659
	0.9	0.8186	2.541	-0.261	2.617	2.468	3.014	2.617	2.328	2.434
	0.95	0.8005	2.281	-0.149	2.338	2.267	2.548	2.338	2.198	2.242
308.15	0.05	1.0094	7.05	-1.002	7.14	6.95	7.22	7.14	6.76	7.03
	0.1	1.0021	6.59	-1.068	6.76	6.42	6.92	6.76	6.10	6.57
	0.15	0.9944	6.15	-1.131	6.38	5.93	6.62	6.38	5.52	6.12
	0.2	0.9864	5.73	-1.185	6.00	5.48	6.32	6.00	5.01	5.70
	0.25	0.9780	5.34	-1.235	5.63	5.07	6.03	5.63	4.55	5.29
	0.3	0.9691	4.97	-1.280	5.27	4.68	5.73	5.27	4.16	4.90
	0.35	0.9599	4.62	-1.319	4.92	4.33	5.43	4.92	3.80	4.54

	0.4	0.9502	4.29	-1.351	4.58	4.00	5.13	4.58	3.49	4.19
	0.45	0.9400	3.96	-1.375	4.25	3.69	4.83	4.25	3.21	3.86
	0.5	0.9293	3.67	-1.393	3.93	3.41	4.53	3.93	2.96	3.55
	0.55	0.9180	3.39	-1.403	3.63	3.15	4.24	3.63	2.74	3.26
	0.6	0.9062	3.12	-1.410	3.34	2.92	3.94	3.34	2.54	2.99
	0.65	0.8936	2.88	-1.396	3.07	2.69	3.64	3.07	2.37	2.75
	0.7	0.8804	2.63	-1.375	2.80	2.49	3.34	2.80	2.21	2.52
	0.75	0.8663	2.41	-1.335	2.56	2.30	3.04	2.56	2.07	2.31
	0.8	0.8513	2.20	-1.286	2.33	2.13	2.74	2.33	1.94	2.12
	0.85	0.8355	2.01	-1.216	2.11	1.96	2.45	2.11	1.83	1.94
	0.9	0.8186	1.86	-1.126	1.91	1.82	2.15	1.91	1.72	1.79
	0.95	0.8005	1.69	-1.012	1.72	1.68	1.85	1.72	1.63	1.66
318.15	0.05	0.9942	4.95	-0.125	4.98	4.86	5.03	4.98	4.74	4.91
	0.1	0.9868	4.65	-0.200	4.72	4.51	4.83	4.72	4.31	4.60
	0.15	0.9790	4.37	-0.268	4.47	4.19	4.62	4.47	3.92	4.30
	0.2	0.9708	4.10	-0.328	4.21	3.88	4.42	4.21	3.58	4.01
	0.25	0.9623	3.85	-0.383	3.97	3.61	4.22	3.97	3.28	3.74
	0.3	0.9534	3.60	-0.435	3.73	3.35	4.02	3.73	3.01	3.48
	0.35	0.9440	3.36	-0.478	3.49	3.11	3.81	3.49	2.77	3.23
	0.4	0.9342	3.13	-0.518	3.26	2.88	3.61	3.26	2.55	3.00
	0.45	0.9239	2.91	-0.551	3.04	2.68	3.41	3.04	2.36	2.78
	0.5	0.9131	2.71	-0.570	2.82	2.49	3.21	2.82	2.19	2.57
	0.55	0.9017	2.52	-0.587	2.62	2.31	3.00	2.62	2.03	2.37
	0.6	0.8897	2.34	-0.592	2.42	2.14	2.80	2.42	1.90	2.19
	0.65	0.8770	2.16	-0.585	2.23	1.99	2.60	2.23	1.77	2.02
	0.7	0.8636	1.99	-0.561	2.05	1.85	2.40	2.05	1.66	1.86
	0.75	0.8494	1.82	-0.523	1.89	1.71	2.19	1.89	1.56	1.71
	0.8	0.8343	1.67	-0.466	1.73	1.59	1.99	1.73	1.47	1.58
	0.85	0.8183	1.53	-0.391	1.58	1.48	1.79	1.58	1.38	1.46

	0.9	0.8013	1.42	-0.297	1.43	1.37	1.59	1.43	1.31	1.36
	0.95	0.7831	1.30	-0.170	1.30	1.27	1.38	1.30	1.24	1.26

Table-4: Values of AAPD for viscosity models at different temperatures.

	T/K	η_{Eyring}	η_{Kndm}	$\eta_{Bingham}$	$\eta_{Frenkel}$	η_{Dey}	η_{Hind}	η_{wijk}
2-Propenol + Benzyl alcohol	298.15	5.719	1.566	10.357	5.719	2.598	1.881	2.598
	308.150	4.766	1.011	9.255	4.766	3.287	1.035	3.287
	318.150	2.743	1.475	7.137	2.743	5.089	1.002	5.089
	T/K	η_{Eyring}	η_{Kndm}	$\eta_{Bingham}$	$\eta_{Frenkel}$	η_{Dey}	η_{Hind}	η_{wijk}
2-propanol + 2-phenylethnol	298.15	4.60	6.60	19.13	4.60	16.45	3.83	16.45
	308.15	5.29	4.66	17.79	5.29	13.55	2.50	13.55
	318.15	2.92	5.83	13.66	2.92	13.74	4.12	13.74

Conclusion

In the above discussion it can be concluded that the system of 2-Propenol with benzyl alcohol shows stronger molecular interactions, likely due to more efficient hydrogen bonding and better molecular packing than 2-propenol and 2-phenyl ethanol. Such system still exhibits strong interactions but is slightly less compact due to steric hindrance from the extra ethyl group. Both systems follow the same general behavior, confirming the dominance of hydrogen bonding and dipole-dipole interactions in alcohol mixtures. The viscosity decreases with increasing temperature, consistent with reduced intermolecular interactions. 2-propenol decreases the viscosity of both benzyl alcohol and 2-phenylethanol mixtures. All the theoretical models follow the same trend as the experimental data but Eyring, Hind, and Frenkel models show the best agreement with experimental data suggesting that these models effectively describe the viscosity behaviour of these mixtures in comparison to others.

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