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Research Article

Viscosities of binary liquid systems: Prediction and correlation

Kumud Dwivedi[*a] and Indra Prasad Tripathi[b]

[*a]PhD Scholar, Department of Chemistry, Mahatma Gandhi Chitrakoot Gramodaya Vishwavidyalaya, Chitrakoot, Satna (Madhya Pradesh), India.
[b]Professor, Department of Chemistry, Mahatma Gandhi Chitrakoot Gramodaya Vishwavidyalaya, Chitrakoot, Satna (Madhya Pradesh), India.

Abstract

The viscosity of binary liquid systems of 1-Butanol, C_4H_9OH with Hexadecane, $C_{16}H_{34}$ and Squalane, $C_{30}H_{62}$, were determined theoretically over the complete concentration range, at 298.15, 303.15, 308.15 K and at atmospheric pressure. Hind's relation and modified Kendall-Monroe method is employed in the calculation. Deviation in viscosity is calculated and the obtained results were analysed in terms of the applied approach, the structure of the investigated system, the nature of components of the binary liquid systems and the interactions in the system.

Keywords: Viscosity, Binary liquid systems, 1-Butanol, Hexadecane, Squalane, interactions.

1. Introduction

The thermodynamic and acoustical properties of binary liquid systems have been studied for several reasons, one of the most important of which is that these properties give us information about the molecular interactions. The viscosity of binary liquid systems is one of the properties widely used in various chemical-engineering correlations regarding the fluid flow, mass and heat transfer calculations, but it is also a very often used property for characterization of pure components. Volumetric and viscometric investigations of binary liquid systems enable determination of some useful thermodynamic and other parameters that are highly sensitive to molecular interactions [1-10].

Therefore in continuation of our earlier work on thermodynamic and acoustical studies of binary liquid systems comprising alcohol with hydrocarbons, in this paper using the experimental data of ultrasonic velocity (u), density (ρ), and viscosity (η) [11], we present the theoretical results of viscosities of binary liquid systems of 1-Butanol + Hexadecane and 1-Butanol + Squalane over the entire range of composition and at 298.15, 303.15, 308.15 K. from the experimental data deviation in viscosity (Δη) have been computed. Theoretical viscosities are calculated by using Hind's relation and Kendall-Monroe relation. In order to get general conclusions for the investigated system, Modified Kendall-Monroe viscosity correlation ($E\eta_m$) and deviation in viscosity (Δη) were applied.

1.2 Theory

The existing theories for the transport properties of binary liquid systems can be broadly differentiated into two groups, statistical mechanical theories and phenomenological theories. Amongst the various statistical mechanical theories, the theories proposed by Kirkwood (1946), Rice and Allnatt (1961) have been the most extensively studied. These theories involves several assumptions and requires considerable computation. While they are found to be in good agreement with the experimental studies. The studies for liquid systems is not so satisfactory. The elaboration of statistical mechanical theories to binary liquid systems requires a knowledge of radial distribution functions which is not usually available. For binary liquid systems phenomenological theories are expected to take preference. In case of pur liquid components, the rate theory proposed by Eyring (1937) is found to be the most successful in correlating theoretical assumptions with experimental studies. Further it has been observed

* Correspondence Info
Kumud Dwivedi
PhD Scholar,
Department of Chemistry,
Mahatma Gandhi Chitrakoot Gramodaya Vishwavidyalaya,
Chitrakoot, Satna (Madhya Pradesh), India.
E mail: kumuddwivedi123@gmail.com

that their rigorous non-equilibrium statistical mechanical theory reduces to Eyring's rate theory under certain well defined approximations, so it provides the significant backing of Eyring's theory. In the same way Bloomfield and Dewan (1971) have studied the viscosity of binary liquid systems. According to this theory, either Eyring's rate theory or Free-volume theory can explain the observed data quite well. A combination of the two, as has been previously proposed by Macedo and Litovitz (1965), is not so satisfactory [12].

Besides these theories, several empirical and semi-empirical expressions have been proposed for prediction of the viscosities of binary liquid systems.

Hind's Equation (η_H):

Hind et al (1960) proposed the following relation for the evaluation of viscosity of binary liquid systems:

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

Where, η = viscosity of the mixture

x_1 and x_2 = mole fractions of component 1 and 2 respectively.

η_1 and η_2 = viscosities of component 1 and 2 respectively.

And η_{12} = constant (for unlike pair interaction), its value is nearly equal to the sum of the viscosities of the pure species composing the binary liquid system. Its value can also be calculated by the following expression:

$$\eta_{12} = 0.5\eta_1 + 0.5\,\eta_2$$

Kendall and Monroe Equation (η_m):

Kendall and Monroe derived an equation for the analysis of viscosity of binary liquid systems based on zero adjustable parameter (13).

$$\eta_m = (x_1\eta_1^{1/3} + x_2\eta_2^{1/3})^3$$

Modified Kendall-Monroe Equation ($E\eta_m$):

It is the modified form of Kendall and Monroe relation, which can be calculated as:

$$E\eta_m = x_1x_2\,(x_1\eta_1^{1/3} + x_2\eta_2^{1/3})^3$$

Viscosity Deviation ($\Delta\eta$):

Deviation in viscosities are calculated by following expression:

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

3. Results and Discussion

The experimental and theoretical viscosities of binary liquid systems of 1-Butanol + Hexadecane and 1-Butanol + Squalane are presented in table-1 and 2. A close look of data presented in tables at different temperatures reveals that for the binary liquid systems (1-butanol+hexadecane and 1-butanol+squalane), Kendall-Monroe relation gives best results followed by Hind's theory due to the closeness in values obtained from these theoretical assumptions with respect to the experimental values. A remarkable change is observed in the values of viscosities at different temperatures.

A comparison of experimental thermodynamic data of binary liquid system with that calculated by means of various theories are very useful fromdifferent point of view-(a). It suggests which theory is more appropriate to the characteristics of the system. (b). It may allow the identification of some theory as a convenient reference for the interpretation of the deviations observed.

The viscosity data have been correlated with semi-empirical equations of modified Kendall and Monroe relation. The values of the modified Kedall-Monroe correlation ($E\eta_m$) equation for both of the systems under study are all positive. The vaues of modified Kedall-Monroe viscosity correlation at different temperatures shows decrease in viscosities with increase in temperature.

The plots of deviation in viscosities against mole fraction of 1-butanol (x1) at 298.15, 303.15, 308.15 K for the binary liquid systems of 1-butanol+hexadecane and 1-butanol+squalane systems are presented in figure-1(a) and 1(b) respectively.

Table 1: Values of Viscosities calculated by Hind's method,η(H), Kendall and Monroe method, η_m, Modified Kendall-Monroe correlation E η_m, and deviation in viscosity Δη, of 1-Butanol(1)+Hexadecane(2) System at 298.15, 303.15 and 308.15 K.

At T = 298.15K.

X1	η(exp)	η(H)	Eη_m	η_m	Δη
0.0000	3.0410	3.041	0.0000	3.0410	0.0000
0.0899	2.9570	2.9989	0.0252	2.9968	-0.0419
0.1048	2.9370	2.99195	0.2805	2.9895	-0.05495
0.1516	2.8990	2.9701	0.3816	2.9667	-0.0712
0.2017	2.8460	2.9466	0.4738	2.9424	-0.1006
0.2494	2.8110	2.9243	0.5465	2.9194	-0.1133
0.3382	2.7530	2.8827	0.6439	2.8769	-0.1297
0.4147	2.7040	2.8469	0.6895	2.8406	-0.1429
0.5057	2.6650	2.8043	0.6994	2.7978	-0.1393
0.5845	2.6350	2.7675	0.6706	2.7611	-0.1325
0.6980	2.5940	2.7143	0.5710	2.7089	-0.1203
0.7945	2.5680	2.6692	0.4351	2.6649	-0.1012
0.8497	2.5580	2.6433	0.3372	2.6400	-0.0853
0.8963	2.5510	2.6215	0.2434	2.6191	-0.0705
0.9530	2.5560	2.59499	0.1162	2.5938	-0.0390
1.0000	2.5730	2.5730	0.0000	2.5730	0.0000

At T = 303.15 K

X1	η(exp)	η(H)	Eη_m	η_m	Δη
0.0000	2.7060	2.7060	0.0000	2.7060	0.0000
0.0899	2.6000	2.6673	0.2181	2.6652	-0.0673
0.1048	2.5820	2.6608	0.2494	2.6585	-0.0788
0.1516	2.5460	2.6407	0.3392	2.6374	-0.0947
0.2017	2.5150	2.6191	0.4211	2.6150	-0.1041
0.2494	2.4780	2.5985	0.4856	2.5938	-0.1205
0.3382	2.4320	2.5602	0.5718	2.5546	-0.1282
0.4147	2.3940	2.5273	0.6119	2.5212	-0.1333
0.5057	2.3440	2.4880	0.6204	2.4818	-0.1440
0.5845	2.3060	2.4541	0.5945	2.4480	-0.1481
0.6980	2.2560	2.4052	0.5059	2.3999	-0.1492
0.7945	2.2230	2.3636	0.3852	2.3595	-0.1406
0.8497	2.2180	2.3398	0.2984	2.3366	-0.1218
0.8963	2.2190	2.3197	0.2154	2.3174	-0.1007
0.9530	2.2280	2.2953	0.1028	2.2942	-0.0673
1.0000	2.2750	2.2750	0.0000	2.2750	0.0000

At T = 308.15 K

X1	η(exp)	η(H)	$E\eta_m$	η_m	Δη
0.0000	2.4090	2.4090	0.0000	2.409	0.0000
0.0899	2.3020	2.3705	0.1938	2.3682	-0.0685
0.1048	2.2870	2.3641	0.2215	2.3615	-0.0772
0.1516	2.2540	2.3441	0.3010	2.3405	-0.0901
0.2017	2.2230	2.3227	0.3733	2.3182	-0.0997
0.2494	2.1890	2.3023	0.4299	2.2970	-0.1133
0.3382	2.1460	2.2643	0.5054	2.2579	-0.1183
0.4147	2.1120	2.2315	0.53999	2.2247	-0.1195
0.5057	2.0680	2.1926	0.5463	2.1856	-0.1246
0.5845	2.0290	2.1588	0.5227	2.1521	-0.1298
0.6980	1.9900	2.1103	0.4436	2.1044	-0.1203
0.7945	1.9600	2.06895	0.3371	2.0644	-0.10895
0.8497	1.9530	2.0453	0.2608	2.0418	-0.0923
0.8963	1.9480	2.0254	0.1880	2.0228	-0.0774
0.9530	1.9530	2.0011	0.0896	1.9999	-0.0481
1.0000	1.9810	1.9810	0.0000	1.9810	0.0000

Table 2: Values of Viscosities calculated by Hind's method,η(H), Kendall and Monroe method, η_m , Modified Kendall-Monroe correlation E η_m, and deviation in viscosity Δη, of 1-Butanol(1)+Squalane(2) System at 298.15, 303.15 and 308.15 K.

At T = 298.15K.

X1	η(exp)	η(H)	$E\eta_m$	η_m	Δη
0.0000	28.257	28.2570	0.0000	28.2570	0.0000
0.0451	26.655	27.0987	1.1286	26.2056	-0.4437
0.1077	24.689	25.4908	2.2609	23.5263	-0.8018
0.1346	23.925	24.7999	2.6131	22.4334	-0.8749
0.1888	22.478	23.4079	3.1145	20.3354	-0.9299
0.2231	21.622	22.5269	3.3067	19.0778	-0.9049
0.3059	19.666	20.4003	3.4519	16.2577	-0.7343
0.4052	17.395	17.8498	3.1959	13.2601	-0.4548
0.5039	15.106	15.3184	2.6674	10.6703	-0.2088
0.6118	12.474	12.5435	1.9597	8.2515	-0.0695
0.7056	10.056	10.1344	1.3444	6.4721	-0.0784
0.7998	7.573	7.71490	0.7947	4.9629	-0.1419
0.8546	6.128	6.3075	0.5224	4.2038	-0.1795
0.9035	4.873	5.0515	0.3135	3.5955	-0.1785
0.9669	3.325	3.4231	0.0928	2.8982	-0.0981
1.0000	2.573	2.5730	0.0000	2.5730	0.0000

At T = 303.15K.

X1	**η(exp)**	**η(H)**	**$E\eta_m$**	**η_m**	**$\Delta\eta$**
0.0000	22.087	22.0870	0.0000	22.087	0.0000
0.0451	20.877	21.1935	0.8845	20.5372	-0.3165
0.1077	19.417	19.9533	1.7787	18.5087	-0.5363
0.1346	18.855	19.4203	2.0594	17.6797	-0.5653
0.1888	17.780	18.3465	2.4636	16.0854	-0.5665
0.2231	17.138	17.6669	2.6220	15.1277	-0.5289
0.3059	15.643	16.0265	2.7547	12.9742	-0.3835
0.4052	13.900	14.0592	2.5725	10.6737	-0.1592
0.5039	12.136	12.1037	2.1684	8.6739	0.0323
0.6118	10.119	9.9660	1.6132	6.7924	0.1529
0.7056	8.276	8.1077	1.1209	5.3964	0.1683
0.7998	6.348	6.2414	0.6728	4.2014	0.1066
0.8546	5.200	5.1557	0.4467	3.5951	0.0443
0.9035	4.186	4.1869	0.2708	3.1060	-0.0009
0.9669	2.912	2.9308	0.0813	2.5407	-0.0188
1.0000	2.275	2.2750	0.0000	2.2750	0.0000

At T = 308.15K.

X1	**η(exp)**	**η(H)**	**$E\eta_m$**	**η_m**	**$\Delta\eta$**
0.0000	17.774	17.774	0.0000	17.774	0.0000
0.0451	16.806	17.0617	0.7129	16.5555	-0.2557
0.1077	15.620	16.0731	1.4375	14.9583	-0.4531
0.1346	15.162	15.6483	1.6663	14.3047	-0.4863
0.1888	14.294	14.7923	1.9981	13.0464	-0.4983
0.2231	13.789	14.2506	2.1301	12.2895	-0.4616
0.3059	12.617	12.9429	2.2473	10.5842	-0.3259
0.4052	11.385	11.3747	2.1105	8.7566	0.0103
0.5039	9.903	9.8159	1.7903	7.1616	0.0871
0.6118	8.307	8.1118	1.3428	5.6537	0.1952
0.7056	6.824	6.6305	0.9408	4.5288	0.1935
0.7998	5.267	5.1428	0.5701	3.5602	0.1242
0.8546	4.344	4.2773	0.3809	3.0661	0.0067
0.9035	3.527	3.5050	0.2324	2.6657	0.02197
0.9669	2.497	2.5037	0.0704	2.2007	-0.0068
1.0000	1.981	1.981	0.0000	1.981	0.0000

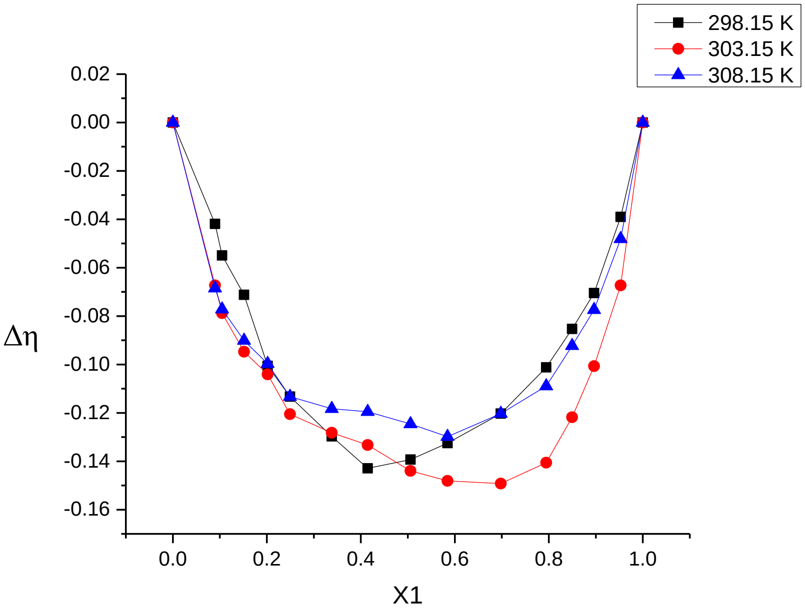

Figure-1(a): Plot of deviation in viscosity (Δη) against mole fraction (x1) of 1-Butanol for the binary liquid system of 1-Butanol+Hexadecane at 298.15, 303.15, 308.15 K.

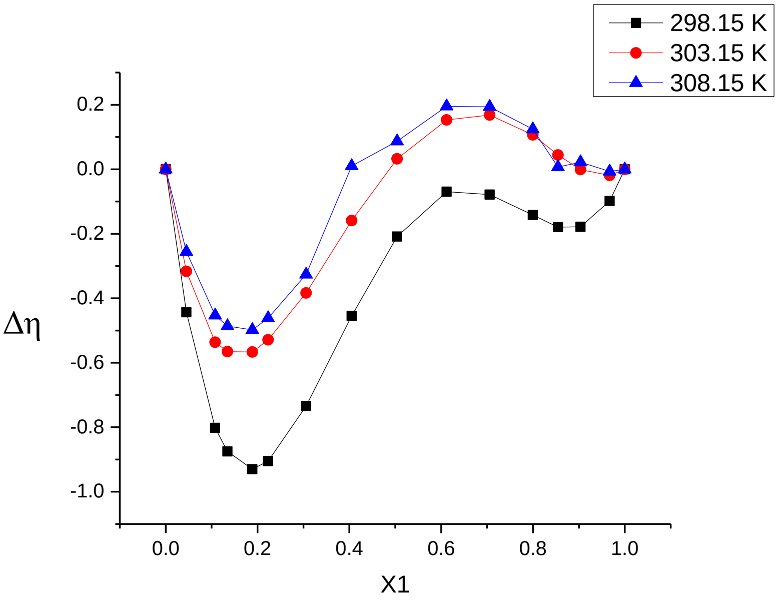

Figure-1(b): Plot of deviation in viscosity (Δη) against mole fraction (x1) of 1-Butanol for the binary liquid system of 1-Butanol+squalane at 298.15, 303.15, 308.15 K.

Deviation in viscosity (Δη) were found to be both negative and positive. The negative deviations are observed for 1-butanol+hexadecane system (except initial and final concentration), while positive deviations were observed for 1-butanol+squalane system (in addition with some negative deviations). The negative values of deviations in viscosities suggests the existence of weak intermolecular interactions upon mixing of 1-butanol with hexadecane, while the positive values of deviations observed in 1-butanol+squalane system for a particular range of concentration, shows the presence of strong intermolecular force of attraction between the respective components of binary liquid system. This leads to suggestions that combinations of some interactive and non-interactive forces are responsible for these positive and negative interactions [14-25]. During the molecular interaction, the rate of collision increases with the increase in temperature. The positive values show strong interaction with the system components [26-27].

4. Conclusion

In this paper we have theoretically evaluated the values of viscosities for the binary liquid systems of 1-Butanol+Hexadecane and 1-Butanol+Squalane at 298.15, 303.15, 308.15 K, over the entire composition range. Viscosity is calculated by using Hind's relation, and Kendall-Monroe theory. It may be concluded that Kendall-Monroe theory gives better results of viscosities than Hind's theory at all observed temperatures. The observed deviation in viscosity values is attributed to the presence of intermolecular interactions in the systems studied.

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