THEORETICAL ESTIMATION OF VISCOSITY OF OXYGENATES WITH QUINARY HYDROCARBON MIXTURES AT 298.15 K

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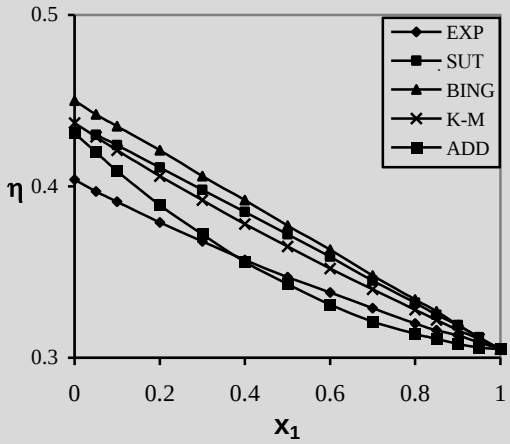
Abstract



On the basis of four different models, the theoretical estimation of viscosity of multicomponent liquid mixtures has been carried out. The mixture under the present investigation is a regular pseudo binary system, all the systems of an oxygenate (acetone, diisopropylether, methyl ethyl ketone, ethanol) interacting with a five component hydrocarbon mixtures containing 25 mol % hexane, 10 mol % heptane, 35 mol % 2,2,4-trimethylpentane, 20 mol % toluene and 10 mol % p-xylene. The six component mixture has been considered as a pseudo binary system. In order to carry out a comparative study, Kendall – Munroe, Bingham and Additive equations have been employed. Furthermore, highlight of the work is the computation of the viscosity by using the scarcely employed Sutherland relation in conjunction with aforementioned viscosity models.

Key words : Viscosity, Hexanary, Multicomponent, Oxygenate

Introduction

The study of viscosity as a transport property is being actively pursued by several workers because of its significance in terms of design calculations from the practical standpoint. It is not without reason that multicomponent liquid systems have attracted the attention of researchers in the past few decades. Viscosity measurements of multicomponent systems are found to exhibit extremely significant multi dimensional industrial applications such as in heat transfer, fluid flow, mixing, agitation, heat exchangers and so forth. Viscosity of photo resistant films play an important role in maintaining the thickness and uniformity of a coating layer on a wafer. Thus, information about the viscosity of pure liquids and liquid mixtures is very useful in several applications of chemical technology. The estimation of viscosity of multicomponent liquid mixture is much more difficult than that of pure liquid.

From the theoretical aspect, it is equally significant as it gives an in depth understanding of

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the structure of liquid mixture. However, there is a distinct scarcity of viscosity data of multicomponent liquid mixtures; one may refer to some of the papers[1-7] on the viscosity of ternary and quaternary solutions. Thus, prediction or computation of viscosities of multicomponent, in this case, hexanary liquid mixtures at different temperatures, is of paramount significance. This investigation becomes more interesting as the methods employed are simple yet deliver reasonably good results.

Over the years, various empirical and semi-empirical equations[8-10] for estimating liquid viscosity have been proposed and developed. These encompass Kendall-Munroe[8-10], Frenkel[8-10], Hind-Ubbelhode[8-10], Bingham[8-10], Sutherland-Wassiljewa[8] and Additive[9] relations. Flory[10]theory and the Bertrand- Acree- Burchfield[10](BAB) approach have also been employed to compute viscosity of multicomponent liquid mixtures. Viscosity of ternary, quaternary and quinary mixtures have also been computed by making use of Pandey-Prajapati[11], Mason-Saxena [11]and the Lindsay-Bromley [11]method. A number of models[12-14] for predicting viscosity have been proposed including Grunberg Nissan[12], Katti-Chaudhry[12], McAllister[12] , Heric Brewer[12], Eyring absolute rate theory model[13], corresponding-state theory [14,] significant structure theory[14], group contribution method[14] and model based on kinetic theory[14]. A critical review of the viscosity data and their estimations has been presented earlier[15]. A comprehensive review of the entire empirical, semi empirical and other methods employed for the estimation of viscosity of binary liquid mixtures has been presented by Lee and Lee[16]. Comparatively lesser work has been done on the experimental and theoretical aspects of viscosity of multicomponent liquid systems. Extremely few studies are available on the viscosity of multicomponent liquid mixtures beyond ternary and quaternary due to the lack of data. Asfour et al[17] measured accurately the density and viscosity of a regular quinary system and its quaternary subsystems at 298.15K. Recently[14], the analysis of viscosity data values of the aforementioned quinary[17] and quaternary systems was carried out by us.

The mixture under the present investigation is a regular pseudo binary system, all the systems of an oxygenate[18] (acetone, diisopropylether, methyl ethyl ketone, ethanol) interacting with a five component hydrocarbon mixtures containing 25 mol % hexane, 10 mol % heptane, 35 mol % 2,2,4-trimethylpentane, 20 mol % toluene and 10 mol % p-xylene. The six component mixture has been considered as a pseudo binary system.

In order to carry out a comparative study, Kendall – Munroe[8], Bingham[8] and Additive[8] equations have been employed. Furthermore, highlight of the work is the computation of the viscosity by using the scarcely employed Sutherland[11] relation in conjunction with aforementioned viscosity models. To the best of our knowledge, such comparative data have not been reported in literature so far.

Theoretical

A number of mathematical equations, based on the viscosity data of pure components, have been proposed by various workers for the computation of viscosity of multicomponent systems.

In the present paper, Sutherland equation[11] is applied to evaluate viscosity of multicomponent liquid solutions. The aforesaid equation can be expressed as,

$$\eta_m = \sum \eta_i \left[1 + \sum A_{ij} \left(x_i / x_j \right) \right]^{-1} \quad \ldots . \ (1)$$

where A_{ij} is given by the expression

$$A_{ij} = \frac{1}{4} \left[1 + \left(\eta_i / \eta_j \right)^{1/2} \left(M_j / M_i \right)^{3/8} \right]^2$$

Here, A_{ij} is the Wassiljewa coefficient interpreted by Dey et al[8] and Pandey et al [11,14] as the ratio of efficiencies with which molecules 'j' and 'i' impede the transport of momentum by molecules 'i'. Sutherland, Wassiljewa and Hirshfelder, using quite different approaches, independently obtained Eq (1).

Bingham[8] relation which takes into account ideal mixing of liquids is given as

$$\eta_m = \sum_{i=1}^{n} x_i \eta_i \qquad \ldots . \ (2)$$

The viscosity of multicomponent systems, according to the Kendall – Munroe equation[8], is

Table 1 Viscosity and density values of the pure components at 298.15 K

Component	(g.cm^{-3})	10^{-3} (Pa.s)
Ethanol	0.7849	1.0826
Acetone	0.7844	0.3029
Methyl ethyl ketone	0.7997	0.378
Diisopropylether	0.7185	0.319
2,2,4-Trimethylpentane	0.6877	0.472
n-Hexane	0.6548	0.307
n-Heptane	0.6795	0.3967
Toluene	0.8622	0.5525
p-Xylene	0.8565	0.605

Table 2 Calculated and experimental values of viscosity of Acetone+Hydrocarbon mixture at 298.15K

x_1	exp 10^{-3} (Pa.s)	SUT 10^{-3} (Pa.s)	BING 10^{-3} (Pa.s)	K-M 10^{-3} (Pa.s)	ADD 10^{-3} (Pa.s)
0.0000	0.404	-	0.450	0.437	0.431
0.0500	0.397	0.430	0.442	0.429	0.420
0.1001	0.391	0.424	0.435	0.421	0.409
0.2000	0.379	0.411	0.421	0.406	0.389
0.3000	0.368	0.398	0.406	0.392	0.372
0.4000	0.357	0.385	0.392	0.378	0.356
0.5000	0.347	0.372	0.377	0.365	0.343
0.6000	0.338	0.359	0.363	0.352	0.331
0.7000	0.329	0.345	0.348	0.340	0.321
0.7999	0.320	0.332	0.334	0.328	0.314
0.8498	0.316	0.325	0.327	0.322	0.311
0.8999	0.313	0.319	0.319	0.316	0.308
0.9500	0.309	0.312	0.312	0.311	0.306
1.0000	0.305	-	0.305	0.305	0.305

Table 3 Calculated and experimental values of viscosity of Diisopropyl ether + Hydrocarbon mixture at 298.15K

x_1	exp 10^{-3} (Pa.s)	SUT 10^{-3} (Pa.s)	BING 10^{-3} (Pa.s)	K-M 10^{-3} (Pa.s)	ADD 10^{-3} (Pa.s)
0.0000	0.404	-	0.450	0.437	0.431
0.0500	0.399	0.432	0.443	0.430	0.421
0.1000	0.394	0.427	0.436	0.423	0.411
0.1999	0.384	0.417	0.423	0.410	0.394
0.3000	0.374	0.407	0.410	0.397	0.378
0.4000	0.364	0.397	0.397	0.384	0.364
0.5000	0.355	0.387	0.383	0.372	0.352
0.5999	0.346	0.377	0.370	0.360	0.341
0.6999	0.337	0.365	0.357	0.349	0.332
0.8000	0.328	0.352	0.344	0.338	0.325
0.8499	0.324	0.345	0.337	0.333	0.322
0.8999	0.320	0.337	0.330	0.327	0.320
0.9499	0.316	0.328	0.324	0.322	0.318
1.0000	0.312	-	0.317	0.317	0.317

Table 4 Calculated and experimental values of viscosity of Methyl Ethyl ketone + Hydrocarbon mixture at 298.15K

x_1	exp 10^{-3} (Pa.s)	SUT 10^{-3} (Pa.s)	BING 10^{-3} (Pa.s)	K-M 10^{-3} (Pa.s)	ADD 10^{-3} (Pa.s)
0.0000	0.404	-	0.450	0.437	0.431
0.0500	0.399	0.435	0.446	0.433	0.424
0.1003	0.396	0.434	0.442	0.430	0.418
0.2003	0.391	0.432	0.435	0.424	0.407
0.3000	0.387	0.429	0.428	0.418	0.398
0.4000	0.384	0.425	0.421	0.412	0.389
0.5000	0.381	0.422	0.414	0.406	0.383
0.6000	0.379	0.417	0.407	0.400	0.378
0.7000	0.377	0.411	0.399	0.395	0.375
0.8000	0.375	0.403	0.392	0.389	0.373
0.8500	0.375	0.399	0.389	0.386	0.373
0.9000	0.375	0.393	0.385	0.383	0.374
0.9500	0.376	0.386	0.382	0.381	0.376
1.0000	0.377	-	0.378	0.378	0.378

given by

$$\eta_m = \sum_{i=1}^{n} x_i \ln \eta_i \quad \ldots . \ (3)$$

According to Additive relation[8], viscosity is given by

$$\ln \eta_m V_m = \sum_{i=1}^{n} x_i \ln \eta_i V_i \quad \ldots \ (4)$$

where V is the molar volume.

Results and discussion

Viscosities of four, six component mixtures (acetone, diisopropylether, methylethyl ketone and ethanol with five component hydrocarbon mixtures) at 298.15K, have been computed by employing various empirical and semi-empirical methods viz Sutherland, Bingham, Kendall – Munroe and Additive relations using Eqs (1), (2), (3) & (4) respectively. The necessary data needed for the computation and comparison have been taken from literature[18]. All the parameters of pure components are listed in Table-1. The systems comprise of an oxygenate (acetone, diisopropylether, methylethyl ketone, ethanol), interacting with a five component hydrocarbon mixture containing 25 mol % hexane, 10 mol % heptane, 35 mol % 2,2,4-trimethylpentane, 20 mol % toluene, and 10 mol % p-xylene. The six component mixtures have been considered as pseudo binary system consisting of a pure component i.e. the oxygenate and another pseudo pure component i.e. the hydrocarbon mixtures. Tables 2, 3, 4 & 5 enlist the computed and experimental values of viscosity of the pseudo binary mixtures viz acetone + hydrocarbon mixture, diisopropylether + hydrocarbon mixture, methyl ethyl ketone + hydrocarbon mixture and ethanol + hydrocarbon mixture respectively. Table 6 records the average percentage deviations of the four aforementioned pseudo binary mixtures computed by the four different approaches at 298.15 K.

Table 5 Calculated and experimental values of viscosity of Ethanol + Hydrocarbon mixture at 298.15K

x_1	exp 10^{-3} (Pa.s)	SUT 10^{-3} (Pa.s)	BING 10^{-3} (Pa.s)	K-M 10^{-3} (Pa.s)	ADD 10^{-3} (Pa.s)
0.0000	0.404	-	0.450	0.437	0.431
0.0500	0.403	0.448	0.481	0.457	0.447
0.1000	0.406	0.460	0.513	0.478	0.465
0.2000	0.425	0.488	0.576	0.524	0.503
0.3001	0.446	0.521	0.640	0.574	0.545
0.4000	0.485	0.559	0.703	0.628	0.594
0.4999	0.532	0.605	0.767	0.688	0.649
0.6001	0.596	0.662	0.830	0.754	0.711
0.7000	0.671	0.731	0.894	0.825	0.783
0.8000	0.768	0.819	0.957	0.904	0.867
0.8500	0.829	0.872	0.989	0.946	0.915
0.8999	0.894	0.933	1.020	0.990	0.966
0.9499	0.977	1.003	1.052	1.036	1.022
1.0000	1.084	-	1.084	1.084	1.084

System-I: Acetone + hydrocarbon mixture: From Table 2, it is clear that theoretically evaluated viscosity values of pseudo binary mixture decrease with increasing the mole fraction of the acetone. Calculated values of viscosity show the same trend as observed experimentally, and the maximum percentage deviations are recorded for the Bingham method and the minimum for the Additive

Table 6 Average percentage deviations by the different methods employed for the four oxygenates + quinary hydrocarbon mixtures at 298.15 K.

Systems Hydrocarbon mixture +	Average Percentage Deviation			
	Sutherland	Bingham	Kendall-Munroe	Additive
Acetone	5.73	7.53	4.76	0.67
Diisopropyl Ether	7.68	7.03	4.67	1.21
Methyl Ethyl Ketone	8.5	7.21	5.48	1.82
Ethanol	10.34	27.97	19.06	15.54

method. The APD values(Table 6) show the following trend:

Additive< K-M< Sutherland< Bingham

System-II: Diisopropylether + hydrocarbon mixture: A close observation of Table 3 indicates that the viscosity values computed by four different methods follow the same trend as observed experimentally. For this pseudo binary system the viscosity values show a gradually decreasing trend with increasing mole fraction of oxygenate for all the methods employed under the present investigation. The APD values(Table 6) show the following trend:

Additive< K-M< Bingham< Sutherland

System-III: Methyl ethyl ketone + hydrocarbon mixture: A perusal of Table 4 indicates that the viscosity values follow the general trend as observed in the systems (I) and (II). For these system, the viscosity values decrease with increasing the mole fraction of first component i.e methyl ethyl ketone. The APD values(Table 6) of the pseudo binary system shows that the Additive relation gives the best results while the deviations are maximum in the case of Sutherland model. Following trend is observed for this system:

Additive< K-M< Bingham< Sutherland

System-IV: Ethanol + hydrocarbon mixture: On inspecting the results of Table 5, it has been observed that for the pseudo binary system i.e oxygenate with five hydrocarbon mixtures, the viscosity values increase with increasing mole fraction of ethanol. It is clear from the table that computed values of viscosity are comparable and found to be in good agreement with the experimental findings. The APD values(Table 6) of viscosity also show a very different trend as compared to the other systems and are as follows:

Sutherland < Additive < K-M< Bingham

This discrepancy in the values may be attributed to the presence of hydrogen bond between the alcohol species. Some more factors responsible for these values for the alkanol + alkane mixture may be due to the hydrogen bond juncture and dispersive interaction between unlike molecule which might result in positive contribution to the excess volume, dipole-dipole interaction and geometrical fitting between components which attribute to the negative contribution.

Conclusion

On the whole, a look at the APD values point towards the fact that the values computed by the additive approach are found to be best in terms of agreement for systems(I), (II) and (III) under consideration. Even, in system (IV), it is seen to give the second best agreement. However, the predictive methods employed are basically empirical in nature and hence a completely different trend might be observed for a different set of systems. Overview of the results point out the fact that all the four methods can be employed quite successfully for the computation of viscosity, since there seems to be reasonably good agreement for all the methods employed in the present investigation with exception to system(IV). Thereby the discrepancies arising due to the component present in the system are justified.

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