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Applicability of the statistical mechanical theory for the estimation of viscosity in the organic liquid mixtures

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Abstract

Viscosity of the liquid mixtures play very important role in determining the molecular interactions, thermal expansion, clustering phenomena etc. The statistical model has been tested for its applicability in the prediction of the viscosities of the liquid mixtures. The good agreement between the computed and experimental values of viscosity validates the applicability of the statistical model for the computation of the viscosity of the liquid mixtures.

Keywords: flory statistical theory, molecular interactions, predictive methods, interaction parameter

Introduction

Viscosity is one of the important properties of the liquids and liquid mixtures, which is greatly used to study clustering phenomenon, molecular interaction and thermal expansivity, etc. A chemical engineer mostly requires the predictive methods for its determination. Viscosity is a measure of internal fluid friction, which tends to oppose any dynamic change in the fluid motion.

Various theories of liquid system explain the relations for the evaluation of viscosity in various ways. Several approaches for the estimation of viscosity in liquids and liquid mixtures from other known parameters or viscosities of pure components of a liquid mixture are available. Methods of predicting viscosity of liquids and liquid mixtures based upon Free Volume Theory [1-5], Absolute Rate Theory [6], Statistical Thermodynamic Theory [7-8] and Significant Structure Theory [9-11], are some of the important approaches. Some concepts [12-15] to combine these different theories and making the prediction simpler is worth praising. Some attempts have been made to evaluate viscosity using Statistical model [16, 17]. Studies in viscosities have been of interest in recent past [18-22] also. It has been observed that most of the previous approaches used are based upon empirical relations or on mole fraction additivity assumptions. An attempt has been made to validate the statistical model for the prediction of viscosity of liquid mixtures. This approach is expected to give good results as the relation uses the interaction parameter in its computation, which mainly depends upon the nature of the liquids under consideration.

Theoretical

Though, several predictive methods have been proposed for the evaluation of the viscosity of liquids and liquid mixture, the present study focuses on relation based upon absolute Rate Theory and Free Volume Theory in conjunction with Flory Statistical Theory (FST).

The Free Volume Theory assumes that there are probabilities of occurrence of empty neighboring sites in liquids, into which the molecules can Jump [4, 5]. The derivations of various relations in this assumption are based upon the following partition function of a molecule in a liquid [1, 2].

$$F_l = \frac{(2\pi mkT)^{3/2}}{h^3} V_f b_l e^{-E_0/RT} \qquad \ldots(1)$$

where, b_l is the combined vibrational and rotational contribution and E_o is the difference in energy per mole between the molecule in liquid and in the gas at 0 K, which may be approximated with enthalpy of vaporization (ΔE_{vap}). Other symbols have their usual meanings. The Absolute Rate Theory [6] relates viscosity to the free energy needed for a molecule to overcome the attractive force field of its neighbours, allowing molecule to jump in a new equilibrium position. Since probability of occurring empty neighbouring sites is related with the free volume of the liquid, it seems logical that these theories can be combined [12]. Based upon these concepts, Bloomfield and Dewan [14] examined the expression for the evaluation of viscosity of liquid mixtures. By the combination of the relations from these two theories, following expression can be derived for the evaluation of viscosity of liquid mixtures:

$$\eta = A.\exp\left\{(\Delta G^*/RT) + \gamma'(V^*/V_f)\right\} \qquad \ldots(2)$$

where, the symbols have their usual meanings. For pure components of a liquid mixture, the above equation can be written as:

$$\eta = A.\exp\left\{(\Delta G_i^* / RT) + \gamma'(V_i^* / V_{f,i})\right\} \qquad \ldots(3)$$

Using the assumption of Roseveare *et al.* [13],

$$\Delta G^* = \left(\sum xi \Delta G_i^*\right) - \left(\alpha' \Delta G^R\right) \qquad \ldots(4)$$

where, ΔG^R is residual free energy and is related to excess free energy of mixing. α' is a constant with an order of unity. ΔG^R is given as:

$$\Delta G^R = \Delta H_M - T\Delta S^R \qquad \ldots(5)$$

where, ΔH_M is enthalpy of mixing per mole and ΔS^R is the residual entropy per mole. Reduced volume ($\tilde{V}$) is given by the equation

$$\tilde{V} = V / V^* \qquad \ldots(6)$$

Using eqn (2) to (6) and some adjustments, the following relation can be obtained to evaluate the viscosity of liquid mixtures:

$$\text{In} \qquad \eta = \left(\sum x_i \ln \eta_i\right) - \left(\Delta H_M / RT\right) + (\Delta S^R / R) + \left[\frac{1}{\tilde{V} - 1} - \sum \frac{x_i}{\tilde{V}_i - 1}\right] \quad \ldots(7)$$

The four terms in eqn (7) represent four different contributions, which are ideal mixture viscosity (η_{id}), enthalpy (η_H), residual entropy (η_s) and difference in the free volume between mixture and pure components (η_v). The above equation can be simply expressed in terms of various contributing terms as:

$$\ln \eta = \ln \eta_{id} + \ln \eta_H + \ln \eta_S + \ln \eta_v \qquad \ldots(8)$$

where, contributing terms of eq (8) can be written as.

$$\eta_{id} = \exp\left[\sum x_i \ln \eta_i\right] \quad \eta_H = \exp\left[-\frac{\Delta H_M}{R}\right] \quad \eta_S = \exp\left[\frac{\Delta S^R}{R}\right] \text{ and } \eta_v = \exp\left[\frac{1}{\tilde{V} - 1} - \left(\sum \frac{x_i}{\tilde{V}_i - 1}\right)\right]$$

The residual frequency (ΔS^R) and enthalpy of mixing ΔH_M can be computed using the Flory relation[7,8]:

$$\Delta S^R = \sum\left\{-\frac{3x_i P_i^* V_i^*}{T_i^*} \ln\left(\frac{\tilde{V}_i^{1/3} - 1}{\tilde{V}^{1/3} - 1}\right)\right\} \qquad (9)$$

For binary liquid mixture,

$$\Delta H_M = x_1 P_1^* V_1^* \left[\frac{1}{\tilde{V}_1} - \frac{1}{\tilde{V}}\right] + x_2 P_2^* V_2^* \left[\frac{1}{\tilde{V}_2} - \frac{1}{\tilde{V}}\right] + \frac{X_1 V_1^* \theta_2 X_{12}}{\tilde{V}_1} \qquad (10)$$

For ternary liquid mixture,

$$\Delta H_M = x_1 P_1^* V_1^* \left[\frac{1}{\tilde{V}_1} - \frac{1}{\tilde{V}} \right] + x_2 P_2^* V_2^* \left[\frac{1}{\tilde{V}_2} - \frac{1}{\tilde{V}} \right] + x_3 P_3^* V_3^* \left[\frac{1}{\tilde{V}_3} - \frac{1}{\tilde{V}} \right] + \frac{x_1 V_1^* \theta_2 X_{12}}{\tilde{V}_1} + \frac{x_2 V_2^* \theta_3 X_{23}}{\tilde{V}_2} + \frac{x_3 V_3^* \theta_1 X_{31}}{\tilde{V}_3} \qquad (11)$$

Results and Discussion

Three binary and one ternary liquid mixtures comprising various organic compounds have been considered under investigation. The computed values were compared against the experimental values. The experimental values, computed values and percentage deviations in computed values for the same, have been depicted in tables-1 to 4. The necessary data for the computation of viscosity have been taken from literature. The values of thermal expansion coefficient and isothermal compressibility, which are required for the computation of viscosity using a relation based upon Flory statistical theory, have also been taken from the literature [17-18].

Table-1 lists some of the parameters of pure liquid components and interaction parameters of binary and ternary liquid mixtures. The results of the computations shown in tables 2 to 5 show that the method based upon Flory statistical theory (FST) gives satisfactory results in nearly all the systems under investigation. In most of the system under study, the percentage deviations are low. The reason for this good agreement may be that, Flory theory clearly uses the interaction parameter, Xij, in its relation, which is an important aspect of this theory.

Table 1: Various Parameters of binary and ternary liquid mixtures

Liquid Mixture	**T**	**η_1 /10^{-3}**	**η_2 /10^{-3}**	**η_3 /10^{-3}**	**V_1/ 10^{-6}**	**V_2/ 10^{-6}**	**V_3/ 10^{-6}**
	(K)	**N s m^{-2}**	**N s m^{-2}**	**N s m^{-2}**	**m^{3}mol^{-1}**	**m^{3}mol^{-1}**	**m^{3}mol^{-1}**
a) n-Heptane + n-hexane	298.15	0.3860	0.2940	-	147.50	131.57	-
b) Carbon-tetrachl. + cyclohexane	298.15	0.9004	0.8950	-	97.08	108.76	-
c) Cyclohexane + benzene	298.15	0.8950	0.6036	-	108.76	89.41	-
d) Toluene + n-heptane + n-hexane	298.15	0.6036	0.3860	0.2940	106.88	147.50	131.57

Table 2: Experimental and Computed (FST) values of viscosity (η) in binary liquid mixture: n- heptane (1) + n- hexane

x_1	**x_2**	**T**	**η/10^{-3}**	**FST**	
		(K)	**N s m^{-2}**	η	%Diff.
0.0000	1.0000	298.15	0.2940	0.2940	0.00
0.2069	0.7931	298.15	0.3145	0.3120	0.80
0.2351	0.7649	298.15	0.3160	0.3145	0.48
0.2637	0.7363	298.15	0.3170	0.3170	-0.01
0.2929	0.7071	298.15	0.3190	0.3196	-0.20
0.3129	0.6871	298.15	0.3200	0.3214	-0.44
0.3665	0.6335	298.15	0.3245	0.3262	-0.54
0.3904	0.6096	298.15	0.3250	0.3284	-1.05
0.4267	0.5733	298.15	0.3275	0.3317	-1.28
0.4687	0.5313	298.15	0.3310	0.3355	-1.37
0.5072	0.4928	298.15	0.3345	0.3391	-1.37
0.5526	0.4474	298.15	0.3380	0.3433	-1.56
0.5994	0.4006	298.15	0.3440	0.3476	-1.05
0.6507	0.3493	298.15	0.3500	0.3524	-0.69
0.6881	0.3119	298.15	0.3550	0.3559	-0.27
0.7280	0.2720	298.15	0.3600	0.3597	0.08
1.0000	0.0000	298.15	0.3860	0.3860	0.00
		APD:			-0.50

Table 3: Experimental and Computed (FST) values of viscosity (η) in binary liquid mixture: Carbon tetrachloride (1) + benzene

x_1	**x_2**	**T**	**η/ 10^{-3}**	**FST**	
		(K)	**N s m^{-2}**	η	**%Diff.**
0.0000	1.0000	298.15	0.6036	0.6036	0.00
0.1367	0.8633	298.15	0.6400	0.6368	0.51
0.1809	0.8191	298.15	0.6530	0.6479	0.78
0.2176	0.7824	298.15	0.6640	0.6574	1.00

0.2521	0.7479	298.15	0.6720	0.6664	0.84
0.2882	0.7118	298.15	0.6800	0.6760	0.60
0.3188	0.6812	298.15	0.6880	0.6842	0.55
0.3463	0.6537	298.15	0.6970	0.6917	0.76
0.4713	0.5287	298.15	0.7350	0.7270	1.09
0.6150	0.3850	298.15	0.7750	0.7701	0.63
1.0000	0.0000	298.15	0.9004	0.9004	0.00
		APD:			0.61

Table 4: Experimental and Computed (FST) values of viscosity (η) in binary liquid mixture: Cyclohexane (1) + benzene

x_1	**x_2**	**T**	**$\eta/10^{-3}$**	**FST**	
		(K)	**N s m^{-2}**	**η**	**%Diff.**
0.0000	1.0000	298.15	0.6036	0.6036	0.00
0.2942	0.7058	298.15	0.6780	0.6753	0.40
0.2613	0.7387	298.15	0.6690	0.6668	0.34
0.2368	0.7632	298.15	0.6650	0.6605	0.68
0.1692	0.8308	298.15	0.6600	0.6436	2.49
0.1659	0.8341	298.15	0.6570	0.6428	2.17
0.1226	0.8774	298.15	0.6540	0.6322	3.33
0.1770	0.8230	298.15	0.6540	0.6455	1.30
0.2951	0.7049	298.15	0.6740	0.6755	-0.23
0.6686	0.3314	298.15	0.7870	0.7826	0.56
1.0000	0.0000	298.15	0.8950	0.8950	0.00
		APD:			1.00

Table 5: Experimental and Computed (FST) values of viscosity (η) in ternary liquid mixture: Toluene + heptane + hexane

x_1	**x_2**	**x_3**	**T**	**$\eta/10^{-3}$**	**FST**	
			(K)	**N s m^{-2}**	**η**	**%Diff.**
0.1210	0.1838	0.6952	298.15	0.3354	0.3356	-0.06
0.1459	0.2011	0.6530	298.15	0.3405	0.3429	-0.69
0.1698	0.2170	0.6132	298.15	0.3458	0.3499	-1.19
0.1929	0.2358	0.5713	298.15	0.3528	0.3572	-1.25
0.2160	0.2544	0.5296	298.15	0.3589	0.3647	-1.61
0.2390	0.2726	0.4884	298.15	0.3656	0.3722	-1.81
0.2641	0.2875	0.4484	298.15	0.3723	0.3801	-2.11
0.2849	0.3060	0.4091	298.15	0.3786	0.3875	-2.35
0.3088	0.3222	0.3690	298.15	0.3844	0.3956	-2.91
0.3330	0.3391	0.3279	298.15	0.3926	0.4040	-2.90
0.3559	0.3553	0.2888	298.15	0.3996	0.4122	-3.14
0.3760	0.3735	0.2505	298.15	0.4063	0.4199	-3.35
0.3983	0.3908	0.2109	298.15	0.4146	0.4284	-3.33
0.4204	0.3974	0.1822	298.15	0.4233	0.4358	-2.94
0.4433	0.4045	0.1522	298.15	0.4415	0.4436	-0.47
			APD:			-2.01

Conclusion

The predictive method for the viscosity of the liquid mixtures based upon the statistical method has been found to be highly encouraging. Very good agreements between the computed values and experimental values have been obtained, despite the fact that the method requires minimum input data. This is the importance of the approach under consideration. This statistical method includes the interaction parameter in the relation used for the estimation. The introduction of such parameters instead of using just mole fraction additive approach ensures more accuracy of a predictive method. This is another important aspect of this approach.

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