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Preamble and Applicability of a New Relation for the Estimation of Viscosity of Liquid Mixtures

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Abstract

A New relation for the estimation of viscosity of binary and ternary liquid mixtures has been proposed and tested for its validity. The results obtained from the newly proposed relation have been compared with the experimental values. For comparison, the relation based upon Flory Statistical Theory has also been utilized. Very good agreement between the experimental values and values obtained from the newly proposed relation vouch the applicability of the proposed relation for the estimation of viscosity of liquid mixtures.

Keywords: Chemical industry; Molecular interaction; Multicomponent system; Rheochor; Transport property.

1. Introduction

Viscosity is an important property, which measures internal fluid friction that opposes any dynamic change in the fluid motion. In liquids and liquid mixtures, it is an important transport property as it characterizes momentum transport within them. The knowledge of thermodynamic and transport properties of multicomponent system is essential mainly for design calculations involving fluid flow, heat transfer, mass transfer, sizing and resizing of the storage vessels and separation processes. A chemist, physicist or a research worker utilizes this knowledge for understanding the intermolecular interactions.

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In chemical industries, the multicomponent liquid systems are more important than pure liquids in product formulations. It is also true that the industrial applications require immediate approximates rather than extensive experimental data, for design calculations. This is why such methods have been gaining enormous amount of interest for a long time.

Several approaches for the estimation of viscosity of liquids and liquid mixtures from other known parameters or viscosities of pure components are available. Most of the approaches of predicting viscosity of liquids and liquid mixtures are based upon free volume theory [1-2], absolute rate theory [3], Flory statistical theory [4-5] and significant structure theory [6-7]. The works on simplifying these relations by some workers [8]-[9] are also very important. The single parameter relation proposed by [10] utilizes interaction parameter G_{ij} . It gives reasonably good results. Some empirical and semi empirical relations to evaluate the viscosity of liquid mixtures have also been proposed [11-13]. The predictive methods employed [14] for determining the viscosities of binary liquids mixtures of some molten electrolytes gave satisfactory results. Reference [15] utilized the predictive methods for the estimation of binary organic liquid mixtures. They utilized the computed excess molar viscosities to study molecular interactions. Other workers [16-18] utilized the measured viscosity data to study molecular interactions and to evaluate various relations of predicting the viscosity of organic liquid mixtures. Pandey and his colleagues [19] evaluated viscosities of ternary organic liquid mixtures using the relations based upon Flory statistical theory and significant structure theory. The Flory statistical theory (FST) has also been utilized by workers [20-21] as the basis for the estimation of viscosities of multi-component systems. The research work on the estimation methods for viscosity of liquid mixtures is gaining much interest. Presently, the empirical methods for the estimation of the viscosities of liquid mixture have been compared with the proposed group contribution approach and the relative merits have been analyzed [22]. This approach utilized group contribution method in conjugation with the method proposed by [10]. Similarly, the applicability of the statistical mechanical theory for the estimation of viscosity in the organic liquid mixtures has also been evaluated [23].

In the present work, a new relation has been proposed for the estimation of viscosity of liquid mixture of any composition. This relation has been proposed on the basis of mole fraction additivity assumption in rheochor and molar volume or density. This means, it requires the minimum input data, densities and viscosities of the pure components. As far as author's present knowledge is concerned, no such relation has been proposed earlier. The validity of this relation has been tested in various liquid mixtures of organic compounds. One other relation, based upon Flory statistical theory, has also been utilized here to compute the viscosity data of the liquid mixtures. But this is utilized only for comparison purpose. The presently proposed relation is expected to give good results as it is based upon the relation of viscosity and rheochor, and the rheochor is a property of a liquid which is closely related to the structural feature of a compound. The method proposed here is simple and is expected to provide a noble way of determining viscosity of the liquid mixtures with a very good level of accuracy.

2. Theoretical

Two relations for the estimation of the viscosity of liquid mixtures have been discussed here:

(a) Relation based upon free volume theory and absolute rate theory in conjunction with Flory statistical theory

Free Volume Theory [1-2] and absolute rate theory [3-4] have been already used [8] in conjunction with Flory statistical theory [4-5] for the estimation of viscosity of liquid mixtures. The following relation has been utilized for the estimation.

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

Here, ΔH_M is enthalpy of mixing per mole and ΔS^R is the residual entropy per mole, η_i is the viscosity of i^{th} component of the mixture, x_i is the mole fraction i^{th} component and η is the viscosity of liquid of mixture. The ΔS^R is given by

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

ΔH_M for a binary liquid mixture is given by

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

and ΔH_M for a ternary liquid mixture is given by

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

The variables like P_i^* , V_i^* , T_i^* , \tilde{V}_i , \tilde{V} and X_{ij} have their usual meanings used in Flory statistical theory, which has already been used by several workers [20, 21, 24] in past. Recently, the applicability of this relation has been evaluated for organic liquid mixtures [23].

b. The proposed relation:

Molar volume of liquid, when its viscosity is unity is called rheochor, [R], which is given by

$$[R] = V \eta^{1/8}$$

This property is closely related to the molar volume and thus plays very important role in determining the viscosity. It is an additive and constitutive property. Based upon the mole fraction additivity assumption of

rheochor and molar volume of liquid mixtures, author proposes the following relation, which can be used for the evaluation of viscosity of the liquid mixtures:

$$\eta = \left[\frac{\sum (x_i V_i \eta_i^{1/8})}{\sum (x_i V_i)} \right]^8 \dots (2)$$

Here, η is the viscosity of liquid mixture, η_i is the viscosity of the i^{th} component having the mole fraction of x_i and V_i is the molar volume of the i^{th} component.

As far as author's present knowledge is concerned, no such relation has been proposed earlier. Therefore, this relation can be considered as a new approach for the computation of viscosity of liquid mixtures. The proposed relation is very simple and uses minimum input data for computation.

3. Results and Discussion

Three binary and two ternary liquid mixtures of various organic compounds have been considered for the evaluation of the proposed relation. Some parameters of pure liquid components of binary and ternary liquid mixtures have been listed in table 1. Equations 1 and 2 have been utilized to compute the viscosity of liquid mixtures. These computed values along with the experimental values for binary and ternary liquid mixtures of different compositions have been recorded in tables 2 and 3. The computed values from both the equations have been compared against the experimental values and have been recorded in the same tables as percentage deviations. The necessary data for the computation of viscosity have been taken from literature [16–19]. The values obtained from (1), which is related to Flory statistical theory, have been utilized here only for the comparison purpose.

The tables 2 and 3 reflect that the computed viscosity values of binary and ternary liquid mixtures obtained using newly proposed relation are very close to the experimental values of viscosity in almost all mixtures and all compositions. In some cases, percent deviations from Flory statistical theory are less than the newly proposed relation. This result is obvious because Flory statistical theory uses the interaction parameter, X_{ij} , in its relation, which is an important aspect of this theory. The limitation of the present approach is lack of interaction parameter in the relation. Despite this limitation, the currently proposed relation gives good results and the method has its own merits. One of the merits of this relation is that this relation is very simple and uses minimum input data. Data for viscosities and molar volumes of pure components are sufficient to compute the viscosities of the multi-component systems in all the compositions with reasonably good agreements with the experimental data. Therefore, this newly proposed relation is very useful in engineering applications where they utilise such estimated data for design calculations. The method is equally useful for a theoretical physicist and chemist, who uses these data to study molecular interactions.

4. Conclusion

Very good agreements between computed and experimental viscosity data of liquid mixtures vouch the

applicability of newly proposed relation. The newly proposed relation can be used to estimate viscosity of liquid mixture of various compositions using minimum input data. This method is expected to be very important not only for a theoretical physicist and chemist but also for chemical engineering design calculations in years to come.

5. Recommendation

Viscosity and molar volume data of pure components are easily available. Therefore, the newly proposed relation gives a convenient and relatively accurate method for the estimation of viscosities in multi-component systems of various compositions. Whenever data like viscosity, expansivity and isothermal compressibility are available, Flory statistical theory can be suggested as a good method of choice. But the expansivity and isothermal compressibility of pure components are not easily available data. Therefore, the author recommends further work in convenient estimation methods for the estimation of expansivity and isothermal compressibility data.

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Table 1: Viscosities (η) and molar volumes (V) of liquid mixtures

Liquid Mixture	T (K)	$\eta_1/10^{-3}$ N s m ⁻²	$\eta_2/10^{-3}$ N s m ⁻²	$\eta_3/10^{-3}$ N s m ⁻²	$V_1/10^{-6}$ m ³ mol ⁻¹	$V_2/10^{-6}$ m ³ mol ⁻¹	$V_3/10^{-6}$ m ³ mol ⁻¹
Binary							
a. Carbon tetrachloride+cyclohexane	298.15	0.9004	0.8950	-	97.08	108.76	-
b. Carbon tetrachloride+benzene	298.15	0.9004	0.6036	-	97.08	89.41	-
c. Cyclohexane+benzene	298.15	0.8950	0.6036	-	108.76	89.41	-
Ternary							
a. CCl ₄ +cyclohexane+benzene	298.15	0.9004	0.8950	0.6036	97.08	108.76	89.41
a. Toluene+n-heptane+n-hexane	298.15	0.6036	0.3860	0.2940	106.88	147.50	131.57

Table 2: Experimental values and calculated values of viscosity (η) calculated using Flory statistical theory (FST) and newly proposed relation in binary liquid mixtures

2 (a). Binary liquid mixture of Carbon tetrachloride + cyclohexane

Table 2 a

x_1	x_2	T (K)	$\eta/10^{-3}$ N s m ⁻²	FST		New Relation	
				η	%Diff.	η	%Diff.
0.0000	1.0000	298.15	0.8950	0.8950	0.00	0.8950	0.00
0.2753	0.7247	298.15	0.8903	0.8963	-0.67	0.8964	-0.68
0.3845	0.6155	298.15	0.8916	0.8968	-0.59	0.8969	-0.60
0.4418	0.5582	298.15	0.8929	0.8971	-0.48	0.8972	-0.49
0.4727	0.5273	298.15	0.8928	0.8973	-0.50	0.8974	-0.51
0.5800	0.4200	298.15	0.8943	0.8979	-0.40	0.8980	-0.41
0.6707	0.3293	298.15	0.8955	0.8984	-0.32	0.8985	-0.33
0.6805	0.3195	298.15	0.8956	0.8985	-0.32	0.8985	-0.33
0.7701	0.2299	298.15	0.8969	0.8990	-0.23	0.8990	-0.24
0.8640	0.1360	298.15	0.8982	0.8995	-0.15	0.8996	-0.15
1.0000	0.0000	298.15	0.9004	0.9004	0.00	0.9004	0.00
APD:				-0.33		-0.34	

2 (b). Binary liquid mixture of Carbon tetrachloride + benzene

Table 2 b

x_1	x_2	T (K)	$\eta/ 10^{-3}$ N s m ⁻²	FST		New Relation	
				η	%Diff.	η	%Diff.
0.0000	1.0000	298.15	0.6036	0.6036	0.00	0.6036	0.00
0.1367	0.8633	298.15	0.6400	0.6368	0.51	0.6409	-0.14
0.1809	0.8191	298.15	0.6530	0.6479	0.78	0.6532	-0.03
0.2176	0.7824	298.15	0.6640	0.6574	1.00	0.6635	0.08
0.2521	0.7479	298.15	0.6720	0.6664	0.84	0.6732	-0.18
0.2882	0.7118	298.15	0.6800	0.6760	0.60	0.6835	-0.51
0.3188	0.6812	298.15	0.6880	0.6842	0.55	0.6922	-0.61
0.3463	0.6537	298.15	0.6970	0.6917	0.76	0.7001	-0.45
0.4713	0.5287	298.15	0.7350	0.7270	1.09	0.7366	-0.22
0.6150	0.3850	298.15	0.7750	0.7701	0.63	0.7797	-0.60
1.0000	0.0000	298.15	0.9004	0.9004	0.00	0.9004	0.00
APD:				0.61		-0.24	

2 (c). Binary liquid mixture of Cyclohexane + benzene**Table 2 c**

x_1	x_2	T (K)	$\eta/ 10^{-3}$ N s m ⁻²	FST		New Relation	
				η	%Diff.	η	%Diff.
0.0000	1.0000	298.15	0.6036	0.6036	0.00	0.6036	0.00
0.2942	0.7058	298.15	0.6780	0.6753	0.40	0.6906	-1.86
0.2613	0.7387	298.15	0.6690	0.6668	0.34	0.6809	-1.78
0.2368	0.7632	298.15	0.6650	0.6605	0.68	0.6737	-1.31
0.1692	0.8308	298.15	0.6600	0.6436	2.49	0.6537	0.95
0.1659	0.8341	298.15	0.6570	0.6428	2.17	0.6527	0.65
0.1226	0.8774	298.15	0.6540	0.6322	3.33	0.6399	2.15
0.1770	0.8230	298.15	0.6540	0.6455	1.30	0.6560	-0.31
0.2951	0.7049	298.15	0.6740	0.6755	-0.23	0.6909	-2.51
0.6686	0.3314	298.15	0.7870	0.7826	0.56	0.8001	-1.67
1.0000	0.0000	298.15	0.8950	0.8950	0.00	0.8950	0.00
APD:				1.00		-0.52	

Table 3: Experimental values and calculated values of viscosity (η), calculated using Flory statistical theory (FST) and newly proposed relation in ternary liquid mixtures**3 (a). Ternary liquid mixture of Carbontetrachloride + cyclohexane + benzene**

x_1	x_2	x_3	T (K)	$\eta/ 10^{-3}$ N s m ⁻²	FST		New Relation	
					η	%Diff.	η	%Diff.
0.1005	0.2646	0.6349	298.15	0.6823	0.6949	-1.84	0.7099	-4.05
0.1403	0.2246	0.6351	298.15	0.6825	0.6951	-1.85	0.7092	-3.92
0.1751	0.1953	0.6296	298.15	0.6829	0.6968	-2.04	0.7103	-4.01
0.2132	0.1544	0.6324	298.15	0.6928	0.6964	-0.52	0.7089	-2.32
0.2525	0.1240	0.6235	298.15	0.6942	0.6991	-0.70	0.7109	-2.41
0.2911	0.0869	0.6220	298.15	0.6951	0.6998	-0.67	0.7107	-2.25
0.3284	0.0517	0.6199	298.15	0.7159	0.7006	2.13	0.7108	0.72
0.3859	0.1812	0.4329	298.15	0.7435	0.7541	-1.43	0.7670	-3.16
0.3461	0.4372	0.217	298.15	0.8223	0.8214	0.11	0.8325	-1.24
APD:					-0.76		-2.52	

3 (b). Ternary liquid mixture of Toluene + heptane + hexane**Table 3 b**

x ₁	x ₂	x ₃	T (K)	$\eta / 10^{-3}$ N s m ⁻²	FST		New Relation	
					η	%Diff.	η	%Diff.
0.1210	0.1838	0.6952	298.15	0.3354	0.3356	-0.06	0.3348	0.17
0.1459	0.2011	0.6530	298.15	0.3405	0.3429	-0.69	0.3418	-0.38
0.1698	0.2170	0.6132	298.15	0.3458	0.3499	-1.19	0.3486	-0.81
0.1929	0.2358	0.5713	298.15	0.3528	0.3572	-1.25	0.3556	-0.81
0.2160	0.2544	0.5296	298.15	0.3589	0.3647	-1.61	0.3628	-1.09
0.2390	0.2726	0.4884	298.15	0.3656	0.3722	-1.81	0.3701	-1.23
0.2641	0.2875	0.4484	298.15	0.3723	0.3801	-2.11	0.3777	-1.45
0.2849	0.3060	0.4091	298.15	0.3786	0.3875	-2.35	0.3848	-1.63
0.3088	0.3222	0.3690	298.15	0.3844	0.3956	-2.91	0.3926	-2.12
0.3330	0.3391	0.3279	298.15	0.3926	0.4040	-2.90	0.4007	-2.06
0.3559	0.3553	0.2888	298.15	0.3996	0.4122	-3.14	0.4086	-2.24
0.3760	0.3735	0.2505	298.15	0.4063	0.4199	-3.35	0.4160	-2.40
0.3983	0.3908	0.2109	298.15	0.4146	0.4284	-3.33	0.4242	-2.31
0.4204	0.3974	0.1822	298.15	0.4233	0.4358	-2.94	0.4313	-1.89
0.4433	0.4045	0.1522	298.15	0.4415	0.4436	-0.47	0.4388	0.61
APD:					-2.01		-1.31	