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Comparative study on the empirical methods and group contribution method for the evaluation of the viscosities of liquid mixtures

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Abstract
Viscosities of some binary liquids have been evaluated using empirical relations as well as the group contribution method in conjunction with the Grunberg-Nissan method. This is relatively a new approach. The new approach is also found to give fairly good results. The good agreements between the computed values and experimental data vouch the applicability of these methods for the computation of the viscosities in the liquid mixtures.

Keywords: Molecular interactions, adjustable parameter, interaction parameter, transport properties

Introduction
Viscosity is one of the important properties of the liquids and liquid mixtures, which is greatly used to study the phenomenon like clustering phenomena, molecular interactions, product designing and optimization, etc. Viscosity can be considered as a measure of internal fluid friction, which tends to oppose any dynamic change in the fluid motion. Owing such an important nature of viscosity, it has great number of relationships with various parameters of the liquid system. This means, the viscosity is related with the several properties of liquids and liquid mixtures in several 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 [1-3], Absolute Rate Theory [4] and Significant Structure Theory [5-7], are some of the important approaches. Grunberg and Nissan [8] method (G-N) is another very important method for the prediction of viscosity of liquid mixtures. One constant G-N equation is convenient and reasonably accurate. This method utilizes the interaction parameter (G_{ij}), which has been computed in various ways by various workers. Isdale *et al.* [9] suggested group-contribution method to estimate the binary interaction parameter G_{ij}. Wassiljewa [10] proposed a relation for the evaluation of transport property of gaseous mixtures. Kendall and Munroe [11] proposed a method for the computation of viscosity of liquid mixtures based upon the mole fraction additivity relation. The study viscosity of the liquids and liquid mixture has gained enormous amount of interest in recent years also [12-18].

In most of these studies viscosity of liquid mixtures are evaluated using empirical relations. Some attempts have been made to evaluate viscosity using Statistical model [12] and the model based upon Significant Structure theory also. In the present work, instead of all empirical relations, various categories of the relations for evaluation of viscosity of liquid mixtures have been used and tested in various mixtures of organic compounds. The Grunberg-Nissan method, which comprises the interaction parameter, has been used in conjunction with group contribution approach. As far as author's present knowledge is concerned, no detailed studies have been made in this approach, though the method was proposed earlier. Besides these methods, the model based upon kinetic theory of gases and was proposed for the evaluation of transport properties of gaseous mixture [10], has also been utilized in liquid mixtures of organic compounds.

Theoretical
Grunberg and Nissan [8] proposed a comprehensive relation for the evaluation of viscosity in liquid mixture. Single parameter Grunberg-Nissan

equation for binary liquid mixture can be expressed as:

$$\ln \eta = x_1 \ln \eta_1 + x_2 \ln \eta_2 + x_1 x_2 G_{12} \quad ...(1)$$

Where, G_{12} is an interaction parameter, which is a function of temperature and even composition. There are no direct and convenient relations available for the evaluation of interaction parameter G_{ij}. In present study Group Contribution method proposed by Isdale *et al*. [19] has been utilized to compute G_{ij}. The calculation of G_{ij} based upon this method uses the relation

$$G_{ij} = \sum \Delta_i + \sum \Delta_j + W \quad ...(2)$$

Where, W is a parameter evaluated using the relation

$$W = \frac{(0.3161)(N_i - N_j)^2}{(N_i + N_j)} - 0.1188(N_i - N_j) \quad ...(3)$$

The parameters Δ_i, Δ_j, N_i and N_j for this particular method have to be computed using the contribution of groups on these parameters.

Wassiljewa [10] proposed a relation for the evaluation of viscosity of liquid mixtures. The relation in simplified form can be written as

$$\eta = \sum_i \frac{x_i \eta_i}{\sum_{j \neq i} A_{ij} x_j} \quad ...(4)$$

Where x_i is the mole fraction of i^{th} component and A_{ij} is the adjustable parameter. Simplified relation for the evaluation of A_{ij} can be written as

$$A_{ij} \frac{1}{\sqrt{8}} \left(1 + \frac{M_i}{M_j}\right)^{-1/2} \left[1 + \left(\frac{\eta_i}{\eta_j}\right)^{1/2} \left(\frac{M_j}{M_i}\right)^{1/4}\right]^2 \quad ...(5)$$

Owing some structural similarities of gases and liquids, the Wassiljewa relation is expected to be useful for the evaluation of viscosity of liquid mixture also.

The empirical relation was proposed by Kendall and Munroe [11] method for the computation of viscosity of liquid mixtures can be expressed as:

$$\ln \eta = \sum x_i \ln \eta_i \quad ...(6)$$

Results and Discussion

Four binary and two ternary liquid mixtures comprising various organic compounds have been considered under investigation. Some of the parameters of pure liquid components and interaction parameters of binary and ternary liquid mixtures have been recorded in table 1. The computed values of viscosities of liquid mixtures based upon Wassiljewa relation, Kendall- Munroe relation and the Grunberg-Nissan method in conjunction with group contribution method have been recorded in table 2 to 6. The experimental values, computed values and percentage deviations in computed values for the same, have been depicted in tables 2 to 6. The necessary data for the computation of viscosity have been taken from literature.

The results of the computations shown in tables 2 to 6 show that, in most of the system under investigation, the percentage deviations are not so high. Looking at the overall result, these methods seem to be approximate in nature. The focused new approach of the present work, the Grunberg-Nissan method in conjunction with group contribution method, is also found to give fairly good results, in most of the systems under study. In the case of 1-chloronaphthalene + dodecane, slightly greater percentage differences are observed using group contribution approach. These results indicate that aromatic compounds having such fused rings should be treated in a different way, while considering the contribution due to aromatic ring, in the determination of the parameters like Δ_i and Δ_j. The assumptions like considering the contribution of one naphthalene ring as the contribution of two benzene rings should not be practiced. Wassiljewa relation, though was proposed for estimating transport properties of gaseous mixtures, is surprisingly found to be quite applicable in the evaluation of the viscosity of the organic liquid mixtures of concern. Grunberg-Nissan method in conjunction with group contribution method can be utilized for the computation of the viscosities of the liquid mixtures.

Table 1: Various Parameters of binary liquid mixtures

Liquid Mixture	T	$\eta_1/10^{-3}$	$\eta_2/10^{-3}$	G_{12}	A_{12}	A_{21}
	(K)	N s m^{-2}	N s m^{-2}			
a) n-Heptane + n-hexane	298.15	0.3860	0.2940	0.002	1.064	0.942
b) Carbon-tetrachl. + cyclohexane	298.15	0.9004	0.8950	-0.026	0.729	1.325
c) Carbon tetrachloride + benzene	298.15	0.9004	0.6036	0.324	0.846	1.117
d) Cyclohexane + benzene	298.15	0.8950	0.6036	-0.350	1.182	0.859
d) Chloronaphthalene +dodecane	298.15	3.0750	1.2460	-1.438	1.695	0.657

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

x_1	x_2	T	$\eta/10^{-3}$	Wassil		Grp Contr		K-M	
		(K)	N s m^{-2}	η	%Diff.	η	%Diff.	η	%Diff.
0.0000	1.0000	298.15	0.2940	0.2940	0.00	0.2940	0.00	0.2940	0.00
0.2069	0.7931	298.15	0.3145	0.3120	0.79	0.3111	1.08	0.3110	1.10
0.2351	0.7649	298.15	0.3160	0.3145	0.47	0.3135	0.79	0.3134	0.81
0.2637	0.7363	298.15	0.3170	0.3171	-0.02	0.3160	0.32	0.3159	0.35
0.2929	0.7071	298.15	0.3190	0.3197	-0.21	0.3185	0.16	0.3184	0.19
0.3129	0.6871	298.15	0.3200	0.3215	-0.45	0.3202	-0.08	0.3201	-0.04
0.3665	0.6335	298.15	0.3245	0.3263	-0.55	0.3250	-0.14	0.3248	-0.11
0.3904	0.6096	298.15	0.3250	0.3284	-1.06	0.3271	-0.64	0.3270	-0.61

0.4267	0.5733	298.15	0.3275	0.3317	-1.29	0.3303	-0.87	0.3302	-0.83
0.4687	0.5313	298.15	0.3310	0.3356	-1.38	0.3341	-0.95	0.3340	-0.91
0.5072	0.4928	298.15	0.3345	0.3391	-1.37	0.3377	-0.95	0.3375	-0.91
0.5526	0.4474	298.15	0.3380	0.3433	-1.56	0.3419	-1.14	0.3417	-1.10
0.5994	0.4006	298.15	0.3440	0.3476	-1.05	0.3462	-0.65	0.3461	-0.61
0.6507	0.3493	298.15	0.3500	0.3524	-0.69	0.3511	-0.32	0.3510	-0.28
0.6881	0.3119	298.15	0.3550	0.3559	-0.27	0.3547	0.09	0.3546	0.12
0.7280	0.2720	298.15	0.3600	0.3597	0.08	0.3586	0.40	0.3584	0.43
1.0000	0.0000	298.15	0.3860	0.3860	0.00	0.3860	0.00	0.3860	0.00
		APD:			-0.50		-0.17		-0.14

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

x_1	x_2	T	$\eta/10^{-3}$	Wassil		Grp Contr		K-M	
		(K)	N s m^{-2}	η	%Diff.	η	%Diff.	η	%Diff.
0.0000	1.0000	298.15	0.8950	0.8950	0.00	0.8950	0.00	0.8950	0.00
0.2753	0.7247	298.15	0.8903	0.9036	-1.50	0.8918	-0.17	0.8965	-0.69
0.3845	0.6155	298.15	0.8916	0.9050	-1.50	0.8916	0.00	0.8971	-0.61
0.4418	0.5582	298.15	0.8929	0.9054	-1.40	0.8916	0.14	0.8974	-0.50
0.4727	0.5273	298.15	0.8928	0.9055	-1.42	0.8918	0.12	0.8975	-0.53
0.5800	0.4200	298.15	0.8943	0.9054	-1.24	0.8925	0.21	0.8981	-0.43
0.6707	0.3293	298.15	0.8955	0.9049	-1.05	0.8935	0.23	0.8986	-0.35
0.6805	0.3195	298.15	0.8956	0.9048	-1.03	0.8936	0.22	0.8987	-0.34
0.7701	0.2299	298.15	0.8969	0.9039	-0.78	0.8950	0.21	0.8992	-0.25
0.8640	0.1360	298.15	0.8982	0.9027	-0.50	0.8969	0.14	0.8997	-0.16
1.0000	0.0000	298.15	0.9004	0.9004	0.00	0.9004	0.00	0.9004	0.00
		APD:			-0.95		0.10		-0.35

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

x_1	x_2	T	$\eta/10^{-3}$	Wassil		Grp Contr		K-M	
		(K)	N s m^{-2}	η	%Diff.	η	%Diff.	η	%Diff.
0.0000	1.0000	298.15	0.6036	0.6036	0.00	0.6036	0.00	0.6036	0.00
0.1367	0.8633	298.15	0.6400	0.6548	-2.31	0.6624	-3.49	0.6375	0.39
0.1809	0.8191	298.15	0.6530	0.6705	-2.67	0.6808	-4.26	0.6489	0.63
0.2176	0.7824	298.15	0.6640	0.6832	-2.89	0.6958	-4.79	0.6585	0.83
0.2521	0.7479	298.15	0.6720	0.6949	-3.41	0.7097	-5.61	0.6676	0.65
0.2882	0.7118	298.15	0.6800	0.7069	-3.96	0.7239	-6.45	0.6773	0.39
0.3188	0.6812	298.15	0.6880	0.7169	-4.21	0.7357	-6.93	0.6857	0.34
0.3463	0.6537	298.15	0.6970	0.7258	-4.13	0.7460	-7.03	0.6933	0.54
0.4713	0.5287	298.15	0.7350	0.7643	-3.98	0.7901	-7.49	0.7288	0.84
0.6150	0.3850	298.15	0.7750	0.8053	-3.91	0.8335	-7.54	0.7719	0.40
1.0000	0.0000	298.15	0.9004	0.9004	0.00	0.9004	0.00	0.9004	0.00
		APD:			-2.86		-4.87		0.46

Table 5: Experimental and Computed values of viscosity (η) in binary liquid mixture: Cyclohexane (1) + benzene

x_1	x_2	T	$\eta/10^{-3}$	Wassil		Grp Contr		K-M	
		(K)	N s m^{-2}	η	%Diff.	η	%Diff.	η	%Diff.
0.0000	1.0000	298.15	0.6036	0.6036	0.00	0.6036	0.00	0.6036	0.00
0.2942	0.7058	298.15	0.6780	0.6778	0.03	0.6303	7.04	0.6778	0.03
0.2613	0.7387	298.15	0.6690	0.6691	-0.01	0.6253	6.53	0.6690	-0.01
0.2368	0.7632	298.15	0.6650	0.6627	0.35	0.6220	6.47	0.6626	0.36
0.1692	0.8308	298.15	0.6600	0.6453	2.23	0.6142	6.94	0.6452	2.24
0.1659	0.8341	298.15	0.6570	0.6444	1.91	0.6139	6.56	0.6444	1.92
0.1226	0.8774	298.15	0.6540	0.6335	3.13	0.6101	6.72	0.6335	3.14
0.1770	0.8230	298.15	0.6540	0.6473	1.03	0.6150	5.96	0.6472	1.04
0.2951	0.7049	298.15	0.6740	0.6780	-0.60	0.6304	6.47	0.6780	-0.59
0.6686	0.3314	298.15	0.7870	0.7852	0.23	0.7269	7.64	0.7855	0.19
1.0000	0.0000	298.15	0.8950	0.8950	0.00	0.8950	0.00	0.8950	0.00
		APD:			0.75		5.48		0.76

Table 6: Experimental and Computed values of viscosity (η) in binary liquid mixture: Chloronaphthalene (1) + dodecane

x_1	x_2	T	$\eta/10^{-3}$	Wassil		Grp Contr		K-M	
		(K)	N s m^{-2}	η	%Diff.	η	%Diff.	η	%Diff.
0.0000	1.0000	298.15	1.2460	1.2460	0.00	1.2460	0.00	1.2460	0.00
0.0988	0.9012	298.15	1.3060	1.3492	-3.31	1.1986	8.22	1.3623	-4.31
0.1953	0.8047	298.15	1.3930	1.4600	-4.81	1.1857	14.88	1.4864	-6.71
0.2927	0.7073	298.15	1.4450	1.5834	-9.58	1.2052	16.59	1.6231	-12.33

0.3910	0.6090	298.15	1.5330	1.7215	-12.29	1.2595	17.84	1.7739	-15.71
0.4954	0.5046	298.15	1.6630	1.8857	-13.39	1.3607	18.18	1.9493	-17.22
0.5939	0.4061	298.15	1.7700	2.0601	-16.39	1.5063	14.90	2.1307	-20.38
0.6916	0.3084	298.15	1.9550	2.2555	-15.37	1.7126	12.40	2.3273	-19.04
0.8196	0.1804	298.15	2.2650	2.5525	-12.69	2.1122	6.75	2.6126	-15.35
0.8992	0.1008	298.15	2.5370	2.7658	-9.02	2.4643	2.87	2.8074	-10.66
1.0000	0.0000	298.15	3.0750	3.0750	0.00	3.0750	0.00	3.0750	0.00
		APD:			-8.80		10.24		-11.06

Conclusion

These relations under study have been found to give the good agreement between the experimental and computed values. This shows the applicability of these predictive methods in evaluation of the internal pressure of the liquid mixture with the help of minimum input data. The focused approach, Grunberg-Nissan method in conjunction with group contribution method, can be taken as a good method for the evaluation of the viscosities and may require slight modifications. The importance of this method is that, this uses the interaction parameter, which mainly represents the molecular structural aspects of the compounds under consideration.

References

1. Hirschfelder JO. J Chem Edu. 1939; 16:540.
2. Eyring H, Hirschfelder JO. J Phys Chem. 1937; 41:249.
3. Bosworth RCL. Trans Farad Soc. 1947; 43:308.
4. Glasstone S, Laidler KL, Eyring H. The Theory of Rate Processes, McGrawHill, New York, 1941.
5. Eyring H, Ree T, Hirai H. Proc Nat. Acad Sci USA. 1958; 44:683.
6. Eyring H, John MK. Significant Liquid Structures, Wiley, New York, 1969.
7. Eyring H, Ree T, ibid. 1961; 47:526.
8. Grunberg L, Nissan AH. Nature. 1949; 164:799.
9. Isdale JD, MacGillivray JC, Cartwright G. Natl Eng Lab Rept, Glasgaw, Scotland, 1985.
10. Wassiljewa A. Phys. 1904; 5:737.
11. Kendall J, Munroe KP. J Am Chem Soc. 1917; 39:1787.
12. Pandey JD, Pandey S, Gupta S, Shukla AK. J Soln Chem. 1994; 23:1049.
13. Aminabhavi TM, Banerjee K. Ind J Chem. 2001; 40A:53.
14. Tu C, Lee S, Peng I. J Chem Eng Data. 2001; 46:151.
15. Marigliano AC, Solimo HN. J Chem Eng Data. 2002; 47:796.
16. Ali A, Mohammad T, Firdosa N. Indian Journal of Pure & Applied Physics. 2008; 46:545.
17. Xu Y, Yao J, Wang C, Li H. J. Chem. Eng. Data. 2012; 57:298.
18. Dikko AB, De DK, Alkasim A, Ahmed AD. The Int. Jour. of Eng. and Sci. 2014; 3:57.