



Viscosity and Excess viscosity for non-polar system from 298.15 to 323.15K

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Abstract

Viscosity and excess viscosity for a non-polar liquid mixture cyclohexane (1)+ 2,2,4-trimethylpentane (2) were computed at temperature 298.15,303.15,308.15,313.15,318.15,323.15K with mole fraction of cyclohexane. Calculated theoretical values compared and tested with the measured data of Jose M. Navaza. Prigogine-Flory-Patterson (PFP), Glinski (GLI) and Ramaswamy (RS) model based on non-associated and associated process respectively. Nature and the behaviour of binary system was studied with help of these models. Redlich- Kister relation was utilized to determine the respective parameters and deviation from experimental values in term of standard deviation ($\delta\eta$). Extent of interactions between the like and unlike components and nature of binary system can be predicted by excess viscosity. Estimation of experimental findings were carried out with help of Jouyban Acree Model, McAllister model. Jouyban Acree Model correlate the experimental findings more accurately than McAllister model.

Keywords: Viscosity, Excess viscosity, Prigogine-Flory-Patterson, Jouyban Acree, McAllister, Binary liquid.

Introduction

Viscosity is an important physicochemical property having a wide applicability in industries such as paint, petroleum, pharmaceutical and food. Theoretical study of viscous behaviour of liquids has its strategic importance in designing calculations because many times it is difficult to determine the physicochemical properties experimentally at all external conditions of interests. Literature survey reveals that recently, it has been applied in the study of different fluid systems¹, quartz parameter², hydrodynamics of super cooled liquids³, nano litter viscometer for analysing blood plasma⁴, shear viscosity relaxation of liquid alkanes⁵, viscous shear thinning fluids large reactors⁶, non-ionic C₁₂E₈ solution⁷. R.K Shukla et al⁸ and his co-workers have published a research work on viscosities and excess viscosities for polar binary liquid mixtures at various temperatures. The present work deals with the excess and transport properties for non-polar binary system at various temperatures. Results theoretical models for transport and excess thermodynamic function and the experimental work of Jose M. Navaza et al⁹ for binary system at 298.15, 303.15, 308.15, 313.15, 318.15, 323.15K are presented in the paper. Non-associated (PFP) model depends on additivity of liquids¹⁰⁻¹⁵ and associated liquid model of Ramaswamy (RS)¹⁶ and Glinski¹⁷ (GLI) were used to predict the intermolecular relations. These two associated models depend adjustable coefficients. In present study we used the liquid which are non-polar in nature and having a very weak intermolecular relation. $\Delta\eta$ were calculated and applied to Redlich Kister relation¹⁸ to derive the respective parameters. McAllister model¹⁹ based on Eyring theory was applied to estimate the observation values. The aim of this work was to analyse and compare the different theoretical models

which will able to explain the physicochemical relation between different liquids.

Theoretical models

Theoretical models provide a relation between the viscosity and activation energy of molecule to reduce the intermolecular force of attraction and movement to new site or existing vacant site near a neighboring molecule. Theoretical models are fellows:

Prigogine-Flory-Patterson Model: Macedo and Litovitz²¹ proposed a hypothesis involving the activation energy of molecule and vacant site near the neighboring molecules. The product of these two effects deals with the viscous flow. Solution consists of similar assumption. Using the above hypothesis, a relation has been made between the activation energy of pure component ($\Delta G_K^\#$), residual mixing free energy (ΔG_{Mix}^R) and activation energy of solution ($\Delta G_S^\#$).

$$\Delta G_S^\# = x_1 \Delta G_1^\# + x_2 \Delta G_2^\# - \Delta G_M^R \quad (1)$$

Viscosity of pure component (η_i) and solution can be determined by the following equation

$$\eta_i = A \exp \left[\frac{\Delta G_i^\#}{RT} + (\tilde{v}_i - 1)^{-1} \right] \quad (2)$$

Where \tilde{v}_i is reduced volume, taking logarithms of equation (2)

$$\ln \eta_i = \ln A + \frac{\Delta G_i^\#}{RT} + (\tilde{v}_i - 1)^{-1} \quad (3)$$

Applying equation (3) to solution and pure component one obtained

$$\Delta \ln \eta = \ln \eta_{sol} - (x_1 \ln \eta_1 + x_2 \ln \eta_2) \quad (4)$$

Applying Equation (1) and (2) to Equation (4), we get a relation between $\Delta \ln \eta$ and free energy of mixing (ΔG_M^R)

$$\Delta \ln \eta = -\Delta G_M^R / RT + \frac{1}{\tilde{v}-1} - \frac{x_1}{\tilde{v}_1-1} - \frac{x_2}{\tilde{v}_2-1} \quad (5)$$

Ideality of the solution can be explained on the basis of thermodynamic parameter (\tilde{v}) which is termed as reduced volume. If two liquid components having different reduced volume, they will not form an ideal solution.

The values of ΔG_M^R was evaluated from consideration of Flory theory and may be expressed as follows.

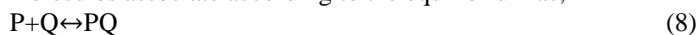
$$\Delta G_M^R = x_1 P_1^* v_1^* \left[\left(\frac{1}{\tilde{v}_1} - \frac{1}{\tilde{v}} \right) + 3\tilde{T}_1 \ln \left(\frac{\tilde{v}_1^{-1/3} - 1}{\tilde{v}^{-1/3} - 1} \right) \right] + x_2 P_2^* v_2^* \left[\left(\frac{1}{\tilde{v}_2} - \frac{1}{\tilde{v}} \right) + 3\tilde{T}_2 \ln \left(\frac{\tilde{v}_2^{-1/3} - 1}{\tilde{v}^{-1/3} - 1} \right) \right] + \frac{x_1 v_1^* \theta_2 X_{12}}{\tilde{v}_1} \quad (6)$$

Put the value of ΔG_M^R from Equation (6) to Equation (5), we get the theoretical viscosity (η) of binary system by the given thermodynamic relation

$$\ln \eta = x_1 \ln \eta_1 + x_2 \ln \eta_2 - [x_1 P_1^* v_1^* \left\{ \frac{1}{\tilde{v}_1} - \frac{1}{\tilde{v}} \right\} + 3\tilde{T}_1 \ln \left\{ \frac{\tilde{v}_1^{-1/3} - 1}{\tilde{v}^{-1/3} - 1} \right\} + x_2 P_2^* v_2^* \left\{ \frac{1}{\tilde{v}_2} - \frac{1}{\tilde{v}} \right\} + 3\tilde{T}_2 \ln \left\{ \frac{\tilde{v}_2^{-1/3} - 1}{\tilde{v}^{-1/3} - 1} \right\} + x_1 v_1^* \theta_2 X_{12} / \tilde{V}_1] / RT + 1 / (\tilde{v}-1) - x_1 / (\tilde{v}_1-1) - x_2 / (\tilde{v}_2-1) \quad (7)$$

In above thermodynamic relation θ , \tilde{T} , v^* and P^* are site fraction, reduced temperature, characteristic volume and characteristic pressure respectively.

Ramaswamy and Anbananthan model: Ramaswamy and Anbananthan model¹⁶ based on the assumption of linearity of acoustic impedance with the mole fraction of components. According to this model when liquid P is added to liquid Q, then molecules associate according to the equilibrium as;



K_{as} can be calculated by the following equation as;

$$K_{as} = \frac{[PQ]}{[P][Q]} \quad (9)$$

Where [P] is concentration of liquid P, [Q] is concentration of liquid Q and [PQ] is concentration of associated system.

By applying the condition of linearity with composition

$$\eta_{exp} = x_P \eta_P + x_{PQ} \eta_{PQ} \quad (10)$$

Since associated component (PQ) cannot be isolated in its pure form and component of non-associated molecules are also present in binary system. So to carry out proper calculations certain assumptions have been made for concentrated solution by replacing concentration term with activity of respective components. The above equation can be treated as

$$\eta_{exp} = x_P \eta_P + x_Q \eta_Q + x_{PQ} \eta_{PQ} \quad (11)$$

Calculations were performed by the following equation by the consideration of the general assumption of the model

$$K_{as} = \frac{[PQ]}{(C_P - [PQ])(C_Q - [PQ])} \quad (12)$$

Since K_{as} is an adjustable parameter. Which can be utilized to calculate the concentration of associated molecule at equilibrium. When certain changes have been made by replacing the concentration term in above equation for concentrated solution. Equation (12) will be represented as

$$K_{as} = \frac{a_{PQ}}{(a_P - a_{PQ})(a_Q - a_{PQ})} \quad (13)$$

Where $a'_P = (a_P - a_{PQ})$ and $a'_Q = (a_Q - a_{PQ})$

Using above equation, we can calculate the value of association constant (K_{as})

$$K_{as} = \frac{a_{PQ}}{a_P a_Q - a_P a_{PQ} - a_Q a_{PQ} + a_{PQ}^2} \quad (14)$$

Sum of the square of deviation (S.S.D.) can be calculated from Equation (15) by comparing the experimental and calculated values of viscosity from Equation (11).

$$S.S.D = \sum \{ (\eta^{Exp} - \eta^{Cal})^2 \} \quad (15)$$

Calculated values of S.S.D. sometimes quite low and sometime its value is quite high depending upon the adjusted parameters. These values changes slowly or rapidly when changes are carried out in adjusted values.

Model of Glinski: J. Glinski¹⁷ modify the theoretical concept derived by Natta and Baccaredda²², by applying the above model to viscosity can be calculated as

$$\eta_{cal} = \frac{\eta_P \eta_Q \eta_{PQ}}{\Phi_P \eta_Q \eta_{PQ} + \Phi_Q \eta_P \eta_{PQ} + \Phi_{PQ} \eta_P \eta_Q} \quad (16)$$

In above equation η_P , η_Q represent the viscosity of pure component P and Q and η_{PQ} is viscosity of associate respectively. η_{cal} is the theoretical viscosity of binary system, Φ_P , Φ_Q , and Φ_{PQ} represents volume fractions of respective components.

The main advantage of Glinski model over Ramaswamy model is that Glinski model requires density of pure liquid to calculate volume fraction while for binary system the density of mixture is not required.

Results and discussion

Experimental and literature values²⁰ of physicochemical properties of cyclohexane and 2,2,4 Trimethylpentane at 298.15K are presented in Table-1. Table-2 presents the Computed values of parameters of Redlich- Kister relation and

their $\delta\eta$ for viscosity. Coefficients calculated from McAllister model and their corresponding $\delta\eta$ are presented in Table-3. Coefficients of Jouyban Acree Model and their corresponding $\delta\eta$ for binary system are presented in Table-4.

Table-5 consist of absolute average % deviation (AAPD) calculated from non-associated and associated model. Theoretical values calculated for different models from Equation (7), Equation (11), and Equation (16) and their respective percentage deviations for binary system over entire range of composition from 298.15 to 323.15K are presented in Table-6.

Table-1: Comparison of experimental density and Viscosity with Literature Data at 298.15K.

	Density g/cc		Viscosity/mPa.s	
	Exp	Lit ²⁰	Exp	Lit ²⁰
Pure Component				
Cyclohexane	0.7711	0.7737	0.8958	0.8923
2,2,4-Trimethylpentane	0.686	0.6878	0.4784	0.462

Table-2: Coefficients of Equation (18) and Standard Deviation ($\delta\eta$) of viscosity.

T/K	A0	A1	A2	A3	$\delta\eta$
298.15	-0.3770	0.3783	-0.8727	-0.2423	0.1561
303.15	-0.4171	0.9458	-1.2078	-0.0408	0.1634
308.15	-0.4282	1.0727	-1.3899	-0.0602	0.1703
313.15	-0.4539	1.2036	-1.5900	0.0382	0.1755
318.15	-0.4556	1.3187	-1.7876	-0.0382	0.1810
323.15	-0.4470	0.9310	-1.8143	-0.0655	0.1854

Table -3: Coefficients calculated from Equation (20), Equation (21) and their Standard Deviations ($\delta\eta$).

T/K	McAllister -3- body ^{(Equation (20))}			T/K	McAllister-4-body ^{(Equation (21))}			$\delta\eta$
	α	β	($\delta\eta$)		α	β	γ	
298.15	0.2965	0.3353	0.0055	298.15	0.6947	0.5924	0.4983	0.0051
303.15	0.2661	0.3269	0.0019	303.15	0.6255	0.5565	0.4806	0.0013
308.15	0.2478	0.3078	0.0018	308.15	0.5823	0.5190	0.4539	0.0012
313.15	0.2324	0.2882	0.0010	313.15	0.5482	0.4790	0.4309	0.0010
318.15	0.2185	0.2758	0.0011	318.15	0.5133	0.4568	0.4100	0.0009
323.15	0.2044	0.2601	0.0014	323.15	0.4853	0.4176	0.3939	0.0012

Table-4: Coefficients of Equation (23) and Standard Deviation ($\delta\eta$) for Viscosity of binary system at various temperatures.

T/K	J_0	J_1	J_2	($\delta\eta$)
298.15	-111.7766	10.2185	-19.0814	0.0051
303.15	-109.0209	-22.7094	-22.9382	0.0013
308.15	-107.3422	-24.5531	-19.9722	0.0012
313.15	-110.9228	-20.7204	-7.6489	0.0010
318.15	-104.9787	-26.5736	-12.3036	0.0009
323.15	-107.4434	-28.8234	10.4965	0.0012

Table-5: Absolute average % deviation.

Absolute Average % Deviation			
T/K	η^{PPF}	η^{RS}	η^{GLI}
298.15	6.2672	2.1725	3.3205
303.15	6.2509	2.7703	3.5192
308.15	6.0235	3.1542	3.5521
313.15	5.9575	2.4688	3.7810
318.15	5.6368	2.3311	3.5952
323.15	5.3821	2.8056	3.5940

Table-6: Experimental Densities, Viscosities, theoretical Viscosities calculated from Equation (7), Equation (11), and Equation (16) and their Percentage Deviations ($\% \Delta\eta$) for binary system at various temperatures.

X_1	$\rho^{Exp}_{(Mix)}$	η^{Exp}	$\eta^{PPF}_{Equation (7)}$	$\eta^{RS}_{Equation (11)}$	$\eta^{GLI}_{Equation (16)}$	$\% \Delta PPF$	$\% \Delta RS$	$\% \Delta GLI$
				298.15K				
0.0762	0.6901	0.4888	0.5006	0.4895	0.4960	-2.42	-0.14	-1.48
0.1483	0.6942	0.5006	0.5228	0.5028	0.5140	-4.44	-0.44	-2.67
0.2166	0.6982	0.5135	0.5449	0.5180	0.5322	-6.11	-0.88	-3.64
0.2815	0.7023	0.5267	0.5669	0.5350	0.5507	-7.63	-1.57	-4.56
0.3431	0.7062	0.5406	0.5887	0.5534	0.5696	-8.90	-2.37	-5.36
0.4018	0.7101	0.5549	0.6104	0.5732	0.5887	-10.01	-3.30	-6.10
0.4577	0.7142	0.5752	0.6320	0.5940	0.6082	-9.88	-3.27	-5.74
0.5109	0.7182	0.5959	0.6534	0.6157	0.6280	-9.65	-3.32	-5.39
0.5618	0.7223	0.6219	0.6747	0.6381	0.6482	-8.48	-2.61	-4.23

0.6105	0.7264	0.6484	0.6958	0.6611	0.6688	-7.30	-1.96	-3.14
0.657	0.7306	0.6717	0.7166	0.6845	0.6897	-6.69	-1.90	-2.67
0.7016	0.7349	0.6954	0.7374	0.7081	0.7109	-6.03	-1.83	-2.23
0.7443	0.7392	0.7147	0.7579	0.7319	0.7326	-6.04	-2.40	-2.50
0.7853	0.7436	0.7344	0.7782	0.7557	0.7546	-5.96	-2.90	-2.76
0.8246	0.7482	0.7572	0.7983	0.7795	0.7771	-5.43	-2.94	-2.62
0.8624	0.7528	0.7806	0.8182	0.8032	0.7999	-4.82	-2.89	-2.47
0.8988	0.7574	0.8041	0.8379	0.8267	0.8232	-4.21	-2.81	-2.38
0.9338	0.762	0.8283	0.8574	0.8500	0.8470	-3.52	-2.62	-2.25
0.965	0.7665	0.8617	0.8753	0.8713	0.8693	-1.57	-1.12	-0.88
				303.15K				
0.0762	0.6851	0.4625	0.4719	0.4630	0.4678	-2.02	-0.10	-1.14
0.1483	0.6893	0.4737	0.4919	0.4759	0.4841	-3.84	-0.47	-2.20
0.2166	0.6935	0.4848	0.5118	0.4904	0.5007	-5.57	-1.16	-3.27
0.2815	0.6977	0.4963	0.5316	0.5063	0.5174	-7.11	-2.01	-4.26
0.3431	0.7019	0.5132	0.5512	0.5232	0.5345	-7.40	-1.95	-4.14
0.4018	0.706	0.5306	0.5706	0.5411	0.5517	-7.54	-1.99	-3.98
0.4577	0.7101	0.5454	0.5899	0.5598	0.5693	-8.16	-2.65	-4.38
0.5109	0.7142	0.5607	0.6090	0.5791	0.5870	-8.61	-3.29	-4.69
0.5618	0.7184	0.5768	0.6279	0.5990	0.6050	-8.85	-3.84	-4.90
0.6105	0.7226	0.5933	0.6466	0.6192	0.6234	-8.98	-4.36	-5.07
0.657	0.7269	0.6129	0.6651	0.6396	0.6419	-8.52	-4.35	-4.74
0.7016	0.7312	0.633	0.6834	0.6602	0.6608	-7.96	-4.30	-4.39
0.7443	0.7357	0.6528	0.7015	0.6809	0.6799	-7.46	-4.30	-4.15
0.7853	0.7401	0.6732	0.7194	0.7015	0.6994	-6.87	-4.21	-3.89
0.8246	0.7446	0.6953	0.7371	0.7221	0.7191	-6.01	-3.85	-3.42
0.8624	0.7491	0.718	0.7546	0.7426	0.7391	-5.09	-3.42	-2.94
0.8988	0.7535	0.741	0.7718	0.7629	0.7594	-4.16	-2.95	-2.49
0.9338	0.7579	0.7645	0.7889	0.7830	0.7801	-3.19	-2.41	-2.04

0.965	0.7623	0.7932	0.8045	0.8013	0.7995	-1.42	-1.02	-0.79
				308.15K				
0.0762	0.6813	0.4368	0.4446	0.4376	0.4411	-1.79	-0.19	-0.99
0.1483	0.6854	0.4475	0.4627	0.4502	0.4560	-3.39	-0.61	-1.90
0.2166	0.6896	0.457	0.4806	0.4640	0.4711	-5.16	-1.53	-3.08
0.2815	0.6938	0.4668	0.4984	0.4788	0.4863	-6.76	-2.56	-4.18
0.3431	0.6979	0.4812	0.5160	0.4944	0.5017	-7.23	-2.73	-4.27
0.4018	0.702	0.496	0.5334	0.5107	0.5174	-7.54	-2.96	-4.31
0.4577	0.7062	0.5098	0.5507	0.5275	0.5332	-8.02	-3.48	-4.59
0.5109	0.7103	0.524	0.5677	0.5448	0.5491	-8.35	-3.97	-4.80
0.5618	0.7145	0.539	0.5846	0.5624	0.5653	-8.47	-4.35	-4.89
0.6105	0.7187	0.5545	0.6013	0.5803	0.5818	-8.45	-4.65	-4.92
0.657	0.7229	0.5717	0.6178	0.5983	0.5983	-8.07	-4.65	-4.66
0.7016	0.7271	0.5895	0.6342	0.6164	0.6152	-7.58	-4.56	-4.35
0.7443	0.7314	0.6066	0.6503	0.6345	0.6322	-7.20	-4.59	-4.21
0.7853	0.7357	0.6242	0.6662	0.6525	0.6494	-6.73	-4.53	-4.04
0.8246	0.74	0.6438	0.6819	0.6704	0.6668	-5.92	-4.13	-3.58
0.8624	0.7442	0.6639	0.6974	0.6882	0.6845	-5.05	-3.66	-3.10
0.8988	0.7485	0.6844	0.7127	0.7059	0.7024	-4.14	-3.14	-2.63
0.9338	0.7528	0.7054	0.7279	0.7233	0.7205	-3.18	-2.54	-2.14
0.965	0.7571	0.7312	0.7416	0.7392	0.7375	-1.43	-1.10	-0.86
				313.15K				
0.0762	0.6775	0.4131	0.4220	0.4143	0.4190	-2.15	-0.29	-1.44
0.1483	0.6816	0.421	0.4382	0.4244	0.4326	-4.08	-0.82	-2.76
0.2166	0.6857	0.4315	0.4543	0.4358	0.4463	-5.27	-0.99	-3.42
0.2815	0.6899	0.4424	0.4702	0.4482	0.4601	-6.27	-1.32	-4.00
0.3431	0.694	0.4546	0.4859	0.4616	0.4740	-6.88	-1.54	-4.27
0.4018	0.6982	0.4671	0.5014	0.4758	0.4881	-7.35	-1.85	-4.50
0.4577	0.7024	0.4781	0.5168	0.4906	0.5023	-8.10	-2.61	-5.06

0.5109	0.7065	0.4895	0.5320	0.5058	0.5166	-8.68	-3.34	-5.54
0.5618	0.7107	0.5029	0.5470	0.5216	0.5311	-8.76	-3.71	-5.60
0.6105	0.7148	0.5166	0.5618	0.5376	0.5457	-8.75	-4.07	-5.63
0.657	0.719	0.5322	0.5764	0.5539	0.5604	-8.31	-4.07	-5.30
0.7016	0.7232	0.5483	0.5909	0.5703	0.5753	-7.76	-4.00	-4.92
0.7443	0.7274	0.5646	0.6051	0.5867	0.5903	-7.17	-3.91	-4.55
0.7853	0.7315	0.5813	0.6192	0.6031	0.6055	-6.51	-3.76	-4.16
0.8246	0.7357	0.6	0.6330	0.6195	0.6207	-5.50	-3.25	-3.46
0.8624	0.7398	0.6192	0.6467	0.6358	0.6362	-4.44	-2.69	-2.74
0.8988	0.744	0.6377	0.6602	0.6520	0.6518	-3.52	-2.25	-2.21
0.9338	0.7483	0.6567	0.6735	0.6680	0.6675	-2.55	-1.73	-1.65
0.965	0.7524	0.6779	0.6856	0.6827	0.6822	-1.13	-0.71	-0.64
				318.15K				
0.0762	0.6723	0.3929	0.3999	0.3930	0.3973	-1.78	-0.03	-1.11
0.1483	0.6766	0.4013	0.4149	0.4025	0.4098	-3.38	-0.30	-2.13
0.2166	0.6808	0.4106	0.4296	0.4131	0.4225	-4.63	-0.60	-2.90
0.2815	0.685	0.4203	0.4443	0.4246	0.4353	-5.70	-1.03	-3.56
0.3431	0.6893	0.4305	0.4587	0.4370	0.4481	-6.55	-1.51	-4.09
0.4018	0.6935	0.4411	0.4730	0.4500	0.4611	-7.22	-2.02	-4.53
0.4577	0.6978	0.4527	0.4871	0.4636	0.4742	-7.59	-2.41	-4.74
0.5109	0.7021	0.4647	0.5009	0.4776	0.4873	-7.80	-2.78	-4.86
0.5618	0.7063	0.4762	0.5147	0.4920	0.5006	-8.08	-3.31	-5.12
0.6105	0.7106	0.488	0.5282	0.5066	0.5139	-8.24	-3.81	-5.32
0.657	0.7149	0.5024	0.5416	0.5214	0.5274	-7.80	-3.78	-4.98
0.7016	0.7191	0.5172	0.5548	0.5363	0.5410	-7.26	-3.69	-4.60
0.7443	0.7234	0.5318	0.5677	0.5512	0.5547	-6.76	-3.65	-4.30
0.7853	0.7277	0.5467	0.5805	0.5661	0.5685	-6.19	-3.56	-3.98
0.8246	0.7319	0.5628	0.5932	0.5810	0.5824	-5.39	-3.23	-3.48
0.8624	0.7362	0.5793	0.6056	0.5958	0.5964	-4.54	-2.85	-2.95

0.8988	0.7404	0.5952	0.6179	0.6105	0.6105	-3.81	-2.57	-2.57
0.9338	0.7447	0.6115	0.6300	0.6250	0.6248	-3.02	-2.21	-2.17
0.965	0.7489	0.6323	0.6410	0.6383	0.6380	-1.37	-0.95	-0.91
				323.15K				
0.0762	0.6689	0.3727	0.3788	0.3736	0.3766	-1.63	-0.25	-1.04
0.1483	0.6732	0.3804	0.3922	0.3830	0.3880	-3.10	-0.68	-2.00
0.2166	0.6774	0.3888	0.4054	0.3932	0.3995	-4.28	-1.13	-2.76
0.2815	0.6816	0.3975	0.4185	0.4041	0.4111	-5.29	-1.65	-3.42
0.3431	0.6859	0.4059	0.4314	0.4155	0.4227	-6.29	-2.36	-4.14
0.4018	0.6901	0.4147	0.4442	0.4274	0.4344	-7.11	-3.06	-4.75
0.4577	0.6944	0.4251	0.4568	0.4396	0.4461	-7.45	-3.41	-4.95
0.5109	0.6986	0.4358	0.4691	0.4521	0.4579	-7.65	-3.74	-5.07
0.5618	0.7029	0.4457	0.4813	0.4648	0.4698	-8.00	-4.29	-5.40
0.6105	0.7071	0.4559	0.4934	0.4777	0.4817	-8.23	-4.78	-5.66
0.657	0.7113	0.4687	0.5053	0.4906	0.4937	-7.80	-4.67	-5.33
0.7016	0.7156	0.482	0.5170	0.5036	0.5058	-7.26	-4.48	-4.93
0.7443	0.7198	0.4944	0.5285	0.5165	0.5179	-6.90	-4.47	-4.75
0.7853	0.7241	0.5072	0.5399	0.5294	0.5301	-6.44	-4.38	-4.51
0.8246	0.7283	0.5235	0.5510	0.5422	0.5423	-5.26	-3.58	-3.59
0.8624	0.7325	0.5402	0.5620	0.5550	0.5546	-4.04	-2.73	-2.66
0.8988	0.7368	0.5565	0.5729	0.5676	0.5670	-2.95	-1.99	-1.88
0.9338	0.741	0.5733	0.5836	0.5801	0.5794	-1.80	-1.18	-1.07
0.965	0.7451	0.5887	0.5935	0.5914	0.5910	-0.81	-0.46	-0.39

Following expressions were used in PFP model to determine the corresponding values

$$\alpha = \frac{75.6 \times 10^{-3}}{T^9 u^2 \rho^3} \quad \text{and} \quad \beta_T = \frac{1.71 \times 10^{-3}}{T^{4/9} u^2 \rho^{4/3}} \quad (17)$$

R.K shukala²³ and others²⁴⁻²⁶ have obtained values of α and β_T have obtained from above expression. Concept of linearity represents the non-associative and associative nature of binary system. Deviation from linearity corresponds to the associative behaviour. Ramaswamy and Anbananthan model predict the

strong association between the like and unlike molecules of liquids which has been trained to predict of viscosity of poor associating liquid mixture. The results obtained from above model were utilized properly. To carry out such calculations we constructed a data sheet in excel. Association constant K_{as} and adjustable Coefficients can be changed manually to determine the theoretical viscosity. Values of viscosity of pure liquids and associate can be used to determine the association constant.

Mathematical representation of Redlich- Kister relation¹⁸

$$y = x_i(1 - x_i) \sum_{i=0}^p A_i(2x_i - 1)^i \quad (18)$$

Where y represents the viscosity deviation ($\Delta\eta$) A_i represents coefficients of polynomial. The values of coefficients A_i were estimated by nonlinear least square method. Values of A_i and $\delta\eta$ are presented in Table-2. Standard deviation ($\delta\eta$) was determined by the following equation

$$\delta\eta = \left[\frac{\sum_{i=1}^n (\eta_{Exp} - \eta_{Cal})^2}{(n-p)} \right]^{1/2} \quad (19)$$

Where p and n represent the adjusting coefficient and data point respectively. $0.1561 < \delta\eta < 0.1854$. Largest deviation occurs at 323.15K.

McAllister model¹⁹, is one of most accurate correlation model for different physicochemical properties follow the method of least square.

McAllister -3-body model is defined as

$$\ln \eta = x_1^3 \ln \eta_1 + 3x_1^2 x_2 \ln \eta_\alpha + 3x_1 x_2^2 \ln \eta_\beta + x_2^3 \ln \eta_2 - \ln[x_1 + x_2 M_2/M_1] + 3x_1^2 x_2 \ln[(2 + M_2/M_1)/3] + 3x_1 x_2^2 \ln[(1 + 2 M_2/M_1)/3] + x_2^3 \ln[M_2/M_1] \quad (20)$$

McAllister-4-body model is defined as

$$\ln \eta = x_1^4 \ln \eta_1 + 4x_1^3 x_2 \ln \eta_\alpha + 6x_1^2 x_2^2 \ln \eta_\beta + 4x_1 x_2^3 \ln \eta_\gamma + x_2^4 \ln \eta_2 - \ln[(x_1 + x_2 M_2/M_1)] + 4x_1^3 x_2 \ln[(3 + M_2/M_1)/4] + 6x_1^2 x_2^2 \ln[(1 + M_2/M_1)/2] + 4x_1 x_2^3 \ln[(1 + 3M_2/M_1)/4] + x_2^4 \ln(M_2/M_1) \quad (21)$$

In above equation η represent calculated viscosity of binary system and α , β and γ are adjustable Coefficients which have been calculated from Equation (20) and (21) for McAllister -3-body and McAllister-4-body model respectively. (x_1 , x_2), (η_1, η_2) and (M_1 , M_2) are the physical parameters of pure components. Values of Coefficients and standard deviation ($\delta\eta$) of respective models are presented in Table-3. It is observed that standard deviation ($\delta\eta$) for McAllister-3- body and McAllister-4-body model lies in the range are (0.0055-0.0014) and (0.0051-0.0012) respectively at various temperatures. Calculated values of viscosity from Equation (21) correlated the experimental viscosity of liquid mixture more accurately in comparison to calculated values from Equation (20). Furthermore, corresponding parameters and respective standard deviation decreases as temperature increases except 323.15K

Jouyban Acree model²⁷⁻²⁸ is a mathematical correlation model was applied to correlate the physicochemical property of binary system at various temperatures:

$$\ln \eta_{m,T} = X_1 \cdot \ln \eta_{1,T} + X_2 \cdot \ln \eta_{2,T} + J_0 \left[\frac{x_1 \cdot x_2}{T} \right] + J_1 \left[\frac{x_1 \cdot x_2 \cdot (x_1 - x_2)}{T} \right] + J_2 \left[\frac{x_1 \cdot x_2 \cdot (x_1 - x_2)^2}{T} \right] \quad (22)$$

where J_0 , J_1 , and J_2 are coefficients of the Jouyban Acree model can be calculated by no -intercept regression method by rearranging Eq.22.

$$\ln \eta_{m,T} - X_1 \cdot \ln \eta_{1,T} - X_2 \cdot \ln \eta_{2,T} = J_0 \left[\frac{x_1 \cdot x_2}{T} \right] + J_1 \left[\frac{x_1 \cdot x_2 \cdot (x_1 - x_2)}{T} \right] + J_2 \left[\frac{x_1 \cdot x_2 \cdot (x_1 - x_2)^2}{T} \right] \quad (23)$$

Where η_m , η_1 and η_2 are viscosity of liquid system, component 1 and 2 respectively. Standard deviation ($\delta\eta$) for Jouyban Acree model lies between 0.0051–0.0009, which shows model correlates the experimental findings with high accuracy in comparison to McAllister model²⁸.

In all the correlation model standard deviation decreases with increase in temperature. Standard deviation order for correlation models is as: Jouyban Acree model < McAllister four body < McAllister three body.

Excess viscosity (η^E) derived from statistical equation of Flory which is generally used to know the behaviour of liquids and to determine the extent of attractive (or repulsive) interactions.

$$\eta^E = \eta - \sum_{i=1}^2 x_i \eta_i \quad (24)$$

where η^E is theoretical excess viscosity, η_i is viscosity for i^{th} component and x_i is the mole fraction for i^{th} component. The plot of excess viscosity with mole fraction x_1 obtained from PFP, Ramaswamy and Glinski at different temperatures are presented in Figure-1. The similar curves were observed in all figures for all the models and show negative changes with different magnitude at different temperatures. PFP Model shows small negative change in excess viscosity whereas for Ramaswamy model a large negative change in excess viscosity was observed as shown in Figure-1. Decreasing order of excess viscosity was observed as *PFP < Glinski < Ramaswamy*. which indicate the molecular interaction between components of binary mixture.

Table-6 predicts that viscosity and excess viscosity decrease as mole fraction of cyclohexane increases for all models with increase in temperatures.

The similar changes were observed and showed negative percentage deviation with increase in temperature. Calculated values of viscosity and excess viscosity obtained from PFP, Ramaswamy and Glinski models and their percentage deviations (% Δ) indicate that PFP model show more Percentage deviation in comparison to Ramaswamy and Glinski model, the order is as follows *PFP > Glinski > Ramaswamy*. Although liquid mixture was non-polar but Considerable good results were observed for Ramaswamy model as compared to PFP and Glinski models, which indicate that packing effect is more dominating than dispersive forces between unlike molecules of binary liquid mixture.

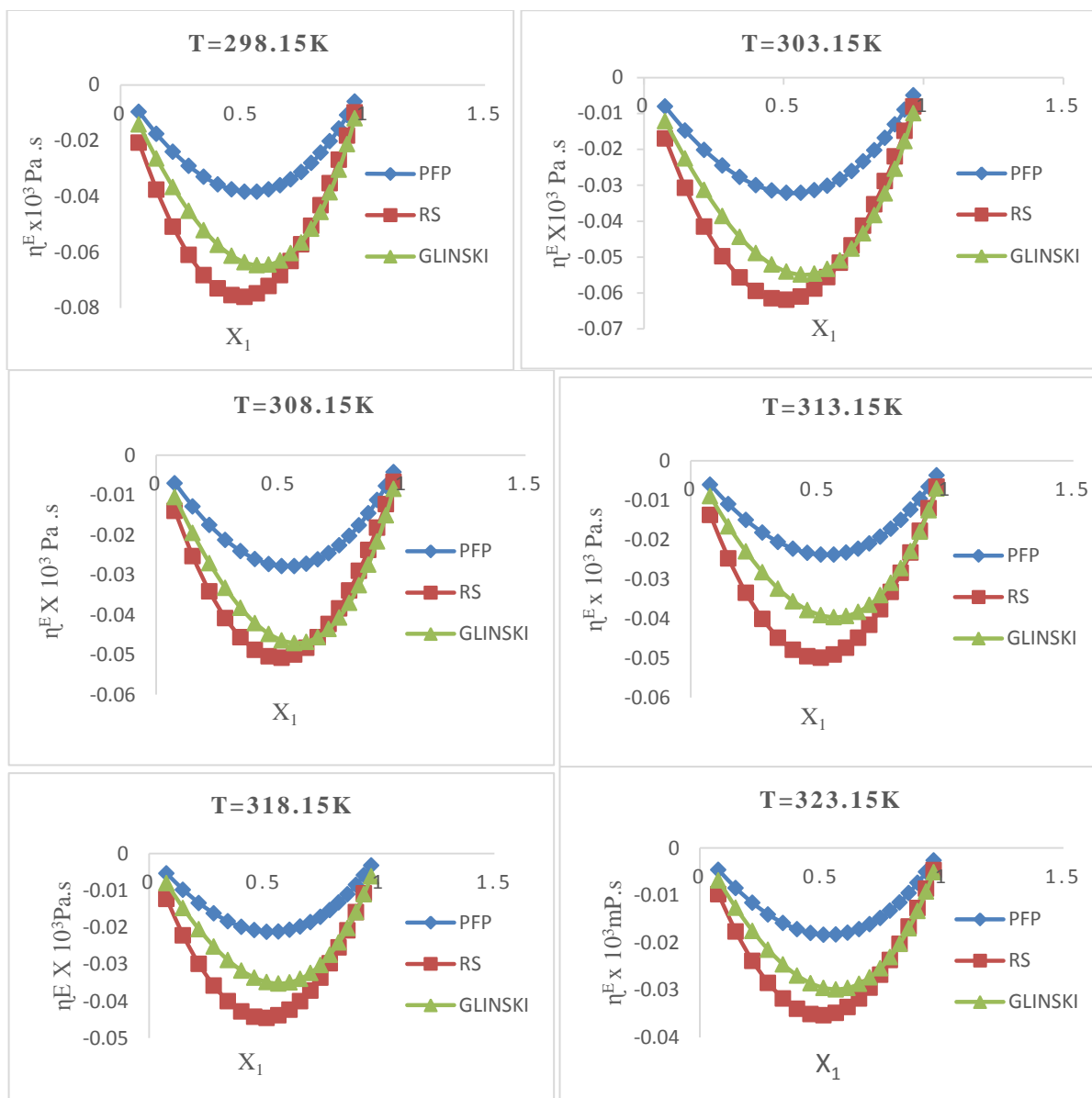


Figure- 1: Variation of excess viscosity with temperatures.

Conclusion

From the above discussion it is concluded that the theoretical results of viscosity and excess viscosity calculated from associated (RS) model gave better results and provide smooth way to determine intermolecular interaction and structure of associates than non-associated (PFP) and Glinski model. Jouyban Acree Model Gave excellent result than other two models. The order is as follows Jouyban Acree Model >McAllister four body>McAllister three body.

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