

Theoretical estimation of viscosity of quinary and its constituent quaternary liquid mixtures

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Abstract : The present work is concerned with the theoretical analysis of quite new and rare data on viscosity of a regular quinary and its quaternary subsystems at 308.15 K and 313.15 K (Nhaesi and Asfour, *J. Chem. Eng. Data*, 2005, 50, 149). For the first time, six different relations, viz. Wassiljewa relation, Sutherland-Wassiljewa (S-W) relation, Arrhenius model, Bingham relation, Kendall-Munroe (K-M) relation and Croenauer-Rothfus-Kermore (C-R-K) relation have been applied to the quinary system (toluene + octane + ethylbenzene + tetradecane + hexadecane) and its quaternary subsystems.

The theoretical results are compared with experimental viscosity data reported in the aforementioned papers. Quite interesting results are obtained.

Keywords : Quinary liquid system, viscosity, Wassiljewa relation, Arrhenius model.

Introduction

Knowledge of transport properties of multicomponent liquid system is essential in many industrial applications. Among the various transport properties (diffusion coefficient, thermal conductivity and viscosity) of liquid, viscosity is the most important due to its applications for process design in petroleum, petrochemical, chemical and other chemical industries involving fluid transportation, mixing, agitation, heat exchange and concentration. Viscosity of photo resistant plays 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 applications in chemical engineering such as in the determination of flow in pipelines, heat transfer operations etc. The estimation of viscosity of liquid mixture is much more difficult than that of pure liquid.

Various empirical and semi-empirical equations¹⁻⁵ for estimating liquid viscosity have been developed. In another attempt, a number of models⁶⁻¹⁶ for viscosity have been proposed. These include Eyring absolute rate theory model⁶, corresponding state theory^{7,8}, significant structure theory^{9,10}, Flory theory¹¹⁻¹⁴, group contribution method¹⁵ and model based on kinetic theory¹⁶. A critical review of viscosity data and their estimations has been presented earlier¹⁷.

A comprehensive review of all the empirical, semiempirical and other methods employed for the estimation of viscosity of binary liquid mixtures has been presented by Lee and Lee¹⁸. Comparatively lesser work has been done on the experimental and theoretical aspects of viscosity of multicomponent liquid systems.

Table 1. Different parameters of pure components

	ρ g cm ⁻³	v 10 ⁻⁶ m ² s ⁻¹	η 10 ⁻³ Pa.s
At 308.15 K :			
Toluene	0.8529	0.5811	0.4956
Octane	0.6904	0.6603	0.4559
Ethylbenzene	0.8539	0.6632	0.5663
Tetradecane	0.7521	2.2770	1.7125
Hexadecane	0.7631	3.2250	2.4610
At 313.15 K :			
Toluene	0.8484	0.5509	0.4674
Octane	0.6864	0.6254	0.4293
Ethylbenzene	0.8496	0.6265	0.5323
Tetradecane	0.7487	2.0920	1.5663
Hexadecane	0.7597	2.9280	2.2244

Table-2. Calculated and experimental values of viscosity along with percentage deviation of quinary liquid mixture at different temperatures

Toluene (x_1) + Octane (x_2) + Ethylbenzene (x_3) + Tetradecane (x_4) + Hexadecane (x_5)																
x_1	x_2	x_3	x_4	η_{mix} W 10^{-3} Pa.s	η_{mix} S-W 10^{-3} Pa.s	η_{mix} Arrh 10^{-3} Pa.s	η_{mix} Bingham 10^{-3} Pa.s	η_{mix} K-M 10^{-3} Pa.s	η_{mix} C-R-K 10^{-3} Pa.s	η_{exp} 10^{-3} Pa.s	% Δ W	% Δ S-W	% Δ Arrh	% Δ Bingham	% Δ K-M	% Δ C-R-K
At 308.15 K :																
0.4716	0.1968	0.1993	0.0781	0.6286	0.9128	0.5665	0.7034	0.6016	0.5903	0.6235	-0.82	-46.40	9.14	-12.82	3.51	5.32
0.0517	0.5990	0.1756	0.1122	0.6368	1.2465	0.6354	0.7416	0.6121	0.6572	0.6461	1.44	-92.93	1.66	-14.79	5.27	-1.72
0.4050	0.2941	0.0855	0.0486	0.7256	0.9907	0.6451	0.8769	0.6787	0.6859	0.7496	3.20	-32.16	13.95	-16.99	9.46	8.49
0.1205	0.0407	0.4157	0.1403	1.0513	1.4535	0.8949	1.2499	0.9775	0.9592	1.0921	3.74	-33.09	18.06	-14.45	10.50	12.17
0.0723	0.1052	0.0655	0.2002	1.6075	2.6440	1.5319	1.8340	1.5504	1.6027	1.7036	5.64	-55.20	10.08	-7.65	8.99	5.92
0.1704	0.0650	0.6029	0.0580	0.7135	1.3437	0.6202	0.8100	0.6778	0.6485	0.7187	0.72	-86.96	13.71	-12.71	5.69	9.77
0.1777	0.3792	0.0931	0.3080	0.8031	1.1092	0.7591	0.9445	0.7618	0.7987	0.8285	3.07	-33.88	8.38	-14.00	8.04	3.59
0.0780	0.1611	0.2941	0.3994	0.9804	1.3585	0.8954	1.1285	0.9296	0.9440	1.0070	2.64	-34.91	11.08	-12.07	7.68	6.26
0.2810	0.0388	0.1701	0.1050	1.1934	1.6365	1.0065	1.4300	1.1017	1.0909	1.2746	6.37	-28.39	21.03	-12.19	13.57	14.41
0.0715	0.0433	0.0603	0.6177	1.5345	3.0264	1.4950	1.6571	1.4925	1.5436	1.5822	3.01	-91.28	5.51	-4.73	5.67	2.44
										APD	3.07	53.52	11.26	12.24	7.84	7.01
At 313.15 K :																
0.6703	0.0806	0.1087	0.0834	0.5986	1.3419	0.5233	0.6632	0.5692	0.5484	0.5961	-0.42	-125.12	12.21	-11.25	4.51	8.00
0.1053	0.5587	0.1805	0.1023	0.5823	1.0329	0.5797	0.6637	0.5611	0.5993	0.5796	-0.47	-78.20	-0.02	-14.51	3.20	-3.40
0.1810	0.0632	0.6065	0.0538	0.6538	1.2484	0.5732	0.7313	0.6231	0.5980	0.6576	0.57	-89.84	12.83	-11.20	5.25	9.06
0.1153	0.1463	0.3038	0.3721	0.8777	1.1943	0.7963	1.0002	0.8302	0.8412	0.8932	1.74	-33.72	10.85	-11.98	7.05	5.82
0.1864	0.1596	0.1485	0.1091	1.0681	1.4147	0.9449	1.2873	0.9955	1.0158	1.1304	5.51	-25.15	16.41	-13.88	11.93	10.14
0.1661	0.1905	0.1980	0.2468	0.9246	1.1355	0.8315	1.0931	0.8670	0.8863	0.9619	3.88	-18.04	13.56	-13.64	9.87	7.86
										APD	2.10	61.68	10.98	12.74	6.97	7.38

Note

Table 3. Average percentage deviation of quaternary liquid mixtures at different temperatures

System	Temp. (K)	APD					
		W	S-W	Arrh	Bingham	K-M	C-R-K
I		Toluene (x ₁) + Octane (x ₂) + Ethylbenzene (x ₃) + Tetradecane (x ₄)					
	308.15	1.93	103.05	5.43	11.43	2.67	4.10
	313.15	1.44	94.37	6.50	9.35	3.95	3.43
II		Toluene (x ₁) + Octane (x ₂) + Ethylbenzene (x ₃) + Hexadecane (x ₄)					
	308.15	3.15	87.13	14.46	15.22	8.55	9.74
	313.15	3.66	86.48	14.89	13.26	9.02	10.19
III		Toluene (x ₁) + Ethylbenzene (x ₂) + Tetradecane (x ₃) + Hexadecane (x ₄)					
	308.15	1.80	-74.11	14.62	-10.99	7.52	9.52
	313.15	3.07	73.93	14.89	9.61	7.83	9.81
IV		Octane (x ₁) + Ethylbenzene (x ₂) + Tetradecane (x ₃) + Hexadecane (x ₄)					
	308.15	2.35	99.94	12.78	10.86	7.46	7.98
	313.15	2.52	100.19	12.94	9.69	7.65	8.14
V		Toluene (x ₁) + Octane (x ₂) + Tetradecane (x ₃) + Hexadecane (x ₄)					
	308.15	4.30	91.94	13.79	11.43	8.80	9.33
	313.15	11.12	78.98	19.96	4.35	15.33	15.81

However, no such studies are available on the viscosity of multicomponent liquid mixtures beyond ternary and quaternary due to the lack of data. For the first time, very recently, Asfour *et al.*¹⁹ measured accurately the density and viscosity of a regular quinary system toluene + octane + ethylbenzene + tetradecane + hexadecane and its quaternary subsystems at 308.15 K and 313.15 K.

In the present work six different methods viz. Wassiljewa (W) relation, Sutherland-Wassiljewa (S-W), Arrhenius model, Bingham relation, Kendall-Munroe (K-M) relation and Croenauer-Rothfus-Kermore (C-R-K) relation have been applied to calculate the viscosity of above mentioned quinary and its constituent quaternary systems. A comparison between experimental and calculated values is also done. The aim of the present investigation is to check the validity of these relations for quinary multicomponent liquid system. As far as our knowledge is concerned, we are the first to apply the gaseous state model and other mentioned equations to compute the viscosity of multicomponent liquid system.

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 work, Wassiljewa equation²⁰ is applied to evaluate viscosity of multicomponent liquid solutions. The aforesaid equation can be expressed as,

$$\eta_m = \sum_i \frac{\eta_i}{1 + \sum_j A_{ij} \left(\frac{x_j}{x_i} \right)} \quad (1)$$

The Sutherland-Wassiljewa equation²¹ for the multicomponent liquid solutions can be expressed as,

$$\eta_m = \sum_i \frac{x_i \eta_i}{\sum_j A_{ij} x_j} \quad (2)$$

Here, A_{ij} is the Wassiljewa coefficient interpreted by Pandey *et al.*²²⁻²⁴ and Gray *et al.*²⁵ 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). Sutherland expression was based on the predictions of simple kinetic theory whereas Wassiljewa derived it on the basis of mean free path. Hirshfelder approximation was based on Chapman and Enskog kinetic theory. In eqs. (1) and (2), A_{ij} is the Wassiljewa coefficient, which is independent of composition. A new empirical form has been given to the Wassiljewa coefficient, A_{ij} ²², for giving the best possible results in the case of liquids. It is expressed as,

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

Additive relation based an Arrhenius model²⁶ for the viscosity of pure liquid can be modified to multi-component system as,

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

Bingham⁵ considering the ideal mixing of solutions, proposed the following equation for a binary solution :

$$\eta_m = x_1 \eta_1 + x_2 \eta_2 \quad (5)$$

In general, the equation for multicomponent liquid solutions is expressed as,

$$\eta_m = \sum_{i=1}^n x_i \eta_i \quad (6)$$

According to Kendall and Munroe⁴, the viscosity of multicomponent system assumes the form,

$$\eta_m = \sum_{i=1}^n x_i \ln \eta_i \quad (7)$$

Croenauer, Rothfus and Kermore²⁷ proposed the following equation for n -component liquid solution :

$$\ln v_m = \sum_{i=1}^n x_i \ln v_i \quad (8)$$

where, v_m = kinematic viscosity.

The kinematic viscosity is related with viscosity by the equation, $v = \eta/\rho$, where ρ is density of the liquid system.

Results and discussion

Viscosity values of one quinary solution (toluene + octane + ethylbenzene + tetradecane + hexadecane) and its five constituent quaternary liquid solutions (toluene + octane + ethylbenzene + tetradecane, toluene + octane + ethylbenzene + hexadecane, toluene + ethylbenzene + tetradecane + hexadecane, octane + ethylbenzene + tetradecane + hexadecane and toluene + octane + tetradecane + hexadecane) at 308.15 K and 313.15 K have been computed by six different methods viz. Wassiljewa (W) relation, Sutherland-Wassiljewa (S-W), Arrhenius model, Bingham relation, Kendall-Munroe (K-M) relation and Croenauer-Rothfus-Kermore (C-R-K) relation by using eqs. (1), (2), (4), (6), (7) and (8) respectively. The theoretically obtained values of viscosity are computed with experimental findings. The necessary data needed, for computation and comparison, have been taken from literature¹⁹. All the parameters of pure components are

listed in Table 1. Table 2 enlists the computed and experimental values of viscosity along with percentage deviation of quinary liquid solution. Average percentage deviation (APD) is also reported. In Table 3 APD values of viscosities by six different methods of five constituent quaternary liquid solutions are reported. Calculated values of viscosity show the same trend as observed experimentally.

On inspecting the results of Table 2, it has been observed that for the quinary system, the average percentage deviations for Wassiljewa relation, S-W relation, Arrhenius model, Bingham relation, K-M relation and C-R-K relation are 53.52, 3.07, 11.26, 12.24, 7.84 and 7.01 at 308.15 K and 61.68, 2.10, 10.98, 12.74, 6.97 and 7.38 at 313.15 K respectively. It is also clear from the table that theoretically evaluated viscosity values of quinary system from all the relations; except those of Sutherland-Wassiljewa, are comparable and found to be in good agreement with the experimental findings. The Wassiljewa relation gives excellent results because the APD values are found to be in the order of 2 to 3 percent from this relation.

A close observation of Table 3 indicated that in all five quaternary systems, the Wassiljewa relation gives the excellent result having APD in the order of 2 to 4 percent. The results obtained from other methods are also comparable except those of Sutherland-Wassiljewa.

For the quinary system, the overall APD values seem to follow the trend,

$$W < K-M < C-R-K < Bingham < Arrhenius < S-W.$$

The quaternary liquid systems follow almost the same trend as followed by the quinary liquid system.

Taking into consideration the inevitable experimental error and limitations of various theories, the results obtained from all the relations except those of Sutherland-Wassiljewa are comparable. From the observation of Tables 2 and 3, it is found that generally percentage deviation is more in cases where contribution of hexadecane and tetradecane molecules are greater in the liquid system. These two components have comparatively bigger size and hence their area of contact will be large. This increases the multi body interactions, which can affect the results.

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