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Kinematic Viscosities of Binary and Ternary Liquid Mixtures Involving Chloroform, 2-Propanol, and 2-Butanol at Several Temperatures

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Experimental kinematic viscosity data are presented for chloroform + 2-propanol + 2-butanol and also for the three constituent binary mixtures at 20, 25, 30, and 35 °C. The binary kinematic viscosities have been correlated by the empirical equation obtained by extension of the model of ideal kinematic viscosity of a liquid mixture. Predicted data agree fairly well with the experimental observations. The ternary kinematic viscosities were fitted by correlations suggested by Al-Besharah et al., Vijayaraghavan et al., and Iulian et al. The best fit was obtained with the relation by Al-Besharah et al.

Introduction

A knowledge of the viscosity of liquids and liquid mixtures is required for the solution of many engineering problems concerning heat transfer, mass transfer, and fluid flow. The viscosity of liquid mixtures is important from a practical point of view, and it is also of great interest from a theoretical view point in that mixture behavior may lead to better understanding of liquid theory. The viscosity of liquid mixtures has attracted much attention in the literature (Glasstone et al., 1941; Reid et al., 1987). It has been recognized that viscosity—composition curves are not linear; they may have a maximum, a minimum, neither, or both.

A number of empirical and semitheoretical equations have been successfully developed for pure components and binary mixtures (Reid et al., 1987), but the literature of correlations of flow properties for ternary and multicomponent liquid mixtures is rather limited.

The aim of the study is to compare some of the models for prediction of kinematic viscosity of binary liquid mixtures suggested in the literature. A new empirical equation for kinematic viscosity of binary liquid mixtures is proposed. A general comparison of the correlations for prediction of kinematic viscosity of ternary liquid mixtures was made.

Experimental Section

Materials. All pure liquids used in this work were commercially available from Zorka, Šabac, Yugoslavia. The liquids were used as received without any further purification. Their purity was assessed by gas—liquid chromatography and was better than 99.4% for 2-propanol and 2-butanol and better than 99.0% for chloroform. The experimental densities and absolute viscosities of the pure liquids were compared with those found in the literature (Table 1). The absolute viscosity data for systems investigated were calculated from the measured kinematic viscosity and density values.

Measurements. An Ubbelohde viscometer was used for measuring the kinematic viscosities of the pure liquids and liquid mixtures. The apparatus was submerged in a thermostatic bath at constant temperature with a resolution of ± 0.1 °C. The viscometer was calibrated with bidistilled water and pure components at each temperature. About 30 min was allowed for temperature equilibra-

Table 1. Comparison of Measured Densities ϱ and Absolute Viscosities η of Pure Components with Literature Values at 20, 25, 30, and 35 °C.

		<i>Q</i> /(g cm ⁻³)		$\eta/(r$	nPa s)
compound	t/°C	exptl	lit.	exptl	lit.
chloroform	20	1.4772	1.4890^{a}	0.576	0.570^{a}
	25	1.4461	1.4727^b	0.545	0.5357^{b}
	30	1.4513	1.4706^{a}	0.534	0.516^{a}
	35	1.4325	1.4611^{a}	0.498	0.514^{a}
2-propanol	20	0.7862	0.7864°	2.292	2.410^a
	25	0.7817	0.7812^{c}	2.015	2.009^{a}
	30	0.7771	0.7769^{a}	1.797	1.789^{a}
	35	0.7731		1.507	
2-butanol	20	0.8046	0.8063^{c}	3.967	4.000^{a}
	25	0.7980	0.8025^{d}	3.501	3.556^{a}
	30	0.7935	0.7987^{d}	2.958	
	35	0.7898	0.7938^{d}	2.475	

 a Irving (1977b). b As four and Dullien (1981). c Šedivec and Flek (1976). d Rigglo et al. (1980).

tion before readings were taken. The time of fall always exceeded 180 s; the accuracy of the measurement of the time was 0.1 s. Consequently the errors of the measured values of the kinematic viscosity may be estimated as less than $\pm 0.5\%$. Densities of pure components were measured with an Anton Paar DMA 46 digital density meter, with an accuracy of ± 0.0001 g cm $^{-3}$. Experiments were generally performed at least in three replicates for each composition, and the results were averaged.

Theory

Correlations for Binary Liquid Mixtures. Continued interest in the viscosity of binary mixtures is shown by the prodigious number of papers reported in the literature (Glasstone et al., 1941; and Reid et al., 1987). As measurements have been made, so have appropriate equations to describe the viscosity of mixtures been sought. Irving (1977a,b) surveyed more than 50 equations for describing the viscosity of binary liquid mixtures and classified them by type. He recommends the one-constant Grunberg—Nissan equation (1949) as being widely applicable yet reasonably accurate for predicting absolute viscosity.

McAllister's (1960) model is based on Eyring's absolute rate theory assuming three-body or four-body interactions. For three-body interactions, the equation reported by McAllister (1960) is

$$\begin{split} \ln \, \nu_{\rm b} &= x_1^3 \ln \, \nu_1 + 3 x_1^2 x_2 \ln \, \nu_{12} + 3 x_1 x_2^2 \ln \, \nu_{21} \, + \\ x_2^3 \ln \, \nu_2 &- \ln (x_1 + x_2 M_2 / M_1) + 3 x_1^2 x_2 \ln [(2 + M_2 / M_1) / 3] \, + \\ 3 x_1 x_2^2 \ln [(1 + 2 M_2 / M_1) / 3] + x_2^3 \ln (M_2 / M_1) \, \, (1) \end{split}$$

where x_1 and x_2 are the mole fractions of components 1 and 2, respectively, M_1 and M_2 are their respective molecular weights, and ν_1 , ν_2 , and ν_b are the kinematic viscosities of the pure components and the liquid mixture, respectively. The model given by eq 1 contains two adjustable parameters (ν_{12} , ν_{21}), and the equation allows for the possibility of having a maximum, a minimum, neither, or both for kinematic viscosity of the binary mixture as a function of mole fraction.

Heric and Brewer (1967) suggested the following relation:

$$\ln(\nu_b M_b) = x_1 \ln(\nu_1 M_1) + x_2 \ln(\nu_2 M_2) + x_1 x_2 [A + B(x_1 - x_2) + C()^2 + ...]$$
 (2)

where M_b is the average molecular weight of the binary mixtures and A, B, and C are unknown constants. Usually three constants in the power series are sufficient to provide a fit better than 0.5% (Irving, 1977a).

Krishnan and Laddha (1968) developed the following model for correlating of kinematic viscosity of binary liquid mixtures:

$$\begin{split} \ln \nu_{\rm b} &= x_1 \ln(\nu_1 M_1) + x_2 \ln(\nu_2 M_2) - \ln(x_1 M_1 + x_2 M_2) - \\ &\quad 2.303 x_1 x_2 [B_{12} + C_{12}(x_1 - x_2) + D_{12}(x_1 - x_2)^2] \ \ (3) \end{split}$$

where B_{12} , C_{12} , and D_{12} are binary constants. The authors show that constants B_{12} , C_{12} , and D_{12} may be predicted from vapor—liquid equilibrium data or calculated from experimental data for kinematic viscosity of binary liquid mixtures

Iulian et al. (1993) fitted the experimental kinematic viscosities for binary liquid mixtures to an empirical equation in the form:

$$\ln \nu_b = x_1 \ln(\nu_1 M_1) + x_2 \ln(\nu_2 M_2) - \ln(x_1 M_1 + x_2 M_2) + x_1 x_2 [A_0 + A_1(x_1 - x_2) + A_2(x_1 - x_2)^2 + A_3(x_1 - x_2)^3]$$
(4)

where A_0 , A_1 , A_2 , and A_3 are unknown constants. The four binary constants in the model given by (4) for the binary liquid mixtures have been calculated from the respective experimental data by a nonlinear estimation method, (Iulian et al., 1993).

In this paper the new equation for the prediction of the kinematic viscosity of binary liquid mixture is proposed as the following:

$$\ln \nu_{\rm b} = x_1 \ln \nu_1 + x_2 \ln \nu_2 \pm x_1 x_2 \sum_{j=0}^4 b_j (x_1 - x_2)^j \qquad (5)$$

where b_j are experimental parameters. To determine the values of parameters b_j , the kinematic viscosities of the pure components and binary liquid mixtures must be measured experimentally.

Correlations for Ternary Liquid Mixtures. The use of eq 3 for correlation and prediction of kinematic viscosity of the binary liquid mixtures has been extended by Vijayaraghavan et al. (1976) for ternary liquid mixtures. This equation is given below:

$$\begin{split} \ln \nu_{\rm t} &= x_1 \, \ln(\nu_1 M_1) + x_2 \, \ln(\nu_2 M_2) \, + \\ &\quad x_3 \, \ln(\nu_3 M_3) - \ln(x_1 M_1 + x_2 M_2 + x_3 M_3) \, - \\ &\quad 2.303 x_1 x_2 [B_{12} + C_{12} (x_1 - x_2) + D_{12} (x_1 - x_2)^2] \, - \\ &\quad 2.303 x_2 x_3 [B_{23} + C_{23} (x_2 - x_3) + D_{23} (x_2 - x_3)^2] \, - \\ &\quad 2.303 x_3 x_1 [B_{31} + C_{31} (x_3 - x_1) + D_{31} (x_3 - x_1)^2] \ \, (6) \end{split}$$

where $\nu_{\rm t}$ is the kinematic viscosity of the ternary mixture, x_3 is the mole fraction of component 3, M_3 is the molecular weight of component 3, B_{12} , C_{12} , D_{12} , B_{23} , C_{23} , D_{23} , B_{31} , C_{31} , and D_{31} are binary constants. The binary constants for each of the corresponding three binary mixtures in eq 6 were determined by analysis of the respective experimental data by eq 3.

In accordance with the approach of Ratcliff and Khan (1971), Al-Besharah et al. (1987) proposed the new equation for the real ternary liquid mixture, as follows:

$$\ln \nu_{t} = \sum_{i=1}^{3} x_{i} \ln \nu_{i} + a_{12}x_{1}x_{2} + a_{23}x_{2}x_{3} + a_{13}x_{1}x_{3}$$
 (7)

where a_{12} , a_{23} , and a_{13} are the interaction parameters between components. The values of interaction parameters were determined from the experimental viscosities of pure components and three corresponding mixtures.

Iulian et al. (1993) extended eq 4 for correlation and prediction of kinematic viscosity of the ternary liquid mixtures, as is given below:

$$\begin{split} \ln\nu_{\rm t} &= x_1 \ln(\nu_1 M_1) + x_2 \ln(\nu_2 M_2) + \\ &\quad x_3 \ln(\nu_3 M_3) - \ln(x_1 M_1 + x_2 M_2 + x_3 M_3) + \\ &\quad x_1 x_2 [A_0 + A_1 (x_1 - x_2) + A_2 (x_1 - x_2)^2 + A_3 (x_1 - x_2)^3] + \\ &\quad x_2 x_3 [B_0 + B_1 (x_2 - x_3) + B_2 (x_2 - x_3)^2 + B_3 (x_2 - x_3)^3] + \\ &\quad x_3 x_1 [C_0 + C_1 (x_3 - x_1) + C_2 (x_3 - x_1)^2 + C_3 (x_3 - x_1)^3] + \\ &\quad x_1 x_2 x_3 \gamma (T) \end{split}$$

where A_0 , A_1 , A_2 , A_3 , B_0 , B_1 , B_2 , B_3 , C_0 , C_1 , C_2 , C_3 , and $\gamma(T)$ are the model parameters. These model parameters have been determined from respective experimental data for three corresponding binary liquid mixtures, (Iulian et al., 1993).

Results and Discussion

The experimental kinematic viscosities of three binary liquid mixtures, namely chloroform(1) + 2-propanol(2), 2-propanol(1) + 2-butanol(2), and chloroform(1) + 2-butanol(2) at several temperatures are presented in Table 2. The experimental kinematic viscosities for the three binary liquid mixtures were fitted by correlations suggested by McAllister (1960), eq 1, Heric-Brewer (1976), eq 2, Krishnan and Laddha (1968), eq 3, Iulian et al. (1993), eq 4, and the new equation which is presented in this paper, eq 5. The model parameters for all equations investigated were calculated from the experimental kinematic viscosity data by Marquard's optimization procedure (Marquardt, 1963). The fit was assessed in terms of the criterion:

$$\delta = \frac{100}{N} \sum_{n=1}^{N} \frac{|(\nu_{b,n} - \nu_{b,n}^{\text{calc}})|}{\nu_{b,n}}$$
(9)

where δ is the average percentage deviation, N is the number of experimental points, and $\nu_b^{\rm calc}$ is the calculated value of kinematic viscosity of the binary mixtures.

Table 2. Experimental Kinematic Viscosities v_b of Binary Liquid System at 20, 25, 30, and 35 °C

		$10^2 \ \nu_b / (\text{cm}^2 \ \text{s}^{-1})$			
system	x_1	20 °C	25 °C	30 °C	35 °C
chloroform + 2-propanol	0.0	2.915	2.578	2.312	2.023
	0.0530	2.256	1.976	1.720	1.537
	0.1118	1.658	1.487	1.304	1.182
	0.1774	1.281	1.158	1.049	0.951
	0.2512	1.066	0.896	0.853	0.768
	0.3348	0.805	0.750	0.683	0.627
	0.4302	0.659	0.628	0.567	0.531
	0.5401	0.569	0.525	0.491	0.477
	0.6681	0.501	0.460	0.447	0.419
	0.8192	0.457	0.416	0.399	0.389
	1.0	0.390	0.377	0.368	0.348
2-propanol $+$ 2 -butanol	0.0	4.930	4.387	3.728	3.134
	0.1205	4.803	4.138	3.635	3.074
	0.2357	4.605	3.872	3.411	2.962
	0.3458	4.460	3.793	3.233	2.803
	0.4513	4.064	3.484	3.080	2.678
	0.5523	3.866	3.292	2.910	2.562
	0.6492	3.550	2.993	2.732	2.371
	0.7421	3.487	2.957	2.609	2.274
	0.8315	3.336	2.854	2.488	2.177
	0.9174	3.158	2.732	2.408	2.104
	1.0	2.915	2.578	2.312	2.023
chloroform + 2-butanol	0.0	4.930	4.387	3.728	3.134
	0.0645	4.229	3.688	3.176	2.744
	0.1344	3.358	2.922	2.566	2.158
	0.2101	2.678	2.348	2.059	1.793
	0.2927	2.065	1.762	1.609	1.411
	0.3830	1.635	1.425	1.306	1.174
	0.4822	1.130	0.999	0.923	0.849
	0.5916	0.833	0.800	0.741	0.695
	0.7129	0.640	0.596	0.561	0.525
	0.8482	0.504	0.469	0.446	0.429
	1.0	0.390	0.377	0.368	0.348

Table 3. Comparison of Different Correlations for the Prediction of Kinematic Viscosity for Binary Liquid Mixtures

			$100~(u_{ m b}- u_{ m b}^{ m calc})\!/ u_{ m b}$			
mixture	t/ °C	McAllister/	Heric and Brewer/ eq 2	Krishnan and Laddha/ eq 3	Iulian et al./ eq 4	new equa- tion/ eq 5
chloro-	20	1.4	1.4	1.4	1.4	1.4
form(1) +	25	2.4	1.1	1.1	1.2	1.8
2-pro-	30	2.3	1.6	1.1	0.9	0.3
panol(2)	35	1.9	1.1	0.9	0.7	0.7
2-pro-	20	1.9	1.1	1.0	0.9	0.9
panol(1) +	25	1.4	1.3	1.3	1.0	1.0
2-bu-	30	0.6	0.5	0.5	0.5	0.1
tanol(2)	35	0.6	0.4	0.4	0.3	0.2
chlorof-	20	1.8	1.9	1.8	1.8	1.4
orm(1) +	25	1.7	1.7	1.7	1.7	1.6
2-bu-	30	1.4	1.7	1.5	1.4	1.3
tanol(2)	35	2.1	2.4	2.2	2.1	1.9

The results of comparison of the calculated and experimental kinematic viscosity data for the three binary liquid mixtures investigated are given in Table 3. The δ values for all five correlations were the lowest for 2-propanol(1) + 2-butanol(2).

The best fit for all of the binary liquid mixtures was obtained when using the new correlation, eq 5, whereas the Iulian et al. (1993), Krishnan and Laddha (1968), and Heric-Brewer (1967) correlations resulted in larger deviations. McAllister's (1960) equation gave the poorest agreement between experimental and calculated kinematic viscosity data for the majority of binary systems.

The agreement of the experimental kinematic viscosities with those obtained by using the new correlation, eq 5, is shown graphically in Figure 1. The experimental kine-

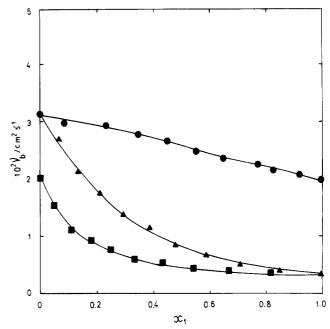


Figure 1. Comparison of experimental viscosity (points) and those calculated by eq 5 (full lines) at 35 °C. Binary liquid systems: ●, chloroform(1) + 2-propanol(2); ♠, 2-propanol(1) + 2-butanol(2); and ■, chloroform(1) + 2-butanol(3).

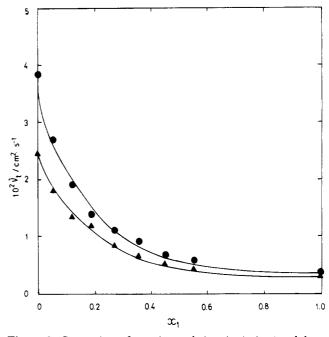


Figure 2. Comparison of experimental viscosity (points) and those calculated by the Al-Besharah et al. (1987) correlation (full lines) for chloroform(1) + 2-propanol (2) + 2-butanol(3) at (\bullet) 20 and (\triangle) 35 °C.

matic viscosity data for chloroform(1) + 2-propanol(2) + 2-butanol(3) at several temperatures are given in Table 4.

The experimental kinematic viscosities for the ternary liquid system are fitted by the empirical correlations suggested by Vijayaraghavan et al. (1976), eq 6, Al-Besharah et al. (1987), eq 7, and Iulian et al. (1993), eq 8. The binary constants in eq 6 were calculated from experimental kinematic viscosity data for the three corresponding binary systems by the Krishnan-Laddha (1968) correlation, eq 3. On the other hand, the binary constants in eq 7 were calculated from experimental kinematic viscosity data for those systems using the Iulian et al. (1993) correlation, eq 4. The results of comparison of experimen-

Table 4. Experimental Kinematic Viscosities v_t of the Ternary Liquid System Chloroform(1) + 2-Propanol(2) +2-Butanol(3) at 20, 25, 30, and 35 °C

		$10^2 \ v_t / (cm^2 \ s^{-1})$			
x_1	x_2	20 °C	25 °C	30 °C	35 °C
0.0	0.5523	3.843	3.312	2.891	2.476
0.0575	0.5717	2.677	2.372	2.055	1.793
0.1193	0.5925	1.927	1.744	1.493	1.341
0.1901	0.5036	1.469	1.328	1.255	1.182
0.1948	0.3870	1.464	1.318	1.189	1.098
0.2704	0.4029	1.129	1.122	0.931	0.844
0.3622	0.2878	0.863	0.857	0.737	0.685
0.3526	0.4203	0.831	0.824	0.710	0.656
0.4547	0.3012	0.685	0.653	0.597	0.564
0.5562	0.3158	0.564	0.523	0.511	0.472
0.8192	0.1808	0.457	0.416	0.399	0.389

Table 5. Comparison of Different Correlations for the Prediction of Kinematic Viscosity for Chloroform(1) + 2-Propanol (2) + 2-Butanol(3)

$100~(u_{ m t}- u_{ m t}^{ m calc})\!/ u_{ m t}$						
t/°C	Vijayaraghavan et al./ eq 6	Al-Besharah et al./ eq 7	Iulian et al./ eq 8			
20	18.2	3.0	3.5			
25	11.2	2.9	4.7			
30	14.3	3.4	3.1			
35	13.4	3.5	3.3			

tal and calculated kinematic viscosities for system chloroform(1) + 2-propanol(2) + 2-butanol(3) are presented in Table 5.

The best fit for the ternary mixture was obtained using the relation by Al-Besharah et al. (1987), whereas the Iulian et al. (1993) and Vijayaraghavan et al. (1976) correlations resulted in larger deviations. Figure 2 represents the agreement of the experimental kinematic viscosities with those obtained by using the Al-Besharah et al. (1987) correlation at 20 and 35 °C.

Conclusions

When comparing the experimental and calculated binary kinematic viscosity data, the best agreement for all systems investigated was obtained by using the empirical correlation proposed in this paper, eq 5. For all five correlations applied, the best agreement between the experimental and calculated kinematic viscosity data was observed for the 2-propanol + 2-butanol binary liquid system. Comparison of the correlation for prediction of kinematic viscosity data of a ternary liquid system revealed that the Al-Besharah et al. (1987) equation gave the best results.

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Received for review January 2, 1995. Accepted April 4, 1995.8

Abstract published in Advance ACS Abstracts, June 1, 1995.

JE950002C