

*Dedicated to the memory of
Professor Mircea D. Banciu (1941–2005)*

PROPERTIES OF THE BINARY AND TERNARY MIXTURES CONTAINING WATER, 1,4 - DIOXANE AND ETHYLENE GLYCOL. VISCOSITY CORRELATIONS

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This paper reports the viscosities measurements for the binary systems water + 1,4-dioxane, water + ethylene glycol and 1,4-dioxane + ethylene glycol and the corresponding ternary system at 293.15K. The experimental viscosities of binary and ternary mixtures were correlated with the equations of Grunberg-Nissan, Katti-Chaudry, Hind, Soliman and McAllister. The deviations in viscosity of the binary and ternary systems were fitted to Redlich-Kister equation.

INTRODUCTION

The solution for many engineering problems involving heat transfer, mass transfer and fluid flow requires quantitative information on the viscosities of pure and mixed liquids. In addition, these properties are useful to understand the behaviour of the liquid mixtures. In these circumstances, the experimental measurements, even if these are expensive and time-consuming, remain an important way to obtain realistic information concerning the dependence of the viscosity on temperature and composition in multicomponent systems.

The present work reports dynamic viscosities for the binary systems of water + 1,4-dioxane, water + ethylene glycol (MEG) and 1,4-dioxane + ethylene glycol and for the ternary system water + 1,4-dioxane + ethylene glycol. The experimental measurements were carried out at 293.15 K, covering the whole composition range. After our knowledge the ternary system has not been studied and the binary system 1,4-dioxane + ethylene glycol has been studied only by one author, but not at 293.15K; ¹ other two systems have been reported quite frequently in literature.²⁻⁴

The dynamic and kinematics viscosity data of the binary systems were used to test the applicability of some correlative equations. Approximately the same correlative equations were extended to the ternary mixtures. The viscosity deviations ($\Delta\eta$) for the binary and ternary systems were correlated by the Redlich-Kister's equation.

EXPERIMENTAL

Materials

The chemicals used in this study were purified by distillation. The analytical-reagent-grade 1,4-dioxane from Merck was distilled at 374.35 K. The water was doubly distilled. The ethylene glycol used was Merck p.a. without further purification. The purity of the compounds was checked not only by comparing the measured densities and viscosities with those reported in the

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literature but also by gas chromatography. The purity found by gas chromatography was better than 99.5 mass %. The properties of the purified solvents, measured at 293.15 K along with literature values at the same temperature are gathered in Tab. 1.

Table 1
Comparison of measured densities, ρ , viscosities, η , with literature values

Component	T, K	ρ , g cm ⁻³		η , mPa s	
		experimental	literature	experimental	literature
Water	293.15	0.9982	0.99822 ² 0.99821 ⁵	1.0050	1.0021 ² 1.0020 ⁵
MEG	293.15	1.1140	1.11323 ² 1.11350 ⁶ 1.1137 ⁷	21.0	20.864 ² 21.0 ⁶ 20.833 ⁷
1,4-Dioxane	293.15	1.0339	1.0334 ⁸	1.3125	
	298.15			1.1902	1.181 ⁹

Apparatus and procedure

Kinematics viscosity measurements of pure solvents and their binary and ternary mixtures were carried out using an Ubbelohde viscosimeter. The viscosimeter was calibrated with double distilled water and pure solvents. The time of fall always exceeded 60 seconds; the accuracy of the flow time was ± 0.1 seconds. Consequently the errors of the measured values of the viscosity may be estimated as less than 1%. At least five time flow measurements were performed for each composition and temperature and the results were averaged. A thermostatically controlled bath was used to keep the temperature within ± 0.05 K.

The mixtures were prepared volumetrically and the accuracy of mole fraction is estimated at 0.002. All mixtures were completely miscible over the whole composition range.

RESULTS AND DISCUSSION

Several relations have been proposed to evaluate the viscosity of liquid binary mixtures by using some semi empirical models with one or more empirical adjustable parameters. The same equations were expanded to the ternary systems.

The equations of Grunberg-Nissan,¹⁰ Katti-Chaudry¹¹ were initially developed only for the binary systems and have one adjustable parameter. Canosa¹² has proposed in 1998 an extension of these equations to the ternary mixtures by introducing of a ternary adjustable parameter. In this case, the equations are:

- Grunberg and Nissan:

$$\ln \eta = \sum_i^n X_i \ln \eta_i + \sum_i^n \sum_{j>i}^n X_i X_j A_{ij} + \sum_i^n \sum_{j>i}^n \sum_{k>j}^n X_i X_j X_k A_{ijk} \quad (1)$$

where η is the dynamic viscosity of the mixture, η_i is the viscosity of pure component i , X_i are the mole fractions, A_{ij} and A_{ijk} are the interaction parameters;

- Katti and Chaudry:

$$\ln(\eta V) = \sum_i^n X_i \ln(\eta_i V_i) + \sum_i^n \sum_{j>i}^n X_i X_j A_{ij} + \sum_i^n \sum_{j>i}^n \sum_{k>j}^n X_i X_j X_k A_{ijk} \quad (2)$$

where V_i is the molar volume of pure component i and V is the molar volume of mixture.

Hind et al.¹³ suggested the following equation:

$$\eta = \sum_i^n X_i^2 \eta_i + \sum_i^n \sum_{j>i}^n X_i X_j A_{ij} + \sum_i^n \sum_{j>i}^n \sum_{k>j}^n X_i X_j X_k A_{ijk} \quad (3)$$

McAllister's two-parameter equation,¹⁴ based on Eyring's theory of absolute reaction rates, takes into account interactions both of like and unlike molecules by a two-dimensional three-body interaction. This equation has expanded to ternary mixtures by Kalidas and Laddha¹⁵:

$$\begin{aligned} \ln \nu &= \sum_{i=1}^n X_i^3 \ln(\nu_i M_i) - \ln \sum_{i=1}^n X_i M_i + 3 \sum_{i=1}^n \sum_{\substack{j=1 \\ j \neq i}}^n X_i^2 X_j \ln(A_{ij} M_{ij}) \\ &+ 6 \sum_{i=1}^n \sum_{\substack{j>i \\ k>j}}^n X_i X_j X_k \ln(A_{ijk} M_{ijk}) \\ M_{ij} &= \frac{2M_i + M_j}{3} \quad M_{ijk} = \frac{M_i + M_j + M_k}{3} \end{aligned} \quad (4)$$

where ν is the kinematics viscosity of the mixture, ν_i is the viscosity of pure component i , ν_{ij} and ν_{ijk} are binary and ternary interaction parameters, respectively, M_i is the molecular mass.

The data were also correlated with a modified form of the McAllister equation proposed by Soliman.¹⁶ The general form of the equation is as follows:

$$\begin{aligned} \ln \nu &= \sum_{i=1}^n X_i^3 \ln \nu_i + 3 \sum_{i=1}^n \sum_{\substack{j=1 \\ i \neq j}}^n X_i^2 X_j \ln \nu_{ij} + \sum_{i=1}^n \sum_{\substack{j=1 \\ j \neq i}}^n \frac{(X_i + X_j)^3 A_{ij} X_i X_j}{\left(\frac{M_i}{M_j}\right)^2 X_i + X_j} \\ &+ 6 \sum_{i=1}^n \sum_{\substack{j>i \\ k>j}}^n X_i X_j X_k \ln A_{ijk} \end{aligned} \quad (5)$$

The viscosity deviations were computed through the following equation:

$$\Delta \eta = \eta - \sum_{i=1}^{N_C} X_i \eta_i \quad (6)$$

where η is the dynamic viscosity of the binary or ternary mixture, η_i are the viscosities of pure components, N_C represents the number of components in the mixture. The viscosity deviation was fitted to Redlich-Kister's equation¹⁷ for the binary systems (eq. (7)) and for the ternary system (eq. (8)).

$$\Delta \eta = X_i X_j \sum_{k=0}^p A_k (X_j - X_i)^k \quad (7)$$

$$\begin{aligned} \Delta \eta &= \Delta \eta_{12} + \Delta \eta_{13} + \Delta \eta_{23} + X_1 X_2 X_3 (B_0 + B_{12} (X_2 - X_1) + B_{13} (X_3 - X_1) + \\ &B_{23} (X_3 - X_2) + C_{12} (X_2 - X_1)^2 + C_{13} (X_3 - X_1)^2 + C_{23} (X_3 - X_2)^2 + \dots) \end{aligned} \quad (8)$$

A_i , B_0 , B_{ij} , and C_{ij} are the adjustable parameters, p is the degree of polynomial expansion, $\Delta \eta_{ij}$ are the viscosity deviations values of the Redlich-Kister equation for the binary systems which are given by eq (7). For obtain a numerical comparison of correlating capability of eqs (1-5, 7, and 8), the standard deviation, σ , was calculated with the equation:

$$\sigma = \left[\frac{\sum (Y_{\text{exp}} - Y_{\text{calc}})^2}{N_{\text{exp}} - N_{\text{par}}} \right]^{0.5} \quad (9)$$

where N_{exp} is the number of experimental data, N_{par} is the number of parameters, and Y is the dynamic viscosity, kinematics viscosity or viscosity deviation, respectively.

Binary systems

The experimental viscosities and densities for the binary systems at 293.15K are given in Tab. 2. Equations (1) to (5) have been used to correlate the viscosity of the binary systems. The values of the

adjustable parameters and the standard deviation are reported in Tab. 3. For all three systems the Soliman model gives the best result, McAllister equation gives approximately the same results. The correlating ability significantly improves as the number of the adjustable parameters increases. The viscosity deviations for the all binary mixtures were calculated. The coefficients A_i and the standard deviations for excess property $\Delta\eta$ are given in Tab. 4. Viscosity deviations versus composition for the binary systems at 293.15K are presented in Fig. 1.

Table 2
Experimental densities and viscosities for the binary systems at 293.15 K

water(1)+1,4-dioxane(2)			water(1)+MEG(2)			MEG(1)+1,4-dioxane(2)		
X_1	ρ^{18} , g cm ⁻³	η^{19} , mPa s	X_1	ρ^{19} , g cm ⁻³	η , mPa s	X_1	ρ^{19} , g cm ⁻³	η , mPa s
0.0000	1.0339	1.3125	0.0000	1.1140	21.0000	0.0000	1.0339	1.3125
0.1007	1.0354	1.3481	0.1005	1.1133	18.3555	0.0997	1.0411	1.5131
0.1995	1.0366	1.4469	0.2006	1.1100	15.8979	0.2021	1.0476	2.0536
0.3422	1.0385	1.6330	0.2452	1.1087	14.6960	0.2983	1.0550	2.2856
0.4256	1.0396	1.7645	0.3963	1.1025	11.1648	0.4096	1.0626	2.9018
0.5378	1.0412	1.9793	0.5010	1.0963	8.8477	0.5023	1.0697	3.9729
0.6640	1.0424	2.2300	0.5984	1.0886	6.8610	0.6021	1.0780	5.1952
0.7530	1.0415	2.2948	0.7039	1.0770	4.9346	0.7009	1.0857	7.3831
0.8197	1.0386	2.2023	0.8072	1.0601	3.3033	0.8054	1.0756	10.8259
0.8710	1.0338	2.0130	0.8992	1.0372	2.0711	0.9002	1.1044	14.8045
0.9130	1.0270	1.7655	0.9500	1.0192	1.4414	0.9495	1.1089	17.7227
0.9470	1.0188	1.5044	1.0000	0.9982	1.0050	1.0000	1.1140	21.0000
0.9760	1.0091	1.2440						
1.0000	0.9982	1.0050						

Table 3
Adjustable parameters and standard deviation of the equations (1) to (5) for the binary systems at 293.15 K

Models Systems	Grunberg-Nissan		Hind		Katti-Chaudry		Soliman			McAllister			
	σ	A_{12}	σ	A_{12}	σ	A_{12}	σ	v_{12}	v_{21}	A_{12}	σ	v_{12}	v_{21}
Water+ 1,4-dioxane	0.441	2.488	0.388	3.140	0.497	3.523	0.046	2.872	0.921	0.500	0.147	9.908	0.713
Water+ MEG	0.647	2.306	0.177	6.717	0.734	2.811	0.041	5.684	10.706	0.398	0.144	10.069	11.917
MEG+ 1,4-dioxane	0.229	-0.975	1.202	-3.900	0.231	-0.896	0.106	1.974	1.115	1.785	0.113	6.246	1.757

Table 4
Coefficients A_i and standard deviation for representation of excess property for the binary systems at 293.15 K

Systems	σ	A_0	A_1	A_2	A_3	A_4	A_5
Water+1,4-dioxane	0.0077	2.747	1.670	-2.099	2.329	-3.048	-1.738
Water+MEG	0.0243	-8.542	-2.439				
MEG+1,4-dioxane	$3.06 \cdot 10^{-5}$	-22.185	-2.382	-5.762	-0.892	2.147	

Variation of $\Delta\eta$ versus X_1 at 293.15 K displayed in Fig. 1, shows a large negative value of $\Delta\eta$ for mixture of MEG + 1,4-dioxane, a relatively small negative deviation for water + MEG system, whereas for water + 1,4-dioxane systems the deviation is relatively small positive. This complex behaviour of the different systems is the result of the structure of the pure compound and interactions between them upon mixing.

Water is an interesting polar protic solvent ($\mu = 1.85$ D) with small size, which is able to support extensive hydrogen-bonding networks.⁴ The ethylene glycol itself as well as glycol with water can also associate by hydrogen bonding; it has high dipole moment ($\mu = 2.31$ D). Dioxane ($\mu = 0.4$ D) is a nonpolar aprotic solvent, but is able to associate by hydrogen bonding, due to its etheric oxygens.

Consequently, the positive $\Delta\eta$ values indicate strong specific interactions between water and 1,4-dioxane molecules, according with the literature.⁴ For the others two systems, the negative values of $\Delta\eta$ may be attributed to the existence of dispersion forces between unlike molecules and the difference in size and shape of unlike molecules. The significantly large negative values of $\Delta\eta$ indicate much weaker interaction between MEG and 1,4-dioxane than the MEG – water system, which probably presents hydrogen bonding. The minimum value of $\Delta\eta$ observed in the MEG – water system is in agreement with the published works.^{2,7}

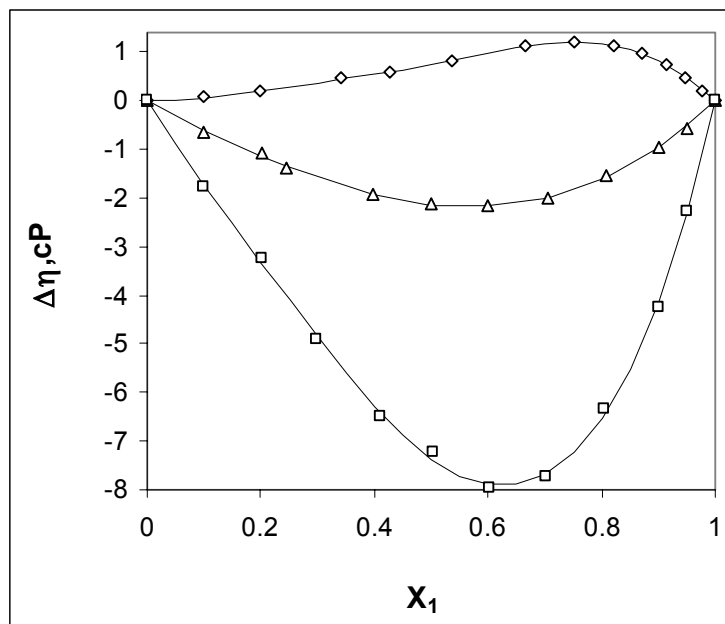


Fig. 1 – Viscosity deviations of the binary systems at 293.15 K for: \diamond water (1)+1,4-dioxane (2), Δ water (1)+MEG (2), \square MEG (1)+1,4-dioxane (2), (—) Redlich-Kister's correlation.

Ternary systems

The experimental viscosities and densities for the ternary system water + 1,4-dioxane + MEG at 293.15 K are listed in Tab. 5. The equations (1, 4 and 5), expanded for the ternary system, were used in the correlation of experimental viscosity data and the results are presented in Tab 6. The comparison of these equations shows that, generally, a rise of number of parameters leads to a smaller standard deviation. Thus, the Soliman model gives the best results. The McAllister model poorly describes the ternary mixture probably because of the differences in molar volumes of the components.

The viscosity deviations data obtained with eq. (6) were fitted with ternary Redlich-Kister polynomials given by eq. (8) and the results are gathered in Tab. 7.

Table 5

Experimental viscosities and densities for the ternary system water (1) + 1,4-dioxane (2) + MEG (3) at 293.15 K

X_1	X_2	$\rho^{19}, \text{g cm}^{-3}$	$\eta, \text{mPa s}$	X_1	X_2	$\rho^{19}, \text{g cm}^{-3}$	$\eta, \text{mPa s}$
0.1465	0.4273	1.0688	4.0634	0.8500	0.1048	1.041	2.3364
0.3031	0.3482	1.0689	4.2160	0.1474	0.2559	1.0832	7.1984
0.4976	0.2507	1.0668	4.2702	0.2984	0.2104	1.083	6.7614
0.6987	0.1507	1.0605	3.6025	0.5000	0.1501	1.079	5.9242
0.8492	0.0754	1.0443	2.4731	0.6999	0.0900	1.0671	4.1825
0.1504	0.7191	1.0443	1.7983	0.8498	0.0451	1.0466	2.5589
0.2963	0.5923	1.046	2.0460	0.1497	0.1303	1.0973	11.1692
0.4988	0.4214	1.0481	2.3771	0.3006	0.1047	1.095	9.8403
0.7005	0.2494	1.0486	2.6534	0.4995	0.0752	1.0874	7.2829
0.8504	0.1250	1.0392	2.2321	0.6990	0.0453	1.0723	4.6117
0.1502	0.5949	1.0552	2.4885	0.8493	0.0199	1.0491	2.6703
0.3007	0.4901	1.055	2.6970	0.0534	0.8976	1.0363	1.5001
0.5021	0.3491	1.0554	3.0273	0.0551	0.0491	1.1086	16.6011
0.7012	0.2096	1.0528	3.0068				

Table 6

Adjustable parameters and standard deviation of the equations (1), (4) and (5) for the ternary system at 293.15 K

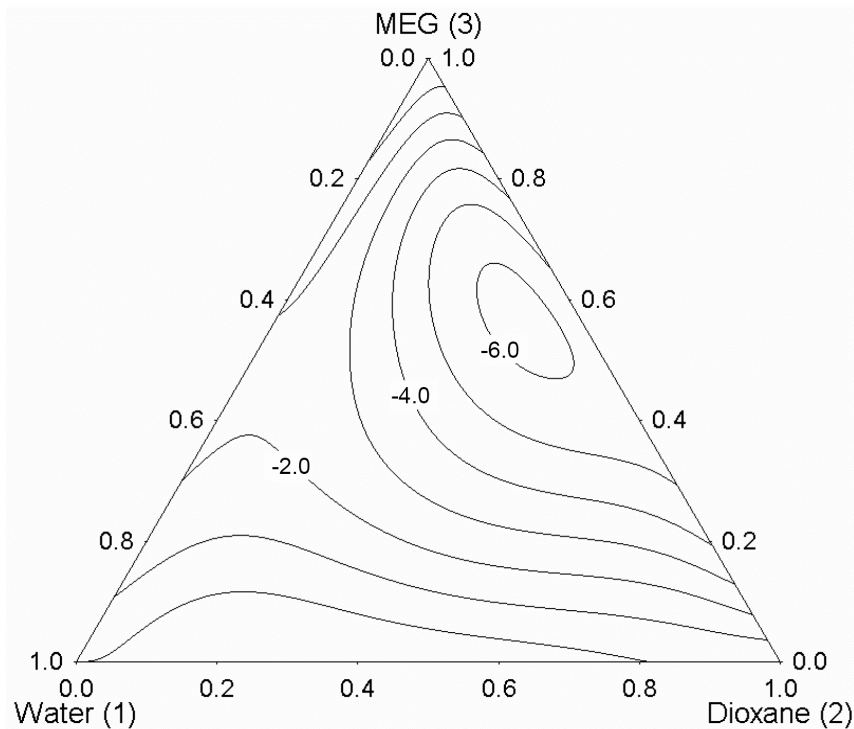
Models	σ	A_{12}	A_{13}	A_{23}	A_{123}	v_{12}	v_{21}	v_{13}	v_{31}	v_{23}	v_{32}	v_{123}
Grunberg-Nissan	0.042	2.294	3.166	-2.490								
	0.034	3.526	3.465	-1.916	-5.927							
Soliman	0.00013	1.150	-0.444	8.799		0.961		13.131		0.493		4.380
	0.00002	0.450	0.237	2.532		3.356	0.718	6.243	12.792	1.506	2.569	5.843
McAllister	0.141					11.766	0.567	11.608	12.625	3.021	6.865	2.499

Table 7

Coefficients A_i and standard deviation for representation of excess property for the ternary system at 293.15 K

Systems	σ	A_0	A_1	A_2	A_3	A_4	A_5	A_6	A_7	A_8	A_9
Water +1,4- dioxane +MEG	0.169	-12.933	29.64 2	48.64 8	2.726	82.77 6	-127.168	66.58 1	-93.414	313.583	5.093

The isolines at 293.15 K at constant values of $\Delta\eta$ calculated with Redlich-Kister equation have been drawn in Fig. 2. The ternary viscosity deviation is negative over the whole composition range presenting a minimum of about - 6 mPa s.

Fig. 2 – Isolines at constant $\Delta\eta$ for the ternary system water (1) + 1,4-dioxane (2) + MEG (3) at 293.15K.

CONCLUSION

Viscosities for the binary systems water + 1,4-dioxane, water + ethylene glycol and 1,4-dioxane + ethylene glycol and for the corresponding ternary system have been measured at 293.15K. Viscosities of binary and ternary systems were calculated by means of the equations of Grunberg-Nissan, Katti- Chaudry, Hind, McAllister and Soliman and the viscosity deviations of the binary and ternary systems were calculated and fitted to Redlich-Kister's equations. The viscosity deviation for the binary water + 1,4-dioxane system is

positive over the entire composition range, which indicate strong specific interactions between molecules. The water + MEG and 1,4-dioxane + MEG mixtures show negative values for $\Delta\eta$; significant larger values in 1,4-dioxane + MEG system indicates much weaker interaction between MEG and 1,4-dioxane than in the MEG – water system. The viscosity deviations of the ternary system water + 1,4-dioxane + MEG are negative over the whole composition range, presenting a minimum.

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