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VISCOSITY OF WATER, 1,4-DIOXANE AND DIMETHYL SULFOXIDE BINARY AND TERNARY SYSTEMS AT TEMPERATURES FROM 293.15 K TO 313.15 K

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The viscosity of the binary water+1,4-dioxane, water+dimethyl sulfoxide and 1,4-dioxane+ dimethyl sulfoxide systems and the corresponding ternary system was measured as function of composition and temperature. The experimental measurements were made at 293.15 K, 303.15 K and 313.15 K for the binary mixtures and at 303.15 K and 313.15 K, for the ternary system. The viscosity data were used to test the applicability of some correlative and predictive equations in literature: Kendall and Monroe, Grunberg-Nissan, Katty-Chaudhri, Tamura-Kurata, McAllister and Soliman. From experimental data the viscosity deviations ($\Delta\eta$) and excess Gibbs energy of activation of viscous flow (G^{*E}) were calculated and correlated by the Redlich-Kister's equations. The results are discussed in terms of the interactions between components.

INTRODUCTION

Many chemical engineering applications require knowledge of thermodynamic and transport properties of the multicomponent systems. In addition, these properties are useful to understand the behavior of the liquid mixtures. Generally, the correlation and prediction of the properties for the multicomponent systems from their constituent binary mixtures is widely used in the study of the liquid state. Estimation of the viscosity could be made by predictive and/or correlative equations. There are developed many empirical and semi-empirical equations to describe the binary mixture viscosity.[1]

Correlation of the viscosity with these equations requires several adjusting parameters. In the last years, the equations for the binary systems have been extended to the ternary mixtures by introducing a ternary adjustable parameter.[2] Many efforts are made to develop the predictive equations of the viscosity for the ternary and multicomponent systems. Some of them are based on a molecular approach,[3,4] while others are based on a group contribution concept.[5,6] However, a general theory for predicting the viscosity of the ternary systems from those of the pure components and constituent binary systems is not yet available.[7,8] 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 composition in systems with many components.

This paper is an extension of our studies on physico-chemical properties of the solvent mixtures. In earlier papers [9-13] we have reported the vapour-liquid equilibrium (VLE) and density data for the binary and ternary systems containing water, 1,4-dioxane and dimethyl sulfoxide (DMSO). For the same systems, in this work we present the viscosity data. Most of the experimental viscosities available in the literature for these systems were reported at few temperatures for binary aqueous systems,[14,15] the ternary water+1,4-dioxane+DMSO system has been partially presented in our previous published work.[16]

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The present work reports dynamic viscosities (η) for the binary water+1,4-dioxane , water+dimethyl sulfoxide (DMSO) and 1,4-dioxane+dimethyl sulfoxide systems and for the ternary water+1,4-dioxane+dimethyl sulfoxide system. The experimental measurements were carried out at 293.15 K, 303.15 and 313.15 K, for the binary systems, and at 303.15 and 313.15, for the ternary mixtures, covering the whole composition range. The kinematic and dynamic viscosity data of the binary and ternary systems were used to test the applicability of some correlative and predictive equations in literature. From the experimental values of viscosity, the viscosity deviations ($\Delta\eta$) and excess Gibbs energies of activation of viscous flow (G^{*E}) for the binary and ternary systems were calculated and correlated by the Redlich-Kister's equation. The variation of these thermodynamic properties with composition and temperature of the mixtures were found to be useful in understanding the nature the interactions between the component molecules.

EXPERIMENTAL

Materials. The chemicals used in this study were purified by distillation. DMSO was distilled under vacuum of 0.8-0.9 kPa at 338.65 K. The analytical reagent grade 1,4-dioxane from Merck was distilled at 374.35 K. The water was doubly distilled. The purity of the compounds was checked not only by comparing the measured densities and viscosities with those reported in the literature but also by gas chromatography. The purity found by gas chromatography was better than 99.8 mass %. The properties of the purified solvents, measured at 298.15, 303.15 and 313.15 along with literature values at the same temperatures are gathered in Table 1.

Table 1

Comparison of experimental values of densities and viscosities of pure liquids with corresponding literature values at different temperatures

Component	T, K	ρ, g cm^{-3}		η, mPa s	
		experimental	literature	experimental	literature
Water	293.15	0.9982	0.9982[17,18], 0.99821[19] 0.98820[20]	1.0050	0.999[17], 1.0032[18] 1.00219[21], 1.0021[20]
	303.15	0.9956	0.9957[18,22], 0.99607[23] 0.99565[24], 0.99564[20]	0.8007	0.797[22], 0.8005[18] 0.7931[23], 0.8075[20]
	313.15	0.9922	0.9922[18], 0.99283[23], 0.99221[24], 0.99222[20]	0.6560	0.6568[18], 0.6382[23] 0.65277[21], 0.6660[20]
1,4-Dioxane	293.15	1.0339	1.0334[25], 1.0317[26]	1.3125	
	303.15	1.0225	1.0222[27], 1.02244[28], 1.0225[29], 1.02221[30]	1.1127	1.0937[27], 1.1000[28] 1.086[29], 1.101[30]
	313.15	1.0121	1.0110[30]	0.9603	0.9425[30]
DMSO	293.15	1.1012	1.10041[17], 1.10040[31] 1.10145[32]	2.2255	2.194[17], 2.216[31]
	303.15	1.0901	1.0907[29], 1.09054[33] 1.09038[23]	1.8180	1.662[29], 1.8034[33] 1.8102[23]
	313.15	1.0804	1.08064[23], 1.0804[34] 1.0806[35]	1.5553	1.5152[23]

Apparatus and procedure. Kinematic viscosity measurements of pure solvents and their binary and ternary mixtures were carried out using an Ubbelohde viscometer for which the accuracy of the flow time was ±0.1 seconds and the corresponding uncertainty in the kinematic viscosity was ± 0.001 10^{-6} m^2 s^{-1}. The time of fall always exceeded 60 seconds. The viscometer was calibrated with double distilled water and pure solvents. 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.

All mixtures were prepared by weighing the appropriate volumes of liquids in airtight stoppered glass bottle. The reproductibility in mole fraction was within ±0.0002. The weightings were done on a HR-120 (A&D Japan) balance with a precision of ±0.1·10^{-3} g. All mixtures were completely miscible over the whole composition range.

RESULTS AND DISCUSSION

Viscosities and their correlation

The experimental data of viscosities for binary and ternary systems containing water, 1,4-dioxane and dimethyl sulfoxide (DMSO) was utilised to test various correlative and predictive viscosity methods in literature. The feasibility of several specific equations to correlate composition-viscosity data for binary and ternary systems was tested. For ternary system the equations incorporate parameters from the binary systems and one or more ternary parameters.

Thus, the equation proposed by Kendall and Monroe[36] is a predictive relation that takes into account only the viscosity of pure components:

$$\eta = \left(\sum_{i=1}^{n} X_i \eta_i^{1/3} \right)^3 \tag{1}$$

The correlative equations of Grunberg-Nissan[37]and Katti- Chaudhri[38] were initially developed only for the binary systems, having one adjustable parameter. Canosa[2] has proposed in 1998 an extension of these equations to the ternary mixtures by introducing of a ternary adjustable parameter. The general form of these equations is done by relations (2) and (3), respectively:

$$\ln \eta = \sum_{i}^{n} X_i \ln \eta_i + \sum_{i}^{n} \sum_{j>i}^{n} X_i X_j A_{ij} + \sum_{i}^{n} \sum_{j>i}^{n} \sum_{k>j}^{n} X_i X_j X_k A_{ijk} \tag{2}$$

$$\ln(\eta V) = \sum_{i}^{n} X_i \ln(\eta_i V_i) + \sum_{i}^{n} \sum_{j>i}^{n} X_i X_j A_{ij} + \sum_{i}^{n} \sum_{j>i}^{n} \sum_{k>j}^{n} X_i X_j X_k A_{ijk} \tag{3}$$

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; V_i is molar volume of pure component i.

In this paper we have taken in consideration the Canosa's contribution and applied it to the Tamura and Kurata equation, [39] also initially developed only for the binary systems. The new mathematical relation of the Tamura and Kurata equation for n-component mixtures is:

$$\eta = \sum_{i}^{n} X_i \phi_i \eta_i + 2 \sum_{i}^{n} \sum_{j>i}^{n} (X_i X_j \phi_i \phi_j)^{0.5} A_{ij} + 2 \sum_{i}^{n} \sum_{j>i}^{n} \sum_{k>j}^{n} (X_i X_j X_k \phi_i \phi_j \phi_k)^{0.5} A_{ijk} \tag{4}$$

where ϕ_i is the volume fraction.

McAllister's two-parameters equation,[40] 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 extended to ternary mixtures by Kalidas and Laddha.[41]

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

ν is the kinematic 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 pure components molecular mass, M_{av} is the molecular mass of mixture.

The McAllister equation of the four-body interactions[40] is more complex and may be used more favorable for mixtures with strong interactions. This equation has three adjustable parameters and for ternary systems is expressed as:[42]

$$\begin{aligned} \ln \nu = {} & \sum_{i}^{3} X_i^4 \ln(\nu_i M_i) - \ln\left(\sum_{i}^{3} X_i M_i \right) + 4 \sum_{i}^{3} \sum_{\substack{j \\ j \neq i}}^{3} X_i^3 X_j \ln\left(A_{iiij} \frac{3M_i + M_j}{4} \right) \\ & + 6 \sum_{i}^{3} \sum_{\substack{j \\ i<j}}^{3} X_i^2 X_j^2 \ln\left(A_{iijj} \frac{M_i + M_j}{2} \right) \\ & + 12 \sum_{i}^{3} \sum_{\substack{j \\ j \neq i}}^{3} \sum_{\substack{k \\ k \neq j, j<k}}^{3} X_i^2 X_j X_k \ln\left(A_{iijk} \frac{2M_i + M_j + M_k}{4} \right) \end{aligned} \tag{6}$$

The data were also correlated with a modified form of the McAllister equation proposed by Soliman.[43] The general form of the equation is as follows:

$$\ln \nu = \sum_{i=1}^{n} X_i^3 \ln \nu_i + 3\sum_{i=1}^{n}\sum_{\substack{j=1 \\ i\neq j}}^{n} X_i^2 X_j \ln A_{ij} + \sum_{i=1}^{n}\sum_{\substack{j=1 \\ j\neq i}}^{n} \frac{\left(X_i + X_j\right)^3 B_{ij} X_i X_j}{\left(\frac{M_i}{M_j}\right)^2 X_i + X_j} + 6\sum_{i}^{n}\sum_{j>i}^{n}\sum_{k>j}^{n} X_i X_j X_k \ln A_{ijk} \quad (7)$$

The values of coefficients were evaluated by method of least-squares, with the corresponding standard deviation, (σ), calculated by using the relation:

$$\sigma = \left[\frac{\sum\left(Y_{\exp} - Y_{calc}\right)^2}{N_{\exp} - N_{par}}\right]^{0.5} \quad (8)$$

where Y is the experimental and calculated viscosity, respectively. N_{exp} is the number of experimental data and N_{par} is the number of parameters.

Binary systems

The experimental values of viscosity at different temperatures for the water + 1,4-dioxane, water + DMSO and 1,4-dioxane DMSO systems over the whole composition range expressed by mole fraction are given in Table 2.

The tabulated data show that the values of viscosity of the both aqueous systems present a maximum at low concentration of 1,4-dioxane and DMSO, respectively. In the 1,4-dioxane+DMSO mixture, the viscosity decreases with the increase of the mole fraction of 1,4-dioxane.

The experimental mixture viscosities were correlated/predicted through the eqs. (1-7). In order to determine the kinematic viscosity in eqs. (5-7), the densities presented in a previous paper[13] were used. The values of the adjustable parameters and the standard deviations are reported in Table 3. The analysis of standard deviations reveals that the capability of these equations to estimate the viscosity of the binary systems depends on the complexity of the mixtures. For a binary system without strong interactions, like 1,4-dioxane+DMSO, any equation can be used to correlate adequately the viscosity data. For the aqueous systems only the three parameters equations of McAllister and Soliman give the best results for these non-ideal systems. The correlating ability significantly improves as the number of the adjustable parameters is increased.

Table 2

Experimental viscosities (η), viscosity deviations ($\Delta\eta$) and excess Gibbs energy of activation of viscous flow (G^{*E}) for the binary systems at different temperatures

T, K	293.15			303.15			313.15		
X_1	η, *mPa s*	$\Delta\eta$, *mPa s*	G^{*E}, *J mol^{-1}*	η, *mPa s*	$\Delta\eta$, *mPa s*	G^{*E}, *J mol^{-1}*	η, *mPa s*	$\Delta\eta$, *mPa s*	G^{*E}, *J mol^{-1}*
water(1)+1,4-dioxane(2)									
0.0000	1.3125	0	0	1.1127	0	0	0.9603	0	0
0.1007	1.3481	0.067	304.2	1.1263	0.045	295.7	0.9753	0.046	329.6
0.1995	1.4469	0.196	693.5	1.1895	0.139	674.4	1.0059	0.106	674.7
0.3422	1.6630	0.426	1262.4	1.3551	0.349	1311.2	1.1020	0.246	1252.3
0.4256	1.7645	0.583	1584.9	1.4920	0.512	1706.4	1.1990	0.368	1641.5
0.5379	1.9793	0.832	2004.9	1.6949	0.750	2191.9	1.3553	0.559	2146.3
0.6640	2.2300	1.122	2381.5	1.8578	0.952	2533.4	1.4830	0.725	2513.2
0.7530	2.2948	1.214	2451.7	1.8470	0.969	2533.3	1.4753	0.744	2528.1
0.8197	2.2032	1.143	2309.2	1.7334	0.876	2338.9	1.3829	0.672	2332.9
0.8710	2.0130	0.968	2024.2	1.5702	0.729	2030.0	1.2495	0.554	2013.1
0.9130	1.7655	0.734	1626.6	1.3795	0.552	1628.2	1.1000	0.418	1606.4
0.9470	1.5044	0.483	1153.8	1.1843	0.367	1161.9	0.9450	0.273	1128.7
0.9760	1.2240	0.232	603.9	0.9868	0.179	614.1	0.7960	0.133	593.1
1.0000	1.0050	0	0	0.8007	0	0	0.6560	0	0

Table 2 (continued)

water(1)+DMSO(2)									
0.0000	2.2255	0	0	1.8180	0	0	1.5553	0	0
0.0915	2.4515	0.338	538.8	1.9550	0.230	499.7	1.6545	0.182	495.6
0.1713	2.6765	0.660	1005.3	2.0820	0.438	922.8	1.7480	0.347	919.4
0.2415	2.8714	0.941	1388.7	2.2237	0.651	1311.7	1.8400	0.502	1290.3
0.3038	3.0658	1.211	1728.0	2.3833	0.874	1675.7	1.9388	0.657	1628.6
0.3594	3.2743	1.487	2041.0	2.5523	1.100	2009.6	2.0457	0.814	1941.0
0.4795	3.8322	2.192	2726.3	2.9441	1.614	2689.2	2.3048	1.181	2594.8
0.5669	4.2124	2.679	3148.3	3.1509	1.910	3064.1	2.4516	1.406	2975.3
0.6541	4.3588	2.932	3394.2	3.1679	2.015	3251.8	2.4679	1.501	3181.2
0.7021	4.2602	2.892	3413.8	3.0584	1.955	3244.4	2.3885	1.465	3184.8
0.7842	3.7056	2.437	3174.9	2.6427	1.623	2986.5	2.0738	1.224	2939.5
0.8637	2.7242	1.553	2481.2	1.9906	1.051	2336.3	1.5702	0.792	2290.9
0.9218	1.8706	0.770	1571.6	1.4343	0.554	1521.6	1.1383	0.412	1473.9
0.9649	1.3067	0.259	677.0	1.0476	0.211	712.6	0.8404	0.153	674.0
1.0000	1.0050	0	0	0.8007	0	0	0.6560	0	0
1,4-dioxane(1)+DMSO(2)									
0.0000	2.2255	0	0	1.8180	0	0.	1.5553	0	0
0.0419	2.1660	-0.021	-11.4	1.7718	-0.017	-14.1	1.5151	-0.015	-17.8
0.1062	2.0800	-0.049	-26.5	1.7035	-0.040	-34.9	1.4560	-0.036	-43.8
0.2171	1.9424	-0.085	-49.5	1.5930	-0.072	-68.2	1.3615	-0.065	-83.1
0.3094	1.8384	-.0105	-64.0	1.5093	-0.091	-90.6	1.2895	-0.082	-110.3
0.4050	1.7402	-0.116	-74.6	1.4295	-0.103	-109.3	1.2227	-0.092	-129.6
0.4541	1.6934	-0.118	-77.7	1.3915	-0.106	-116.3	1.1909	-0.094	-136.4
0.5041	1.6481	-0.117	-79.4	1.3550	-0.108	-121.2	1.1603	-0.095	-141.3
0.6071	1.5621	-0.109	-77.7	1.2864	-0.103	-124.0	1.1034	-0.091	-141.5
0.7139	1.4826	-0.091	-68.0	1.2252	-0.089	-113.7	1.0529	-0.078	-127.5
0.8250	1.4096	-0.063	-49.0	1.1729	-0.063	-85.1	1.0095	-0.055	-94.7
0.9112	1.3592	-0.034	-27.9	1.1394	-0.036	-50.7	0.9824	-0.031	-54.9
0.9530	1.3365	-0.019	-15.6	1.1259	-0.020	-28.7	0.9712	-0.017	-31.1
1.0000	1.3125	0	0	1.1127	0	0	0.9603	0	0

Table 3

Adjustable parameters and standard deviations of the equation (1) to (7) for the binary systems at different temperatures

Equation	Parameters/Standard deviation	Temperature, K			Temperature, K			Temperature, K		
		293.15	303.15	313.15	293.15	303.15	313.15	293.15	303.15	313.15
		Water +1,4-dioxane			Water +DMSO			1,4-dioxane +DMSO		
Kendall-Monroe	σ	0.7136	0.5769	0.4383	1.7448	1.2257	0.9194	0.0522	0.0529	0.0479
Grunberg-Nissan	A_{12}	2.4886	2.5017	2.2948	3.9269	3.5993	3.3366	-0.1347	-0.1807	-0.1950
	σ	0.4242	0.3303	0.2577	0.8287	0.5600	0.4248	0.0017	0.0057	0.0042
Tamura-Kurata	A_{12}	3.7517	3.0457	2.3869	6.9445	4.9781	3.7935	1.5741	1.2728	1.0799
	σ	0.1566	0.1131	0.0913	0.3069	0.2025	0.1466	0.0009	0.0026	0.0013
Katti-Chaudhri	A_{12}	3.5237	3.5479	3.3516	4.6813	4.3448	4.0703	-0.1283	-0.1877	-0.2129
	σ	0.4771	0.3757	0.2956	0.8871	0.6050	0.4597	0.0018	0.0053	0.0038
McAllister (Eq.5)	A_{12}	9.9103	7.9118	6.0287	20.3498	12.7855	9.1909	1.4093	1.1504	0.9952
	A_{21}	0.7127	0.6449	0.5455	1.6789	1.4219	1.1837	1.6642	1.3828	1.1837
	σ	0.1473	0.0939	0.0756	0.1609	0.0835	0.0731	0.0002	0.0003	0.0001
McAllister (Eq.6)	A_{1112}	8.9669	6.6501	5.1729	14.0599	8.2681	6.3167	1.3738	1.1327	0.9826
	A_{1122}	0.7769	0.7800	0.6299	2.7186	2.4914	1.8507	1.5292	1.2639	1.0862
	A_{2221}	1.8919	1.4742	1.2459	2.7591	1.9964	1.7052	1.7479	1.4470	1.2422
	σ	0.0509	0.0463	0.0309	0.0305	0.0083	0.0109	0.0001	0.0001	0.0001
Soliman	A_{12}	2.8715	2.8249	2.2499	9.5711	6.9508	4.9734	1.3346	1.1188	0.9684
	A_{21}	0.9212	0.7844	0.6528	1.7521	1.4599	1.2109	1.5525	1.3345	1.1432
	B_{12}	0.5004	0.3943	0.3719	0.3474	0.2532	0.2577	0.2080	0.1048	0.1026
	σ	0.0459	0.0192	0.0241	0.1135	0.0492	0.0481	0.0001	0.0003	0.0002

From the measured viscosities, the viscosity deviations and excess Gibbs energies of activation of viscous flow were calculated and presented in Table 2. The viscosity deviations ($\Delta\eta$) were computed through the equation (9) and the excess Gibbs energies of activation of viscous flow (G^{*E}) were calculated on the basis of the theory of absolute reaction rate with the relation (10).

$$\Delta\eta = \eta - \sum_{i=1}^{n} X_i \eta_i \qquad (9)$$

$$G^{*E} = RT\left[\ln(V\eta) - \sum_{i=1}^{N} X_i \ln(V_i \eta_i)\right] \qquad (10)$$

η and η_i are the dynamic viscosity of the mixture, and of the pure component i, respectively; V and V_i are the molar volume of the mixture, and of the pure component i, respectively. X_i are the mole fractions, R and T have their usual meaning. Both excess properties (Y^E) were fitted to Redlich-Kister's equation: [44]

$$Y^E = X_i X_j \sum_{k=0}^{p} A_k \left(X_j - X_i\right)^k \qquad (11)$$

where A_i are the adjustable parameters and p is the degree of polynomial expansion. The choice of the number of parameters was based on the standard deviation (σ) calculated using type (8) equation. The obtained coefficients and the standard deviations at three temperatures are given in Table 4. The experimental and calculated excess properties at 303.15 K are plotted in Figures 1 and 2.

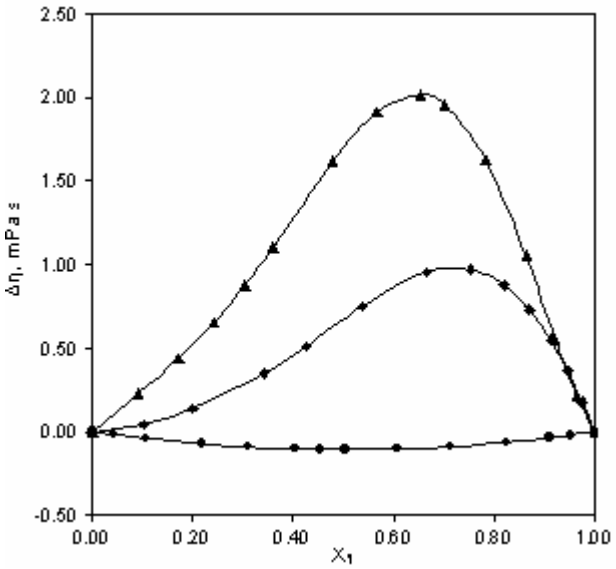

Fig. 1 – Viscosity deviations of the binary systems at T=303.15 K for: ♦ water(1) +1,4-dioxane(2), ▲ water(1) +DMSO(2), ● 1,4-dioxane(1) + DMSO(2), (——) Redlich-Kister's correlation.

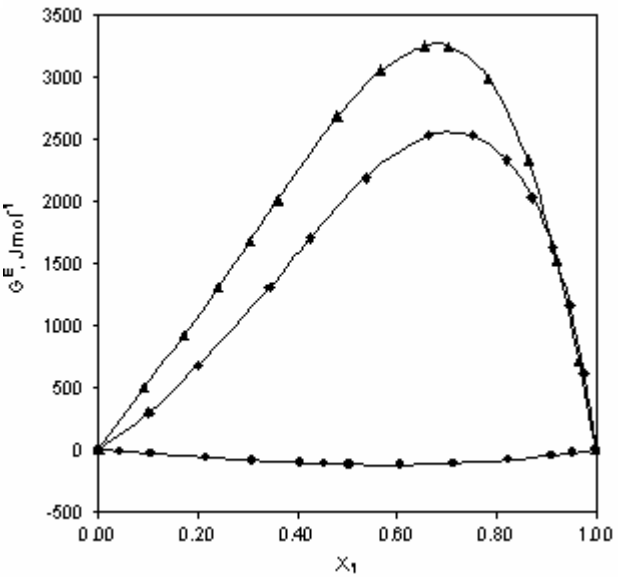

Fig. 2 – Excess molar Gibbs of activation of viscous flow of the binary systems at T=303.15 K for: ♦ water(1) +1,4-dioxane(2), ▲ water(1) +DMSO(2), ● 1,4-dioxane(1) + DMSO(2), (——) Redlich-Kister's correlation.

The viscosity deviations and excess Gibbs energies of activation of viscous flow for the binary water +DMSO and water+1,4-dioxane systems are positive over the entire composition range as shown in Table 2 and figures 1-2. An increase of temperature considerably modifies the viscosity deviations of these binary mixtures; however, G^{*E} scarcely changes. The water +DMSO system presents the viscosity maxima between 2.9–1.5 mPa s at X_{water}=0.6541 and water+1,4-dioxane system, between 2.29-0.74 mPa s at X_1=0.7530 at studied temperatures. The aqueous systems present asymmetrical curves with the maximum values in the water-rich region. The 1,4-dioxane+DMSO mixture shows small negative deviations for both $\Delta\eta$ and G^{*E}, decreasing their algebraic values as temperature raised. Temperature has a strong influence on the excess Gibbs energies of activation of viscous flow. The viscosity minima lies between –0.117 and -0.095 mPa s at X_{water}=0.5041.

Table 4

Coefficients A_i of eq. (11) and standard deviations $\sigma(Y^E)$ for the binary systems at different temperatures

T, K	293.15		303.15		313.15	
	$\Delta\eta$, mPa s	G^{*E}, J mol^{-1}	$\Delta\eta$, mPa s	G^{*E}, J mol^{-1}	$\Delta\eta$, mPa s	G^{*E}, J mol^{-1}
Water + 1,4-dioxane						
A_0	2.9757	7495.7	2.6859	8185.4	1.9753	7953.3
A_1	-4.6205	-7611.7	-4.2819	-8613.4	-3.4384	-8942.6
A_2	4.5891	5345.2	1.9576	2838.9	1.7866	3560.5
A_3	-2.0360	-1585.0	0.8783	938.3	1.0617	1563.4
A_4	-2.4882	1463.3	-0.7122	3636.1	-0.7129	3228.6
A_5	1.7579	-3989.1	-0.5498	-5694.1	-0.3516	-4844.4
σ	0.0008	7.722	0.0006	8.741	0.0008	6.054
Water + DMSO						
A_0	9.2637	11374.3	6.7769	11173.9	4.9629	10796.6
A_1	-11.9166	-10139.0	-7.5905	-9373.7	-5.6851	-9369.3
A_2	4.6181	3926.5	0.1196	2274.3	0.9978	3124.4
A_3	11.1256	-918.2	6.5416	-1179.6	5.0220	-647.4
A_4	-10.3609	8959.2	-3.2653	5702.3	-3.4444	5460.8
A_5		3334.1		2480.5		2420.0
A_6		-13400.3		-6203.6		-7575.0
σ	0.0003	13.756	0.0001	6.080	0.0004	7.189
1,4-dioxane +DMSO						
A_0	-0.4691	-316.1	-0.4299	-483.9	-0.3804	-565.0
A_1	-0.0541	40.4	0.0152	158.8		135.7
A_2	-	-		-15.3		
σ	0.0001	0.301	0.0001	0.2919	0.0001	0.326

The viscosity deviations are functions of size and shape of molecules as well as molecular interactions between the components. Fort and Moore[45] state that a positive viscosity deviation is characteristic of systems with strong interaction between components whereas mixtures where dispersion forces are predominant present negative viscosity deviations. Similarly to the case of viscosity deviation, the excess molar volume and deviations from Raoult's law are related to the molecular interactions between components of the mixture.

The binary systems with water show important negative values V^E over the whole composition range at temperatures between 293.15 and 313.15 K and asymmetrical curves V^E - composition.[11,13] Thus, the binary water + DMSO system presents the V^E minima between –0.85 and –1.25 cm^3 mol^{-1} at X_{water}≈0.6 at mentioned temperatures; the binary system water+1,4-dioxane presents V^E minima between -0.65 and –0.75 cm^3 mol^{-1}at X_{water} ≈0.7, in the same domain of temperatures.[13] Binary mixture of 1,4-dioxane+DMSO presents lower V^E than aqueous systems with symmetrical minima between –0.2 and –0.7 cm^3 mol^{-1} in the range 293.15 - 313.15 K temperatures.[13]

Binary systems of water and organic solvents are systems with strong deviations from Raoult's law; the binary water+DMSO mixtures are characterized by strong negative deviations from Raoult's law; [9-10] the water+1,4-dioxane mixtures have an azeotropic point and show strong positive deviations from ideality. Binary mixture of 1,4-dioxane+DMSO presents positive deviations from Raoult's law.[10]

The system behavior is the result of the pure components structure and interactions between them upon mixing. The structural information shows that water is an interesting solvent with small size, quadruple moment which is able to support extensive hydrogen-bonding network.[46.] At ambient pressure, DMSO exists in the liquid state over a wide temperature range (T_f=291 K and T_b=462 K) and is completely miscible with water. The high boiling temperature has been attributed to the large dipole moment of DMSO molecule (μ=3.96 D at 298.15 K). In the strongly polar S=O bond, oxygen is the most electronegative site of DMSO. Dipole or ionic interactions are responsible for self-association DMSO molecules. Acting as a proton acceptor, it can alter the structure of water. From thermodynamic consideration, Lindberg[47] has argued that the water-

DMSO hydrogen bond is stronger than the water-water hydrogen bond. The studies indicate a strong interaction between water and DMSO, and the general conclusion is that in the mole fraction range $0.7 < X_{water} < 0.6$ the interactions due to hydrogen bonds are at maximum, suggesting the existence of stoichiometrically well-defined $1DMSO:2H_2O$ aggregates.[17,45-48] The water+DMSO mixtures are interesting because of their microheterogeneity indicating cluster formation.[49] Infrared spectroscopy shows that small quantities of DMSO have little effect on the water structure.[50] Other methods[51,52] even lead to the conclusion that small amounts of DMSO act as a "structure breaker" in water.

1,4-Dioxane (μ = 0.4 D) and water are miscible at all solvent compositions and some of their physical properties, such as boiling points, vapor pressures and densities, are approximately identical, but their dielectric constants and dipole moments are very different. Dioxane is an aprotic solvent, whereas water is both an electron donor and acceptor. The X-ray diffraction, mass spectrometry and NMR relaxation were used to investigate the structure of the mixtures containing water and 1,4-dioxane.[53] The investigation results show that in the water-rich region ($X_{water} > \sim 0.9$) the water-water hydrogen bonded network is predominantly formed in the mixtures. When $X_{water} <\sim 0.6$, the clusters characteristic of pure 1,4 dioxane are gradually formed. In this domain the structure of pure 1,4-dioxane is dominant; the water molecules forms hydrogen bonds with pure 1,4-dioxane clusters without altering its bulk structure. Between the mentioned molar fractions, because of unlike interactions, both opened ice-like structure of water and inherent structure of 1,4-dioxane are broken down, and the hydrogen-bonded clusters of 1,4- dioxane and water molecules are the main species in the binary solutions.

The positive $\Delta\eta$ and negative V^E, with accentuated maxima or minima and the structural informations characterise the aqueous binary systems as complex systems, with strong interactions of hydrogen bond and dipole –dipole type. This behaviour is in accordance to Fort and Moore idea[45] and corresponds to systems containing associated components. In the case of DMSO + 1,4-dioxane system, the poor unlike dipole-dipole interactions between SO groups of the DMSO and the O group of 1,4-dioxane, and the capability of 1,4-dioxane molecules to break the polymer chains of DMSO molecules[54], are responsible of small negative $\Delta\eta$ and moderate negative V^E.

Vogel and Weiss[55] affirm that, generally, the mixtures with strong interactions between different molecules present positive viscosity deviations and negative deviations from Raoult's law; whereas, for mixtures without strong specific interactions, the viscosity deviations are negative and deviations of Raoult's law are positive. From the investigated systems, only those containing DMSO present this type of behaviour.

Ternary systems

The experimental viscosities as well as the computed properties: viscosity deviation and excess Gibbs energies of activation of viscous flow for the ternary water+1,4-dioxane+DMSO at 303.15 K and 313.15 K are listed in Table 5. The viscosity deviations and the excess Gibbs energies of activation were computed with eqs. (9) and (10) and fitted to the Redlich-Kister equation:

$$Y^E = Y^E_{bin} + X_1X_2X_3\left(A + B_{12}\left(X_2 - X_1\right) + B_{13}\left(X_3 - X_1\right) + B_{23}\left(X_3 - X_2\right) + C_{12}\left(X_2 - X_1\right)^2 + C_{13}\left(X_3 - X_1\right)^2 + C_{23}\left(X_3 - X_2\right)^2 + \ldots\right) \quad (12)$$

where $Y^E_{bin} = Y^E_{12} + Y^E_{13} + Y^E_{23}$; Y^E_{ij} are given by eq. (11).

Table 5

Values of viscosities (η), viscosity deviation ($\Delta\eta$) and excess Gibbs energies of activation of viscous flow (G^{*E}) as function of composition for the ternary system at different temperatures

T, K		303.15			313.15		
X_1	X_2	η^*, *mPa s*	$\Delta\eta$, *mPa s*	G^{*E}, *J mol^{-1}*	η^*, *mPa s*	$\Delta\eta$, *mPa s*	G^{*E}, *J mol^{-1}*
0.0999	0.8001	1.1898	0.038	301.7	1.0098	0.021	279.8
0.1000	0.5998	1.3323	0.039	329.4	1.1248	0.017	294.2
0.0998	0.4010	1.4929	0.059	358.8	1.2624	0.036	334.6

Table 5 (continued)

0.1000	0.1999	1.7147	0.140	458.4	1.4425	0.097	418.8
0.1997	0.6000	1.3734	0.182	766.8	1.1562	0.138	753.3
0.1998	0.4020	1.5594	0.228	825.6	1.3070	0.171	798.8
0.2000	0.2001	1.8276	0.354	958.4	1.5280	0.272	931.7
0.1998	0.1000	2.0070	0.463	1059.6	1.6727	0.357	1028.5
0.3002	0.5999	1.3707	0.281	1109.8	1.1450	0.217	1098.8
0.3000	0.4000	1.6407	0.410	1288.1	1.3521	0.305	1246.0
0.3000	0.2000	1.9866	0.615	1489.0	1.6072	0.441	1410.7
0.2999	0.1002	2.1884	0.746	1595.4	1.7822	0.557	1536.0
0.3997	0.5001	1.5287	0.470	1571.5	1.2496	0.351	1531.5
0.4000	0.4002	1.6858	0.557	1672.6	1.3794	0.422	1640.1
0.4002	0.1998	2.1482	0.878	1987.1	1.7417	0.666	1941.7
0.3998	0.1002	2.3846	1.044	2104.3	1.9165	0.781	2041.3
0.5000	0.4001	1.6947	0.668	1980.9	1.4011	0.534	1999.3
0.5001	0.3000	1.9655	0.868	2197.9	1.5599	0.633	2117.4
0.5002	0.1998	2.1389	0.971	2253.9	1.7757	0.789	2291.8
0.4998	0.1002	1.5017	1.348	2576.5	2.0477	1.002	2501.5
0.5997	0.3002	1.9354	0.939	2417.5	1.5260	0.689	2342.5
0.6001	0.1997	2.2278	1.161	2603.4	1.7683	0.872	2546.6
0.6000	0.1000	2.6597	1.523	2880.8	2.0747	1.119	2793.9
0.7000	0.2001	2.0698	1.105	2628.5	1.6438	0.837	2590.9
0.6998	0.1000	2.6479	1.612	3064.9	1.9612	1.095	2860.4
0.8001	0.1500	1.9214	1.023	2504.2	1.4854	0.739	2406.8
0.7990	0.0500	2.3545	1.385	2816.4	1.7634	0.957	2645.1
0.9000	0.0500	1.5247	0.658	1786.5	1.2107	0.495	1745.2
0.9000	0.0250	1.5640	0.679	1795.2	1.2463	0.515	1762.9

[*] Iulian et al.[9]

The eqs. (1)-(7), extended for the ternary system, were used to predict/correlate the experimental viscosity data. For the ternary systems, three procedures were used in the fitting of these equations. In the first, we predicted the viscosity of the ternary mixtures using only the binary parameters, without any ternary parameters. In the second procedure we fixed the binary parameters and fitted only the ternary parameters. Finally, in the third procedure, we fitted all parameters. Table 6 shows the complete results of the prediction and correlation with these equations, at 303.15 and 313.15 K.

Table 6

Adjustable parameters and standard deviations of the equation (1) to (7) for the ternary system at different temperatures

Eq.	T, K	A_{12}	A_{13}	A_{23}	A_{21}	A_{31}	A_{32}	B_{12}	B_{13}	B_{23}	A_{123}	σ
(1)	303.15											0.8692[a]
	313.15											0.6461[a]
(2)	303.15											0.4189[a]
											-5.1695	0.3567[b]
		3.8702	4.9454	-1.1898							-14.215	0.3080[c]
	313.15											0.3009[a]
											-4.7109	0.2539[b]
		3.4647	4.4445	-1.1559							-11.733	0.2193[c]
(3)	303.15											0.4603[a]
											-5.5386	0.3955[b]
		5.0468	5.8129	-1.4400							-14.881	0.3409[c]
	313.15											0.3349[a]
											-5.0827	0.2860[b]
		4.6423	5.3064	-1.4056							-12.408	0.2463[c]
(4)	303.15											0.1666[a]
											-2.7764	0.1294[b]
		2.7477	5.0399	0.6909							0.7707	0.1106[a]
	313.15											0.1146[a]
											-2.0699	0.0829[b]
		2.0802	3.6889	0.6523							1.4704	0.0678[c]

Table 6 (continued)

(5)	303.15												0.2638[a]
										0.7644			0.1314[b]
		6.5361	14.871	1.7975	0.7700	1.4929	2.1842			0.4323			0.0902[c]
	313.15												0.1273[a]
										0.5649			0.1001[b]
		4.8479	9.2734	1.4736	0.6479	1.3135	1.6575			0.4618			0.0579[c]
(7)	303.15												0.0932[a]
										0.9741			0.0946[b]
		1.6691	8.9739	1.4037	0.8531	1.6076	1.8937	0.6447	-0.0342	-0.3185	0.9512		0.0529[c]
	313.15												0.0865[a]
											0.8310		0.0806[b]
		1.7197	5.8165	3.9964	0.6892	1.3449	6.5603	0.4706	0.0224	-4.9986	0.5721		0.0207[c]
(6)		A_{1112}	A_{1113}	A_{2221}	A_{2223}	A_{3331}	A_{3332}	A_{1122}	A_{1133}	A_{2233}	A_{1123}	A_{2213}	A_{3312}	
	303.15													0.1739[a]
											1.1015	1.4885	2.0693	0.0385[b]
		5.8683	9.6320	1.3372	0.9242	2.1571	1.3835	0.8431	2.4386	1.1297	0.8701	2.4456	1.9325	0.0368[c]
	313.15													0.0849[a]
											0.8130	1.3632	1.7842	0.0302[b]
		4.2828	6.0177	1.1578	0.8051	1.7543	1.1517	0.7262	2.0109	1.0461	0.8759	1.7288	1.5973	0.0135[c]

[a] prediction from binary parameters; [b] optimization of the ternary parameters; [c] optimization of all model parameters

The prediction results obtained with McAllister and Soliman equations are better than those obtained with the other equations, because, probably of great parameter number and their advanced theoretical support. The viscosity prediction using only binary parameters gives inferior results. Generally, a rise of number of parameters leads to a smaller standard deviation and, especially, the increase of number of ternary parameters improves the viscosity predictions. The optimization of all parameters leads to an improvement of the computational results.

The computed properties: viscosity deviation and excess Gibbs energies of activation of viscous flow at two temperatures for the ternary system, presented in Table 5, show that they are positive over the whole composition range, as we expected from binary values. Also, it can be observed that an increase of the temperature affects considerably the viscosity deviation, while the excess Gibbs energy hardly modifies. The isolines at constant values of $\Delta\eta$ and G^{*E} at 303.15 K have been drawn in Figures 3 and 4, respectively. The results of correlation with Redlich-Kister equation (eq.12), the coefficients and the standard deviations are gathered in Table 7.

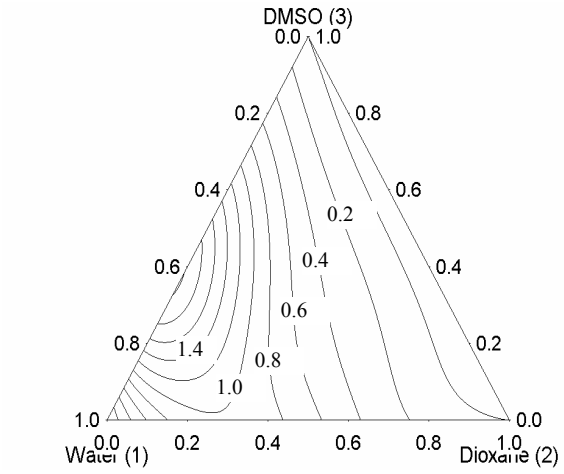

Fig. 3 – Isolines at constant $\Delta\eta$ for the ternary water(1)+1,4-dioxane (2)+DMSO(3) system at 303.15 K.

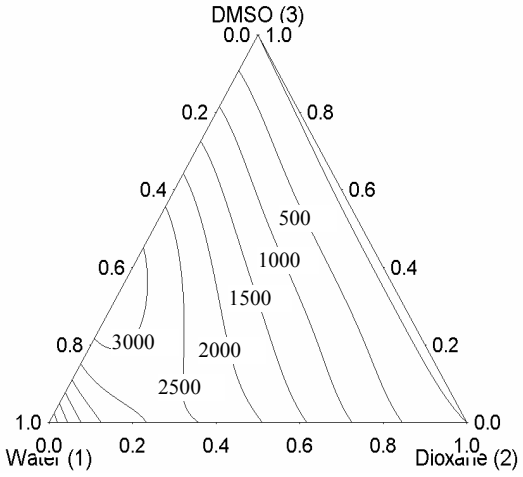

Fig. 4 – Isolines at constant G^{*E} for the ternary water(1)+1,4-dioxane (2)+DMSO(3) system at 303.15 K.

Table 7

Coefficients of Redlich-Kister's equation and standard deviation for excess properties of the water +1,4-dioxane +DMSO ternary system

T, K	303.15		313.15	
	$\Delta\eta$, *mPa s*	G^{*E}, *J mol*$^{-1}$	$\Delta\eta$, *mPa s*	G^{*E}, *J mol*$^{-1}$
A	-13.9193	-16954.5	-9.2993	-15218.0
B_{12}	15.3267	14975.0	10.1514	13817.9
B_{13}	14.9566	15337.5	10.1738	13894.3
B_{23}	-0.2701	363.5	0.1224	69.7
C_{12}	7.8328	9035.1	-0.6326	-1658.1
C_{13}	1.9931	-14057.4	-2.4038	-19984.9
C_{23}	7.4440	5301.5	5.8324	5810.2
D_{12}	-37.5280	-18526.7	-13.4328	-4430.8
D_{13}	-27.7109	3283.6	-18.6658	7790.7
D_{23}	7.8709	14597.1	6.2618	13234.1
σ	0.0431	42.755	0.0147	18.995

CONCLUSION

Viscosities of binary and ternary systems with water, 1,4-dioxane, and DMSO were experimentally measured at various temperatures and correlated by means of Kendall and Monroe, Grunberg-Nissan, Katti-Chaudhri, Tamura-Kurata, McAllister and Soliman equations. For the 1,4-dioxane+DMSO binary system without strong interactions, any equation can be used to correlate adequately the viscosity data; for the systems with water only the three parameters equations of McAllister and Soliman give better results. The viscosity prediction for the ternary system with the same models leads to the best results.

Excess functions have been calculated and fitted to the Redlich-Kister equations. For binary and ternary systems, the deviations in viscosity and the excess Gibbs energy of activation for viscous flow are positive over the whole composition range, except for the binary 1,4-dioxane + DMSO which show small negative deviations for both excess properties. The magnitude of viscosity deviations vary in order: water+DMSO > water+1,4-dioxane> 1,4-dioxane+ DMSO, corresponding with excess volumes behavior.[13]

The systems present important deviations, as a consequence of their structures and interactions. The aqueous binary systems are complex systems with strong interactions of hydrogen bond and dipole – dipole type. The DMSO+1,4-dioxane binary system present poor unlike dipole-dipole interactions.

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