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On the reduced Redlich-Kister excess properties for 1,2-dimethoxyethane with propylene carbonate binary mixtures at temperatures (from 298.15 to 318.15) K

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Abstract: Values of excess properties in 1,2-dimethoxyethane + propylene carbonate binary liquid mixtures at different temperatures from experimental density and viscosity values presented in earlier work, were used to test the applicability of the correlative reduced Redlich-Kister functions and the Belda equation, and to reveal eventual specific interaction hidden by the classical treatment of direct excess Redlich-Kister functions. Their correlation ability at different temperatures, and the use of different numbers of parameters, is discussed for the case of limited experimental data. The relative Redlich-Kister functions are important to reduce the effect of temperature and, consequently, to reveal the effects of different types of interactions. Values of limiting excess partial molar volume at infinite dilution deduced from different methods were discussed. Also, the activation parameters and partial molar Gibbs free energy of activation of viscous flow against compositions were investigated. Correlation between the two Arrhenius parameters of viscosity shows the existence of main different behaviors separated by a stabilized structure in a short range of mole fraction in 1,2-dimethoxyethane (0.45 to 0.83). In this context, the correlation Belda equation has also been applied to the present system for thermodynamic properties in order to reveal eventual solute-solvent interaction at high dilution.

Keywords: Binary liquid mixture; viscosity; Reduced Redlich-Kister equation; Molecular interaction; 1,2-dimethoxyethane ; propylene carbonate.

Introduction

Study of transport and thermodynamic properties of binary mixtures versus temperature or pressure have attracted much attention from several years, most such studies have concerned mixtures containing small molecules.

Generally, examination of the trends of the dependence of excess properties on molar composition in binary mixtures (curves with extrema around the middle of composition range) [1-8], suggested that many of these systems are similar. So, the excess quantity gives an overall view of the origin of the non-ideality in the mixtures but still can be quite misleading. Then, elimination of the factor (molar fraction product $x_1.x_2$) preceding the Redlich-Kister power series removes this similarity effect and gives a specific reduced function [9-16] characterizing the studied physicochemical property and also gives evidence to the existence of important interactions hidden in the precedent classical investigations.

In the present study the excess molar properties and viscosity deviations [1-8] are fitted to the reduced Redlich-Kister (R-K) equation along with its corresponding relative properties and the Herráez [17,18] and Belda correlative equations [19-21]. In addition, the reduced R-K function relative to the viscosity Arrhenius activation energy which is equivalent to the apparent molar property gives more information because it is more sensitive than the excess property to interaction [22,23].

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For 1,2-dimethoxyethane (DME) and propylene carbonate (PPC) molecules, the interpretations in our present study are based on the predominance of hydrogen bonding over dissociation effects present in the components [24]. A thorough survey of literature shows that PPC behaves as a polar liquid with strong dipole-dipole interactions with little or no specific association present in it [24].

Redlich-Kister equations

Excess properties results

The measured values of density and viscosity in binary mixtures of DME and PPC were taken from literature [24] and used in the present work to calculate the excess molar volumes (V^E) and Gibbs free energy of activation of viscous flow (ΔG^{*E}), and viscosity deviations ($\Delta\eta$) (Table 1 and Fig. 1) of this system and then fitted to the R-K equation, at fixed temperature T.

$$Y^E = x_1(1\text{-}x_1).\sum_{p=0}^{p=n} A_{n,p,T}(2x_1-1)^p \qquad (1)$$

where Y^E denotes V^E, $\Delta\eta$ and ΔG^{*E}, and n is the optimal number of parameters (n = 3 or 4). The coefficients $A_{n,p,T}$ in Eq. 1 and Table 2 are regressed by applying the least-square fit method. The corresponding standard deviation $\sigma(Y)$ was calculated by Eq. 2:

$$\sigma(Y) = \sqrt{\sum_{i=1}^{i=N}\frac{\left(Y_{i,\exp} - Y_{i,calc}\right)^2}{N-m}} \qquad (2)$$

where N and m are the numbers of data points and of adjustable parameters, respectively.

In the Fig. 1 we plotted the variation of excess properties (Y^E), deviations in the viscosity $\Delta\eta$ with the mole fraction of DME (x_1). We note that all these functions (V^E, $\Delta\eta$ and ΔG^{*E}), exhibit negative deviations.

Let's remember that in general we have the three following considerations: (i) The chemical effects, such as the breaking of molecular association present in the pure liquids results in the positive values of V^E, and negative ΔG^{*E}, on the other hand charge transfer forces, formation of hydrogen bonds and other complex forming interactions result in the negative values of V^E, and positive ΔG^{*E}. (ii) Physical contributions arise from dispersion forces or weak dipole-dipole interactions causing the positive values of V^E, and negative ΔG^{*E}. (iii) The structural contribution arising from the geometrical fitting of one component into the other because of the differences in the size and shape of the component molecules resulting in the negative values of V^E, and positive ΔG^{*E}.

The factors that are mainly responsible for the contraction of volume causing the V^E values to be negative are due to strong specific interactions like the association of component molecules through hydrogen bonds, due to dipole-dipole interactions or it may be due to the induced dipole-dipole interactions. Due to the effect of thermal agitation, in general the increase in temperature attenuates the volume contraction. So, in the present study as the temperature is increasing the V^E values are becoming more negative, indicating that the interactions are becoming stronger. This can be interpreted by the fact that the intermolecular interactions between unlike molecules are predominate over the intermolecular interactions between like molecules.

These negative values (Table 1) of ΔG^{*E} indicate the existence of weak interaction between the component molecules of the liquid mixtures under study. As the temperature is increasing the ΔG^{*E} values are becoming less negative indicating the predominance of structural effect over the interactional effect upon mixing.

Deviations in viscosity are negative which may be due to mutual loss of dipolar association and the difference in size and shape of unlike molecules. We can say that it's a generalized statement because much clarity will come with excess values only as the unlike sizes may cause fitting of one component molecules in the gaps of the other molecules. So, negative values of $\Delta\eta$ over whole composition range suggest that, viscosities of bonded associates formed between unlike molecules are relatively less than those of pure components, which is exhibited by decreased values of viscosity with mole fraction. This decrease in viscosity attributed to breaking of bonds. Weak types of dipole-induced dipole type of interactions are not sufficient to produce bulky or less mobile entities in system and hence decreased trend of viscosity is observed in the present binary liquid mixtures.

Table 1 Experimental excess properties (Eq. 3) relative to (a): the viscosity $\Delta\eta$ / mPa·s, (b): the molar volume V^E / cm^3·mol^{-1} and (c): the Gibbs free energy of activation of viscous flow ΔG^{*E} / kJ.mol^{-1} for DME (1) + PPC (2) mixtures against the mole fraction x_1 in DME at the temperatures: (298.15, 308.15 and 318.15) K.

x_1	298.15	308.15	318.15	298.15	308.15	318.15	298.15	308.15	318.15
	$\Delta\eta$ / mPa.s			V^E / cm^3.mol^{-1}			ΔG^{*E} / kJ.mol^{-1}		
0	0	0	0	0	0	0	0	0	0
0.0493	-0.1575	-0.1233	-0.0943	-0.11851	-0.14843	-0.17803	-0.05919	-0.06110	-0.05518
0.0999	-0.3066	-0.2226	-0.1696	-0.28330	-0.32194	-0.36063	-0.14075	-0.11540	-0.10172
0.1524	-0.4073	-0.2987	-0.2321	-0.35908	-0.43810	-0.51758	-0.18946	-0.15710	-0.14642
0.1867	-0.4547	-0.3370	-0.2644	-0.45285	-0.54872	-0.64532	-0.21326	-0.18078	-0.17338
0.2298	-0.4931	-0.3758	-0.2942	-0.55147	-0.64570	-0.77774	-0.22509	-0.20802	-0.19711
0.2769	-0.5387	-0.4043	-0.3218	-0.67110	-0.78529	-0.90088	-0.24967	-0.23032	-0.22192
0.3128	-0.5498	-0.4218	-0.3309	-0.72759	-0.87277	-1.0196	-0.26964	-0.25097	-0.23604
0.3708	-0.5597	-0.4323	-0.3412	-0.79680	-0.95085	-1.1358	-0.27854	-0.26387	-0.25272
0.4036	-0.5573	-0.4318	-0.3417	-0.85193	-1.0362	-1.2228	-0.28032	-0.26765	-0.25813
0.4686	-0.5389	-0.4224	-0.3354	-0.93001	-1.1477	-1.2982	-0.27309	-0.27422	-0.26373
0.5193	-0.5140	-0.4040	-0.3212	-0.97140	-1.1711	-1.3123	-0.26125	-0.26366	-0.25556
0.5704	-0.4800	-0.3813	-0.3022	-0.96471	-1.1320	-1.3029	-0.24326	-0.25850	-0.24415
0.6382	-0.4272	-0.3399	-0.2700	-0.89369	-1.0611	-1.2326	-0.21900	-0.23513	-0.22252
0.6767	-0.3971	-0.3118	-0.2489	-0.82864	-0.98411	-1.1440	-0.20893	-0.21510	-0.20794
0.7589	-0.3104	-0.2458	-0.1958	-0.68126	-0.80770	-0.93921	-0.17037	-0.17522	-0.16508
0.8103	-0.2531	-0.2007	-0.1587	-0.57444	-0.67062	-0.77226	-0.14839	-0.15201	-0.13533
0.8432	-0.2140	-0.1702	-0.1335	-0.51895	-0.60416	-0.69509	-0.13029	-0.13378	-0.11550
0.9035	-0.1340	-0.1071	-0.0852	-0.34897	-0.40538	-0.46795	-0.07892	-0.08561	-0.07803
0.9483	-0.0731	-0.0591	-0.0464	-0.15104	-0.17586	-0.20720	-0.04203	-0.04990	-0.04095
1.0000	0	0	0	0	0	0	0	0	0

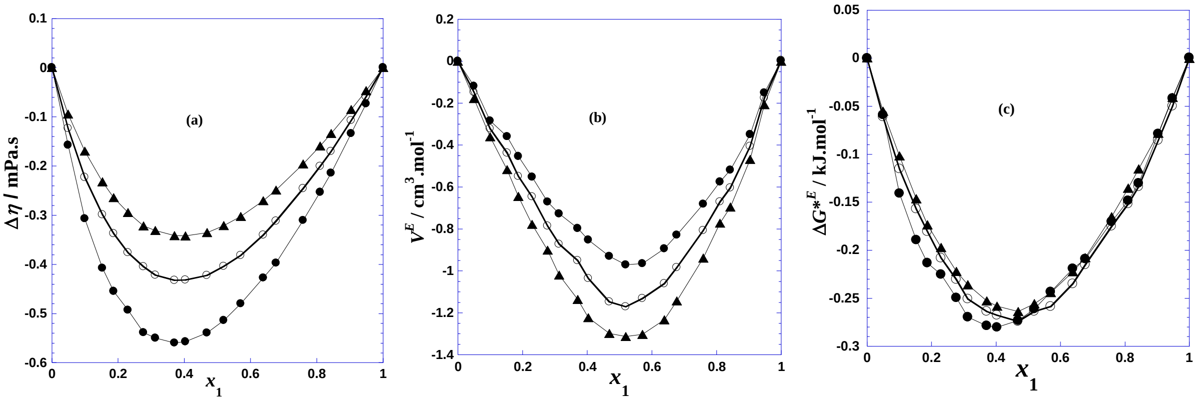

Figure 1 Experimental excess properties (Eq. 1) relative to (a): the viscosity $\Delta\eta$ / mPa·s, (b): the molar volume V^E / cm^3·mol^{-1} and (c): the Gibbs free energy of activation of viscous flow ΔG^{*E} / kJ.mol^{-1} for DME (1) + PPC (2) mixtures against the mole fraction x_1 in DME at the temperatures, (●): 298.15 K; (○): 308.15 K; (▲): 318.15 K.

Table 2 Variation of Redlich-Kister constants $A_{n.p}$ for the experimental excess properties (Eq. 3) and corresponding correlation coefficient R and standard deviation $\sigma(Y)$ relative to the viscosity $\Delta\eta$ / mPa·s, the molar volume V^E / cm^3·mol^{-1} and the Gibbs free energy of activation of viscous flow ΔG^{*E} / kJ.mol^{-1} for DME (1) + PPC (2) mixtures against the mole fraction x_1 in DME at the temperatures: (298.15, 308.15 and 318.15) K.

T / K	$A_{n.0}$	$A_{n.1}$	$A_{n.2}$	$A_{n.3}$	$A_{n.4}$	R	σ
				$\Delta\eta$			
298.15	-2.0939	0.98053	-0.5804	0.2666	0	0.99973	0.0056543
308.15	-1.6420	0.69286	-0.3274	0.1207	0	0.99983	0.0081518
318.15	-1.3068	0.5457	-0.2035	0.04853	0	0.99985	0.015194
				V^E			
298.15	-3.7862	-0.5320	1.4714	-0.4122	-1.1318	0.99063	0.068299
308.15	-4.5193	-0.6607	2.0176	-0.1839	-1.5720	0.98578	0.084467
318.15	-5.2379	0.6924	1.9963	-0.1872	-1.4524	0.98954	0.016449
				ΔG^{*E}			
298.15	-1.0876	0.3135	-0.2041	0.03849	-0.0968	0.99461	0.0048824
308.15	-1.0689	0.2252	0.0553	-0.0545	-0.1859	0.99672	0.0021284
328.15	-1.0367	0.2418	0.1733	-0.1292	-0.2313	0.99739	0.0016653

The reduced Redlich-Kister equations

We note that the extrema observed in all curves of Fig .1 around 0.50 mole fraction, are due principally to the effect of the molar fraction product expressed by the Eq. 1 ($x_1(1-x_1)$) while the phenomenal effects are weak.

In the same context, Desnoyers et al. [9] showed that an examination of the trends of the dependence of V^E, $\Delta\eta$ and ΔG^{*E} on x_1 suggested that many of these systems are similar, and the differences in interactions are mostly significant in solutions very rich in component 2. From the treatment of excess thermodynamic quantities for liquid mixtures proposed by Desnoyers et al. [9], we can conclude that the excess quantity (V^E, $\Delta\eta$ and ΔG^{*E}) gives an overall view of the origin of the non-ideality in the mixtures but still can be quite misleading, especially for systems that show strong interactions at high dilution. Desnoyers et al. [9] suggested that, in agreement with the original statements of Redlich and Kister [1], it is better to use the ratio $V^E / x_1(1 - x_1)$, $\Delta\eta / x_1(1 - x_1)$ or $\Delta G^{*E} / x_1(1 - x_1)$ for this purpose.

So, this ratio is so called the experimental reduced R-K excess properties $Q_{Y,\exp,T}(x_1)$ which is expressed by Eq. 3,

$$Q_{Y,\exp,T}(x_1) = Y^E/(x_1(1-x_1)) \qquad (3)$$

where Y^E denotes V^E, $\Delta\eta$ and ΔG^{*E}.

Also, the excess thermodynamic quantities have the advantage of illustrating the sign and magnitude of their non-ideality, but the reduced Redlich and Kister function $Y^E / x_1(1 - x_1)$ gives a much better handle on the origin of the non-ideality. The experimental reduced R-K excess values (Eq. 3) relative to the molar volume $Q_{V,T}(x_1)$, the viscosity $Q_{\eta,T}(x_1)$ and the Gibbs free energy of activation of viscous flow $Q_{\Delta G^*,T}(x_1)$ for DME (1) + PPC (2) mixtures against the mole fraction x_1 in DME at temperatures 298.15, 308.15 and 318.15 K are presented in Table 3 and plotted in Fig. 2.

We note that the reduced R-K excess property is more sensitive than the direct excess property V^E, $\Delta\eta$ or ΔG^{*E} to interactions that occurs at low concentrations [9-16]. So, we observe that the shape of curves is totally different of those in Fig. 1 because Redlich and Kister treated the data with a power series, putting all the weight on data near 0.5 mole fraction [9-16]. As Desnoyers et al. have shown [9], this is not always the best approach for mixtures having specific interactions such as association at low concentration. Therefore, elimination of the factor $[x_1(1 - x_1)]$ in the reduced R-K excess function $Q_{Y,\exp,T}(x_1)$ (Eq. 3) removes this effect and gives a specific reduced function $Q_{Y,\exp,T}(x_1)$ characterizing the studied physicochemical property and also gives evidence to the existence of important interactions. In fact, taking into account the absolute values of the reduced R-K excess function $Q_{Y,\exp,T}(x_1)$ (Table 3 , Fig. 2), we see that the viscosity effect is due principally to pure PPC while the volume effect is due principally to the pure DME. In the case of the Gibbs free energy of activation of viscous flow and due to the strictly monotonous character of logarithm expressing this property (Eq. 4), we can conclude that the viscosity effect globally dominates on the volume one in all the range of the DME (1) + PPC (2) mixtures.

$$\Delta G^*(x_1,T,P) = RT\cdot ln\left(\frac{\eta(x_1,T,P)\cdot V(x_1,T,P)}{hN_A}\right) \qquad (4)$$

where η, h, R, N_A and V are the shear viscosity of binary liquid mixture, the Plank's constant, the perfect gas constant, the Avogadro's number and the molar volume of mixture, respectively [26,27],

In addition, monotonous variation the reduced R-K viscosity $Q_{\eta,\exp,T}(x_1)$ in curve (*a*) of Fig. 2, suggests that there is a progressively change of solvent's structure when we introduce one component into other in the mixture, while the existence of extremum in curves (*b*) and (*c*) show the eventual existence of preferential clustering at fixed molar composition.

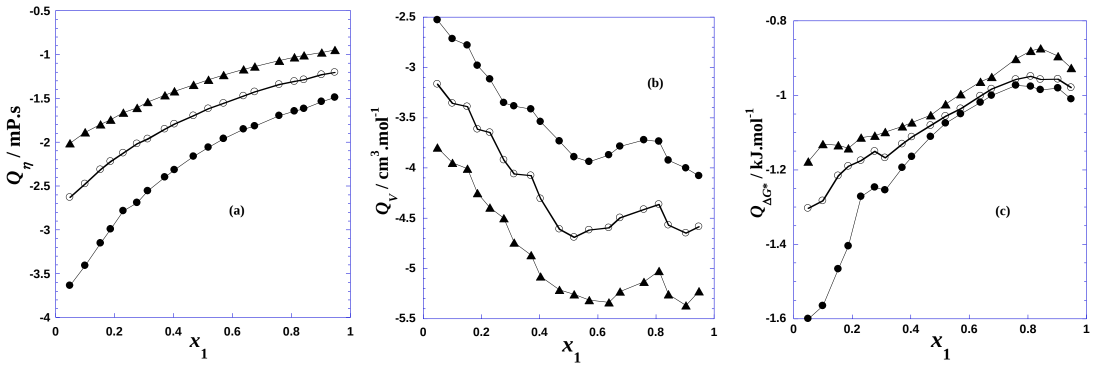

Figure 2. Experimental reduced Redlich-Kister excess properties (Eq. 1) relative to (a): $Q_{\eta,T}(x_1) = \Delta\eta/x_1(1-x_1)$ / mPa·s of viscosity deviation, (b): $Q_{V,T}(x_1) = V^E / x_1(1-x_1)$ / cm^3·mol^{-1} of excess molar volume, and (c): the Gibbs free energy of activation of viscous flow $Q_{\Delta G^*,T}(x_1) = \Delta G^{*E} / x_1(1-x_1)$ / kJ.mol^{-1} of the Gibbs free energy of activation of viscous flow for DME (1) + PPC (2) mixtures against the mole fraction x_1 in DME at the temperatures, (●): 298.15 K; (○): 308.15 K; (▲): 318.15 K.

Table 3. Experimental reduced Redlich-Kister excess values (Eq. 3) relative to the viscosity $Q_{\eta,T}(x_1)$ / mPa·s, the molar volume $Q_{V,T}(x_1)$ / cm^3·mol^{-1} and the Gibbs free energy of activation of viscous flow $Q_{\Delta G^*,T}(x_1)$ / kJ.mol^{-1} for DME (1) + PPC (2) mixtures against the mole fraction x_1 in DME at the temperatures: (298.15, 308.15 and 318.15) K.

x_1	$Q_{\eta,T}(x_1)$ / mPa.s			$Q_{V,T}(x_1)$ / cm^3.mol^{-1}			$Q_{\Delta G^*,T}(x_1)$ / kJ.mol^{-1}		
	298.15 K	308.15 K	318.15 K	298.15 K	308.15 K	318.15 K	298.15 K	308.15 K	318.15 K
0*	-3.9407	-2.8303	-2.1302	-2.4922	-3.1591	-3.7812	-1.7033	-1.3878	-1.1931
0.0493	-3.6360	-2.6304	-2.0114	-2.5286	-3.1670	-3.7983	-1.5999	-1.3036	-1.1773
0.0999	-3.4092	-2.4753	-1.8856	-2.7150	-3.3580	-3.9501	-1.5653	-1.2834	-1.1312
0.1524	-3.1528	-2.3122	-1.7965	-2.7798	-3.3915	-4.0068	-1.4667	-1.2162	-1.1335
0.1867	-2.9943	-2.2190	-1.7413	-2.9823	-3.6137	-4.2499	-1.4045	-1.1906	-1.1418
0.2298	-2.7859	-2.1233	-1.6622	-3.1158	-3.6482	-4.3942	-1.2717	-1.1753	-1.1137
0.2769	-2.6904	-2.0194	-1.6072	-3.3517	-3.9220	-4.4993	-1.2470	-1.1503	-1.1084
0.3128	-2.5575	-1.9625	-1.5395	-3.3848	-4.0602	-4.7435	-1.2544	-1.1675	-1.0981
0.3708	-2.3991	-1.8528	-1.4624	-3.4152	-4.0755	-4.8683	-1.1939	-1.1310	-1.0832
0.4036	-2.3154	-1.7937	-1.4197	-3.5393	-4.3047	-5.0800	-1.1646	-1.1120	-1.0724
0.4686	-2.1643	-1.6961	-1.3467	-3.7348	-4.6090	-5.2134	-1.1110	-1.0810	-1.0529
0.5193	-2.0591	-1.6183	-1.2866	-3.8914	-4.6916	-5.2572	-1.0747	-1.0562	-1.0237
0.5704	-1.9589	-1.5560	-1.2332	-3.9369	-4.6195	-5.3170	-1.0499	-1.0355	-0.99633
0.6382	-1.8501	-1.4722	-1.1694	-3.8705	-4.5953	-5.3381	-1.0195	-1.0018	-0.96368
0.6767	-1.8149	-1.4253	-1.1375	-3.7876	-4.4982	-5.2292	-0.99995	-0.98321	-0.95046
0.7589	-1.6965	-1.3432	-1.0698	-3.7233	-4.4144	-5.1331	-0.97311	-0.95761	-0.90224
0.8103	-1.6466	-1.3053	-1.0327	-3.7370	-4.3628	-5.0240	-0.97653	-0.94889	-0.88041
0.8432	-1.6187	-1.2870	-1.0100	-3.9251	-4.5696	-5.2573	-0.98542	-0.95701	-0.87355
0.9035	-1.5367	-1.2280	-0.97688	-4.0026	-4.6495	-5.3672	-0.98052	-0.95682	-0.89501
0.9483	-1.4901	-1.2049	-0.94673	-4.0807	-4.5870	-5.2262	-1.0101	-0.97902	-0.92678
1.0000*	-1.4225	-1.1660	-0.91132	-4.2412	-4.7173	-5.4137	-1.0519	-1.0022	-0.9541

* Extrapolated values calculated using nonlinear regression fit with fifth polynomial degree and an average of the regression coefficient (*R*) about 0.99992 for viscosity and 0.9991 for the rest.

Table 4. Comparison of calculated values-with four methods-of the limiting excess partial molar volume (10^{-6} m^3·mol^{-1}) and the Gibbs free energy of activation of viscous flow at infinite dilution relative (kJ.mol^{-1}) of DME (1) and of PPC (2) in their corresponding binary mixture at the temperatures: (298.15, 308.15 and 318.15) K.

$\bar{Y}_i^{E,\infty}$ / 10^{-6} m^3·mol^{-1}	***T***	Extrapolation	Redlich-Kister	Derivation	Belda
	K	Table 3	Eqs. 5 and 6	Eqs. 8 and 9	Eqs. 12 and 13
$\bar{V}_1^{E,\infty}$	298.15	-2.4922	-2.5024	-2.4962	-2.4126
	308.15	-3.1591	-3.2291	-2.6375	-2.9196
	318.15	-3.7812	-2.2955	-2.7792	-3.4714
$\bar{V}_2^{E,\infty}$	298.15	-4.2412	-4.3908	-3.4426	-3.5413
	308.15	-4.7173	-4.9183	-3.9742	-4.9607
	318.15	-5.4134	-4.1888	-4.5047	-4.3722
$\overline{\Delta G}_1^{*E,\infty}$	298.15	-1.7033	-1.7405	-1.6504	-1.6836
	308.15	-1.3878	-1.3702	-1.2068	-1.2741
	318.15	-1.1931	-1.2073	-1.0962	-1.0654
$\overline{\Delta G}_2^{*E,\infty}$	298.15	-1.0519	-1.0365	-1.1128	-1.0912
	308.15	-1.0022	-1.0287	-1.0336	-1.0807
	318.15	0.95414	-0.98195	-0.83384	-0.87538

In addition, values of reduced Redlich-Kister functions $Q_{Y,T}(x_i)$ (Eqs. 1 and 3) at infinite dilution represent values of the equivalent of the partial excess physical magnitudes at infinite dilution ($x_1 \rightarrow 0^+$), which can be also calculated from the adjustable parameters using Eqs. 5 and 6:

$$Q_{V,T}(x_1{=}0) = A_{0,T} - A_{1,T} + \ldots + (-1)^p \cdot A_{p,T} + \ldots + (-1)^n \cdot A_{n,T} \quad = \bar{V}_1^{\mathrm{E},\infty} = \bar{V}_1^{\infty} - V_1 \qquad (5)$$

and

$$Q_{V,T}(x_1{=}1) = A_{0,T} + A_{1,T} + \ldots + A_{p,T} + \ldots + A_{n,T} \quad = \bar{V}_2^{\mathrm{E},\infty} \quad = \bar{V}_2^{\infty} - V_2 \qquad (6)$$

where V_i is the molar volume of pure component ‘i’, (V) the molar volume of the mixture and, ($\bar{V}_1$) and ($\bar{V}_2$) partial molar volumes of DMA and EOE in DME (1) + PPC (2) mixtures for each mole fraction x_1 in DME at the temperatures 298.15, 308.15 and 318.15 K. The limiting values of $\bar{V}_i^{E,\infty}$ calculated by using Eqs. 5 and 6 are listed in Table 4.

As discussed in literature [9-16], it can also readily be shown that, for many thermodynamic properties, such as enthalpies, heat capacities, volumes, compressibilities and expansibilities, this quantity ($Q_{Y,T}(x_1)$) is directly related to the apparent molar quantities of both components:

$$Q_{Y,T}(x_1) = Y^E/x_1(1-x_1) = \frac{(Y_{2,\varphi} - Y_2^*)}{x_1} = \frac{Y_{1,\varphi} - Y_1^*}{x_2} \qquad (7)$$

This function is therefore equivalent to an apparent molar quantity over whole mole fraction range, and its extrapolation to $x_1 = 0$ and $x_1 = 1$ (parameters sum $Q_{Y,T}(x_1{=}0)$ and $Q_{Y,T}(x_1{=}1)$ of Eqs. 5 and 6) will give the two excess partial molar quantities $\bar{Y}_i^{E,\infty}$ (where i = 1 or 2). These two limiting parameters are of fundamental importance since they are by definition measures of the solute-solvent interactions of both components.

It is therefore important to determine precisely the R-K interaction parameters, and especially those corresponding to $x_1 = 0$ and $x_1 = 1$. Desnoyers et al. [9] suggested that one of the simplest ways of determining these parameters was from a plot of $Y^E/x_1(1-x_1)$ (or dY^E/dx_1 for free energies). Note that the Redlich Kister excess quantity (Eq. 1) cannot appropriately represent the composition dependence of viscosity.

We can add that these parameters can be obtained from three other manners:
A local extrapolation by fitting partially the curves $Q_{V,T}(x_1)$ separately in each rich-region of one component (1) or (2). The obtained values are truer than those given from Eqs. 5 and 6.
The fit of the molar volume $V(x_1)$ against the molar fraction (x_1) gives directly the partial molar volume V of the component ‘i’ by the following equation:

$$\bar{V}_i = V(x_i) - x_j \cdot \left(\frac{\partial V(x_j)}{\partial x_j}\right)_{T,P} \qquad (12/8)$$

when we proceed to operations of limits of Eq. 8 at infinite dilution ($x_1 \to 0^+$ or $x_1 \to 1^-$), we can easily obtain the values of the excess partial molar volume at infinite dilution of the component ‘i’ in the other one ($\bar{V}_i^{E,\infty}$) :

$$\bar{V}_1^{E,\infty} = \bar{V}_1^{\infty} - V_1 = -(V_1 - V_2) + \left(\frac{\partial V(x_1)}{\partial x_1}\right)_{T,P,x_1=0} \qquad (9)$$

and,

$$\bar{V}_2^{E,\infty} = V_2^{\infty} - V_2 = (V_1 - V_2) - \left(\frac{\partial V(x_1)}{\partial x_1}\right)_{T,P,x_1=1} \qquad (10)$$

We note that in recent work, Belda [19] propose a new empirical correlation equation for four properties (density, viscosity, surface tension, and refractive index) (Eq. 11) which introduces a correcting Factor to linearity as an homographic function acting upon the molar fraction of one component of the binary mixture (x_1).

$$Y_B(x_1) = Y_2 + (Y_1 - Y_2) \cdot x_1 \cdot \frac{1 + m_1 \cdot (1 - x_1)}{1 + m_2 \cdot (1 - x_1)} \qquad (11)$$

where $Y_B(x_1)$ is the mixture property, m_1 and m_2 are the two introduced empirical adjustable parameters. Belda coefficients m_i for (Eq. 11) and corresponding errors of molar volume (V) for DME (1) + PPC (2) mixtures at the temperatures 298.15, 308.15 and 318.15 K are given in Table 5

Table 5 Belda coefficients m_i for (Eq. 13) and corresponding errors, standard deviation $\sigma(Y)$ (Eq. 2) of molar volume (V) for DME (1) + PPC (2) mixtures at the temperatures: (298.15, 308.15 and 318.15) K.

Property	T / K	m_1		m_2		σ_B (Y)
		value	Error	value	Error	
V / cm^3.mol^{-1}	298.15	-0.99654	0.00114	0.21097	0.00405	0.00411
	308.15	-0.99676	0.00135	0.24858	0.00484	0.00429
	318.15	-0.99694	0.00181	0.28808	0.00654	0.00433
ΔG^* / kJ.mol^{-1}	298.15	-0.9949	0.00187	-0.24084	0.00588	0.00288
	308.15	-0.99913	0.00052	-0.24974	0.00163	0.00123
	318.15	-0.9995	0.00071	-0.24518	0.00226	0.00136

In previous papers [20,21], we have discussed the validity of this equation for some physicochemical properties in the 1,4-dioxane-water and isobutyric acid-water mixtures and we conclude that this equation can give better results than the R-K one with the same number of free parameters. We have also, given physical significance [11] for their corresponding parameters (m_1 and m_2). In fact, when we proceed to some mathematical operations of limits and derivations on the Belda equation by injecting Eq. 11 in Eqs. 9 and 10, we can easily obtain the values of partial excess property at infinite dilution of the component “i” in the other one ($\bar{Y}_i^{E,\infty}$) through the following equations:

$$\overline{V}_1^{E,\infty} = \bar{V}_1^{\infty} - V_1 = \frac{m_1 - m_2}{1 + m_2}\cdot(V_1 - V_2) \qquad (12)$$

and,

$$\overline{V}_2^{E,\infty} = \bar{V}_2^{\infty} - V_2 = (m_1 - m_2)\cdot(V_1 - V_2) \qquad (13)$$

Comparison of calculated values-with three methods-of the limiting excess partial molar volume (10^{-6} $m^3\cdot mol^{-1}$) at infinite dilution relative to DME (1) and of PPC (2) in their binary mixture at the temperatures 298.15, 308.15 and 318.15 K are given in Table 4.

The Relative Reduced Redlich-Kister Equation

Nevertheless, like the relative deviation, we can consider the relative reduced R-K function as following,

$$Q_{Y,\mathrm{rel},T}(x_1) = Q_{Y,T}(x_1)/Y(x_1) \qquad (14)$$

The plot of $Q_{Y,\mathrm{rel},T}(x_1)$ versus mole fraction x_1 (Fig. 3) shows that the curves reproach each other and temperature has a small marked effect on $Q_{\mathrm{rel},V,T}(x_1)$ and $Q_{\mathrm{rel},\eta,T}(x_1)$ while in the curve (c) we observe the inverse case. We can conclude that the temperature effect in molar Gibbs free energy dominate the activation of viscous flow effect. We note that, at higher temperature, there will be a competition between molecular interactions and thermal agitation. At higher temperature the increase in viscosity in the entire composition range is due to the breaking up of the hydrogen bonds between the unlike molecules. Inspecting the effect of temperature in Fig. 3 we conclude that the nearness and then the larger separation of curves at the two limits of infinite dilution do not depend only on the value of the solute-solvent parameters but are also affected by temperature shown in Fig. 3. We remark that the differences between their Arrhenius activation energy of viscosity Ea can play an important role in this effect [25]. Note that the relative reduced R-K function $Q_{Y,\mathrm{rel},T}(x_1)$ is also a good tool, like the reduced R-K function $Q_{Y,T}(x_1)$, for interpreting different types of interactions.

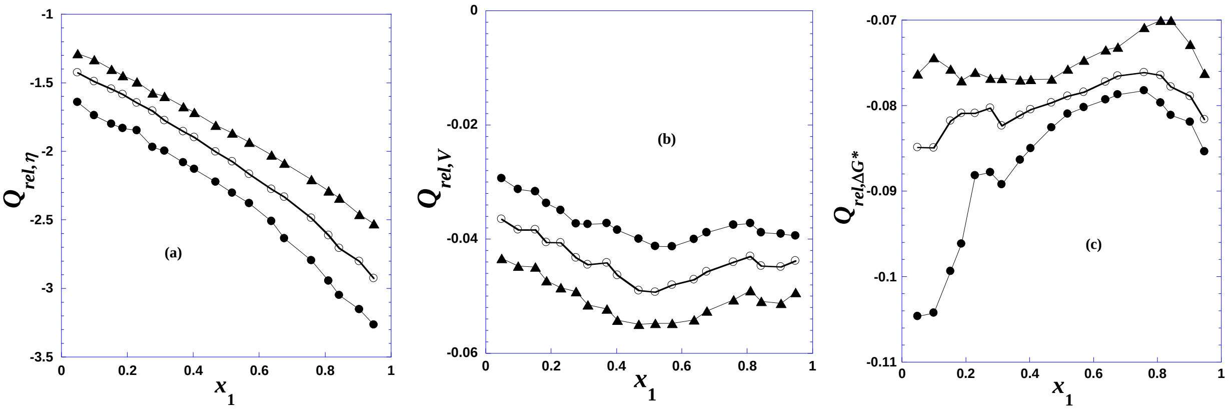

Figure 3 Experimental relative reduced Redlich-Kister excess properties (Eq. 1) relative to (a): $Q_{\mathrm{rel},\eta,T}(x_1)$ for the ratio = $Q_{\eta,T}(x_1)/\eta$ of viscosity deviation, (b): $Q_{\mathrm{rel},V,T}(x_1)$ for the ratio = $Q_{V,T}(x_1)/V$ of excess molar volume, and (c): the Gibbs free energy of activation of viscous flow $Q_{\mathrm{rel},\,\Delta G^*,,T}(x_1)$ for the ratio = $Q_{\Delta G^*,T}(x_1)/\,\Delta G^*$ of the Gibbs free energy of activation of viscous flow for DME (1) + PPC (2) mixtures against the mole fraction x_1 in DME at the temperatures, (●): 298.15 K; (○): 308.15 K; (▲): 318.15 K.

Finally, considering the Eqs. 1, 3, 4 and 15:

$$\Delta G^* = \Delta H^* - T\,\Delta S^* \qquad (15)$$

We can add that the reduced RK excess function $Q_{Y,T}(x_1)$ can be also an excellent indicator, within the mixture, of cluster formation, structure change, etc, and can provide the corresponding particular molar compositions (Figs. 4 and 5) in which occurs the phenomenon. More the average slope of a linear regression, can give an equivalent of temperature which it's in close correlation with the boiling temperatures of the two pure components or the temperature of phase transition in the isobaric vapor liquid diagram of the studied DME–PPC system at atmospheric pressure [25]. We found 342.2 K in Fig. 4 and 325.9 K for Fig. 5 with correlation factor 0.955 and 0.999, respectively while the boiling temperatures of DME and PPC are 358.15 K and 515.15 K, respectively.

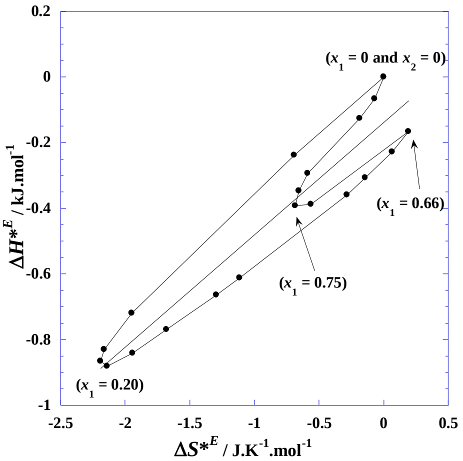

Figure 4 Correlation between The excess Redlich-Kister quantities relative to the enthalpy ΔH^* / kJ·mol^{-1} of the entropy ΔS^* / J·K^{-1}·mol^{-1} of activation of viscous flow for DME (1) + PPC (2) mixtures in the temperature range (298.15 to 318.15 K).

Conclusion

Reduced R-K excess functions have been calculated for DME + PPC binary mixture at three different temperatures (298.15, 308.15 and 318.15) K from their experimental densities and viscosities values reported earlier. In fact, the reduced Redlich-Kister function is a real thermodynamic quantity equivalent to an apparent molar quantity over the whole mole fraction range. Also, at the two limits of infinite dilution, this function gives the two excess standard thermodynamic quantities of the corresponding pure components, which depend only on solute-solvent interactions. In addition, the introduced relative reduced Redlich-Kister equation reduce the temperature effect for revealing the other effects, and can also be good tools, like the reduced Redlich-Kister function, for interpreting different types of interactions. Correlation between the reduced RK excess functions related to the two parameters of activation of viscous flow (ΔH^*) and entropic factor (ΔS^*) for DME+PPC mixtures can give an approximately linear behavior i.e., no observable clear change in curvature. This quasi-straight line behavior suggests us to make an empirical linear equation by introducing a new parameter T_A denoted as viscosity Arrhenius temperature that characterizes each binary system and it's closely correlated to the transition temperature of its isobaric diagram. The results show that there will be a significant degree of H-bonding between unlike molecules leading to progressively change of solvent's structure when we introduce one component into other in the mixture. The negative excess values in our present study indicate the existence of weak interaction between the component molecules of the liquid mixtures. Limiting excess partial molar volume at infinite dilution relative to DME and of PPC in their binary mixture at the temperatures: (298.15, 308.15 and 318.15) K were deduced through different techniques.

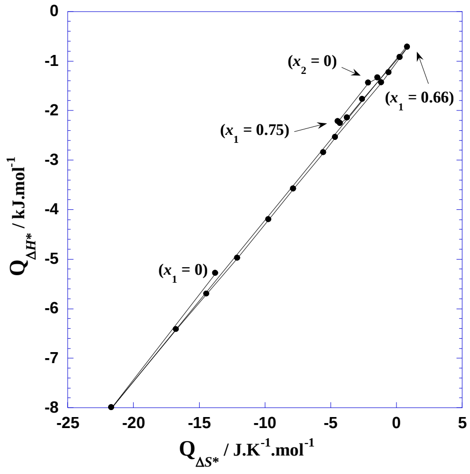

Figure 5 Correlation between The reduced Redlich-Kister functions relative to the enthalpy $Q_{\Delta H^*}$ / kJ·mol^{-1} of the entropy $Q_{\Delta S^*}$ / J·K^{-1}·mol^{-1} of activation of viscous flow for DME (1) + PPC (2) mixtures in the temperature range (298.15 to 318.15 K).

It is also observed that at all temperatures the interaction term of PPC-PPC-DME dominates the interaction term of DME-DME-PPC . The disruption of the intermolecular dipolar forces in PPC is the reason for the negative values of V^E .

In next works, these revealed specific interactions in the present binary mixture will be studied and confirmed by spectroscopic techniques.

In addition, among these techniques, the use of Belda parameters is introduced here and will allow us to give physical significance of the recent proposed empirical Belda equation in the present system.

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