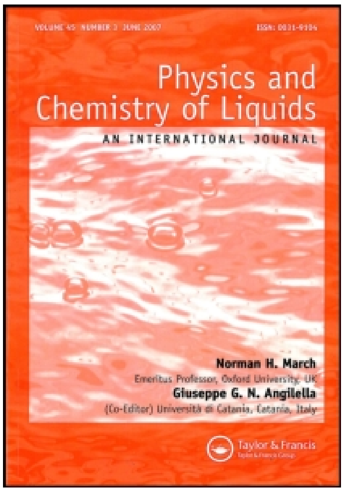

Physics and Chemistry of Liquids
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

Excess Molar Volume and Excess Viscosity of Benzyl Alcohol 4-Hydroxy-4-Methyl-2-Pentanone and Water 4-Hydroxy-4-Methyl-2-Pentanone Binary Systems at 298.15K

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To cite this Article De Doz, Mónica B. Gramajo and Solimo, Horacio N.(1995) 'Excess Molar Volume and Excess Viscosity of Benzyl Alcohol 4-Hydroxy-4-Methyl-2-Pentanone and Water 4-Hydroxy-4-Methyl-2-Pentanone Binary Systems at 298.15K', Physics and Chemistry of Liquids, 29: 2, 79 — 86

To link to this Article: DOI: 10.1080/00319109508028412

URL: http://dx.doi.org/10.1080/00319109508028412

Phys. Chem. Liq., 1995, Vol. 29, pp. 79–86
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EXCESS MOLAR VOLUME AND EXCESS VISCOSITY OF BENZYL ALCOHOL + 4-HYDROXY-4-METHYL-2-PENTANONE AND WATER + 4-HYDROXY-4-METHYL-2-PENTANONE BINARY SYSTEMS AT 298.15 K

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(Received 2 September 1994)

Densities, viscosities and refractive indices have been measured at 298.15 K for water + 4-hydroxy-4-methyl-2-pentanone and benzyl alcohol + 4-hydroxy-4-methyl-2-pentanone binary mixtures over the whole concentration range. From experimental densities and viscosities, excess molar volumes and excess viscosities, respectively have been calculated. These results are fitted with a Redlich-Kister polynomial relation and their coefficients were estimated. The experimental and calculate excess quantities are used to discuss the mixing behaviour of the components.

KEY WORDS: Benzyl alcohol + diacetone alcohol, water + diacetone alcohol, binary systems, excess molar volume, excess viscosity.

1 INTRODUCTION

Studies of molecular interactions in binary mixtures are subject of active investigation. The extensive use 4-hydroxy-4-methyl-2-pentanone (also called diacetone alcohol) in the chemical industry[1] has stimulated our attraction to obtain physical properties of systems where this chemical is included.

To gain some understanding about the nature of interactions in water (W) + 4-hydroxy-4-methyl-2-pentanone (DAA) and benzyl alcohol (BA) + 4-hydroxy-4-methyl-2-pentanone (DAA) mixtures, properties such as density, refractive index and viscosity have been measured at 298.15 K over the whole concentration range. These data were used to calculate the excess molar volume and excess viscosity of the mixtures. The dependence of these excess quantities with the concentration were fitted to a Redlich-Kister-type polynomial relation[2] in order to estimate the coefficients and standard errors.

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2 EXPERIMENTAL SECTION

A. Chemicals

Water was bidistilled in an all-glass apparatus. Benzyl alcohol (Mallinckrodt, A.R.) was dried over activated CaO and fractionally distilled at reduced pressure. 4-hydroxy-4-methyl-2-pentanone (Sintorgan, technical grade) was five times fractionally distilled over CaH_2 at reduced pressure[3]. All middle organic fractions were collected and passed through a glass column packed with 4 nm molecular sieves, and stored over activated molecular sieves to prevent water absorption.

The purities of the samples were checked by comparing the measured densities, viscosities and refractive indices of the components with those reported in the literature[4], and they are shown in Table 1.

B. Apparatus and procedure

Binary mixtures were prepared by mixing accurately weighed quantities of the pure liquids.

Densities of the pure components and their binary mixtures were measured with an Anton Paar electronic densimeter, DMA 45, with an appreciation of ± 0.1 Kg m^{-3}; refractive indices with an aus Jena Abbe refractometer with an accuracy of $\pm$ 0.0001, and viscosities with a Schott-Gerätte AVS 400 viscosimeter with an accuracy of $\pm$ 0.001 mPa s.

3 RESULTS AND DISCUSSION

Table 2 lists experimental values of densities, viscosities and refractive indices of (W + DAA) and (BA + DAA) systems at 298.15 K. Figure 1 and 2 plot these properties against water or benzyl alcohol mole fraction.

Density, refractive index and viscosity show a little deviation from the additivity law when these properties are plotted against the mole fraction of one component for the (BA + DAA) binary system, while for the (W + DAA) binary system the strong deviation is a consequence of their higher polarity and the presence of specific interactions between the components. The maximum in the viscosity curve at $x_W = 0.6$ corroborates this conclusion (see Fig. 1).

Table 1 Densities (ρ), refractive indices (n_D) and viscosities (η) of pure components at 298.15 K.

Compound	ρ (*Kg* m^{-3})		n_D		η (*mPa s*)	
	exptl.	*lit.*	*exptl.*	*lit.*	*exptl.*	*lit.*
W	997.1	997.1	1.3328	1.3328	0.997	0.9971
BA	1041.4	1041.27	1.5340	1.53837	5.737	5.687
DAA	934.2	934.2	1.4223	1.4213	2.902	2.9[a]

[a] At 293.15 K

Table 2 Experimental densities (ρ), viscosities (η), and refractive indices (n_D) for the systems W + DAA and BA + DAA at 298.15 K*.

$x^{@}$	ρ	η	n_D
	W + DAA		
0.0000	934.2	2.902	1.4223
0.2547	943.6	4.143	1.4227
0.4824	958.4	5.758	1.4198
0.6067	968.2	6.204	1.4162
0.7114	977.4	5.917	1.4105
0.7760	984.3	5.315	1.4046
0.8342	989.2	4.609	1.3971
0.8860	995.1	3.616	1.3863
0.9237	998.0	2.698	1.3743
0.9508	998.9	2.022	1.3636
0.9511	998.9	2.022	1.3636
0.9717	998.8	1.516	1.3521
0.9830	997.9	1.261	1.3453
1.0000	997.1	0.997	1.3328
	BA + DAA		
0.0000	934.2	2.902	1.4223
0.0518	938.1	2.886	1.4281
0.1087	944.1	3.021	1.4338
0.1705	950.8	3.199	1.4402
0.2406	959.4	3.410	1.4474
0.3325	969.3	3.670	1.4575
0.3445	970.7	3.703	1.4590
0.4344	979.9	3.968	1.4692
0.5378	991.4	4.295	1.4810
0.6345	1003.0	4.596	1.4934
0.7171	1010.7	4.831	1.5036
0.7554	1014.9	4.935	1.5080
0.8122	1020.9	5.096	1.5152
0.8780	1028.2	5.303	1.5227
0.9123	1032.2	5.420	1.5265
0.9146	1031.7	5.430	1.5267
1.0000	1041.4	5.737	1.5340

* Units: ρ, (Kg m^{-3}); η, (mPa s); V^E, (10^6 m^3 mol^{-1}); η^E, (mPa s)
$^{@}$ $x = x_W$; $x = x_{BA}$ for (W + DAA) and (BA + DAA) systems, respectively.

The excess molar volumes (V^E) are calculated with the following equation:

$$V^E = x_1 M_1(\rho^{-1} - \rho_1^{-1}) + x_2 M_2(\rho^{-1} - \rho_2^{-1}) \tag{1}$$

where x_1 and x_2 are the mole fractions of the components, M_1 and M_2 are their molecular weights, ρ, ρ_1 and ρ_2 are the densities of the solution and of the pure components, respectively.

Excess viscosities (η^E) were obtained by the following equation:

$$\eta^E = \eta - \exp(x_1 \ln \eta_1 + x_2 \ln \eta_2) \tag{2}$$

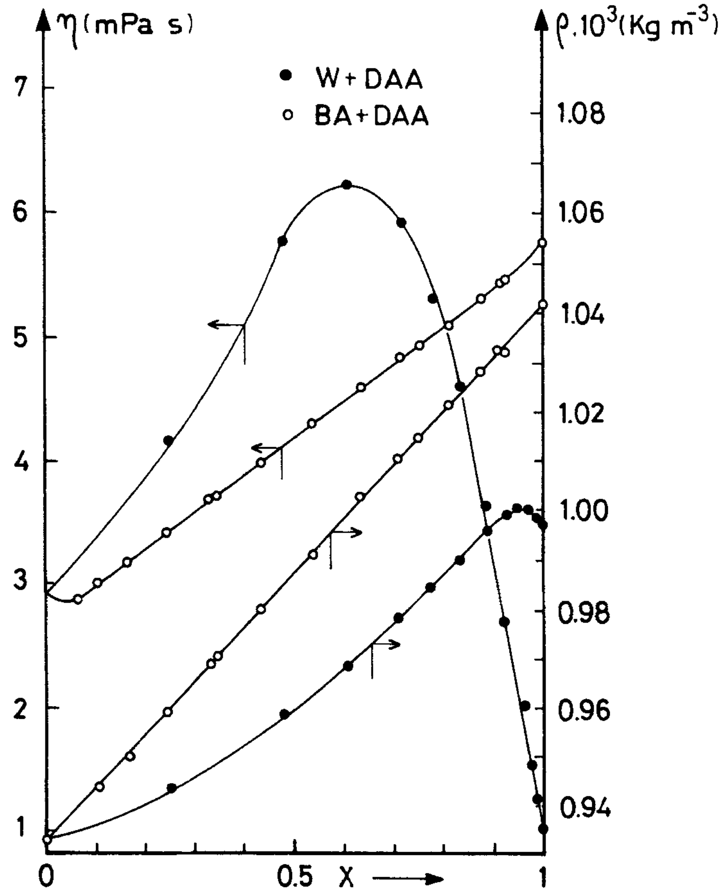

Figure 1 Experimental densities (ρ) and viscosities (η) against mole fraction (x) of: x_W for (W + DAA) and x_{BA} for (BA + DAA) systems.

where η, η_1 and η_2 are the viscosity of the solution and of the pure components, respectively. The additivity law represented in a logarithmic form was taken for ideal mixtures, according to the Eyring model[5].

Excess functions were fitted with a Redlich-Kister equation of the type:

$$X^E = x_1(1-x_1)\sum_{j=1}^{n} a_j(1-2x_1)^{j-1} \tag{3}$$

where X^E is the excess quantity (V^E or η^E), and a_j are the coefficients obtained by a linear least squares fitting procedure. In each case the optimum number of coefficients was ascertained from an examination of the variation of the standard error of estimate (σ)

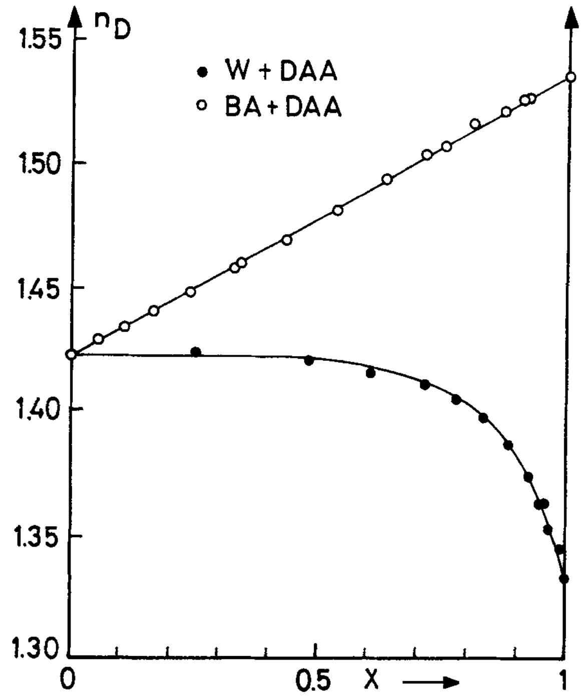

Figure 2 Experimental refractive indices (n_D) against mole fraction (x) of: x_W for (W + DAA) and x_{BA} for (BA + DAA) systems.

with n (calculated with a VAX 11/780 computer):

$$\sigma = \left[\sum (X^E_{\text{obs}} - X^E_{\text{cal}})^2 / (n_{\text{obs}} - n) \right]^{1/2} \tag{4}$$

where $n_{\text{obs.}}$ is the number of experimental points. The values adopted for the coefficients a_j and the standard error of estimates associated with Eq. (4) are summarized in Table 3.

Figure 3 shows the experimental values of V^E and η^E as a function of the mole fraction of water or benzyl alcohol for the two binary systems. The continuous curves were calculated from Eq. (3) using the adopted values of the coefficients.

Table 3 Coefficients, a_j, and standard errors, σ, for representations of the excess functions by Eq. 3*.

System	a_1	a_2	a_3	a_4	a_5	a_6	σ
W + DAA 10^6 V^E	−5.1966	2.8019	0.3879	2.1521			0.01
η^E	17.0893	−16.8449	−14.9223	0.9572	59.7343	59.9284	0.02
BA + DAA 10^6 V^E	−2.0406	0.7987	−0.5223	−3.7805	3.9926	7.3885	0.04
η^E	−0.5811	−0.7220	−0.1632	0.2532	−0.2014	−0.4284	0.0004

* Units: V^E, m^3 mol^{-1}; η^E, mPa s

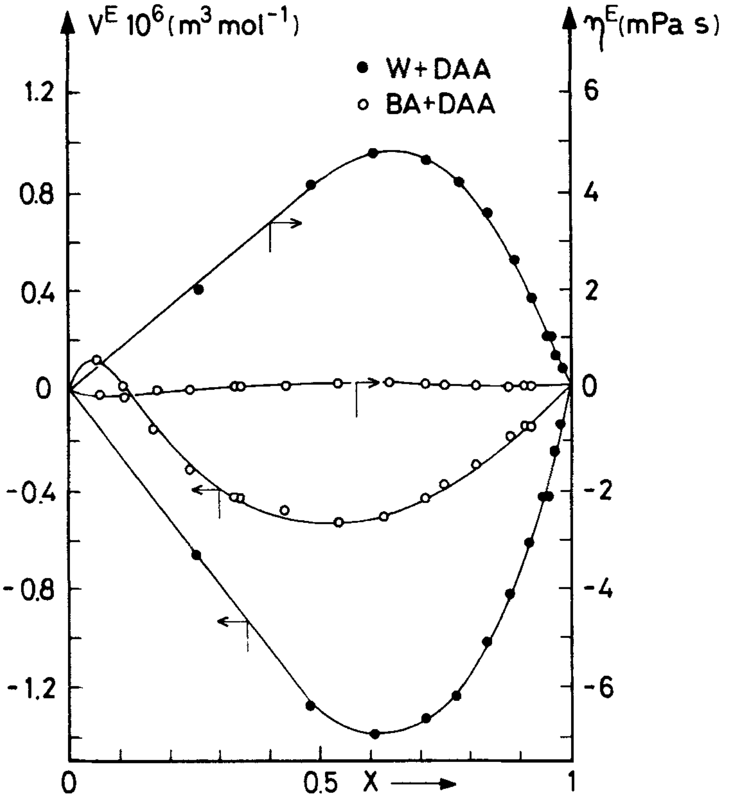

Figure 3 Excess molar volumes (V^E) and excess viscosities (η^E) against mole fraction (x) of: x_W for (W + DAA) and x_{BA} for (BA + DAA) systems.

Water, benzyl alcohol and diacetone alcohol are polar molecules associate through hydrogen bond in their pure state, but only DAA has an intramolecular hydrogen bond[6,7] which is more difficult to be broken by the addition of other specie when the mixture is produced. However, there is spectroscopic evidence[6] that DAA has at least one quarters of its molecules with this type of linkage broken in the pure state.

Several effects may contribute to the values of V^E in these systems, such as: (i) breaking of the hydrogen-bonded structure of the liquids, which gives a positive contribution to V^E, (ii) unfavorable interaction between groups which also produce a positive contribution, (iii) interstitial accommodation of the smaller component within the remain hydrogen-bonded structure of the bigger one, (iv) specific interactions with formation of new chemical species in the solution[8]. These last two effects give a negative contribution to V^E.

From the experimental results we deduce that the negative effects mentioned above are more important than the positive ones, since the excess molar volume for the binary system (W + DAA) is negative over the whole concentration range which means a volume contraction when the mixture is made. This situation could be explained accepting that intermolecular association complexes between both species have been formed, since the interstitial acommodation between both molecules is less probable due to the size and structure of them.

A sigmoid curve was obtained for (BA + DAA) binary systems when V^E is plotted against x_{BA}. The positive values could be explained in terms of the disruption of the intermolecular hydrogen bond of BA, where the maximum positive interactions are present at $x_{BA} = 0.05$. On the other hand, an intermolecular association between both species could be explain the negative values.

For both systems, negative excess viscosities correspond to positive excess molar volumes, as usually, which means that association forces are dominant[9]. This effect is marked for the binary system (W + DAA), where a pronounced maximum is observed at $x_W \cong 0.66$, while for the other system the maximum is not well defined because their values are close to zero, presenting a slightly sigmoid cuve. Fialkov[10] conclude that for systems whose excess viscosities show a behavior similar to (W + DAA) system, the composition of the intermolecular complex can be fixed, at least to a first approximation, according to the molar relation indicated by the maxima. These complexes are more stable when the positive values of the maxima of η^E are bigger. The stoichiometric relation of the formed complex can be obtained from Figure 3 for (W + DAA) system; it is 2W.DAA, but its probable structure (if it is true) can not be given analyzing only these macroscopic properties.

Complexes solute-solvent have also been investigated by methods based upon the deviation from additivity of the refractive indexes[11,12]. For mixtures of two liquids, (W + DAA or BA + DAA), the excess refractive index (n_D^E) is given by:

$$n_D^E = n - (\phi_1 n_1 + \phi_2 n_2) \tag{5}$$

where n, n_1 and n_2 are the refractive index of the solution and pure components, respectively. ϕ_1 and ϕ_2 their corresponding volume fractions. For many binary systems, in which spectroscopic or other methods indicate that molecular interactions occurs, it is found that $n_D^E > 0.004$. Therefore, these authors conclude that $n_D^E > 0.004$ is indicated of complex formation. For (W + DAA) system, we have observed that n_D^E exceed this value over the whole concentration range which is in agreement with the conclusions arrived with the other excess properties. On the other hand, (BA + DAA) system n_D^E scarcely exceed the above value at $0.7171 \leqslant x_{BA} \leqslant 0.8780$ in agreement with the slightly positive values of excess viscosity in the same concentrarion range, indicating that some intermolecular complexes have been formed, concordantly with the conclusions obtained from excess molar volumes and excess viscosity.

Acknowledgement

We wish to thank the CIUNT-UNT-Argentina, for financial support.

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