EXCESS MOLAR VOLUMES OF BINARY MIXTURES
(ACETIC ACID + WATER, BENZENE, *N*-HEXANE AND *N*-HEPTANE) AT SEVERAL TEMPERATURES

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The densities for the binary mixtures (acetic acid with water, or benzene, or n-hexane, or n-heptane) at several temperatures T = (296.15, 302.15, 308.15, 314.15, 319.15) K have been measured over the whole composition range and atmospheric pressure along with the properties of the pure components. The experimental values of excess molar volumes, V^E_m, were obtained for the same set of systems and are correlated with a suitable parametric equation[1] which is function of the so-called active fraction. All systems studied are positive, $V^E_m > 0$, except for acetic acid – water where the deviation is negative over the composition range.

INTRODUCTION

This article presents other experimental information, to continue on from a working project carried out in our laboratory.[2-4] In the current literature, there are multiple study mixtures containing acetic acid and a variety of organic or inorganic liquids studied by different authors[5-12] with respect to different properties. With the contribution of the information from this study and others taken from the literature, we aim to analyze one aspect on these mixtures; we attempt to enlarge our knowledge on the behaviour of this kind of systems, because is difficult to explain owing to the presence of specific interactions. In the chemical industry, the information based on the densities of pure liquids and liquid mixtures is important from both practical and theoretical points of view, in applications in chemical engineering, in order to determine excess thermodynamic properties[13-15] such as volumes, viscosity, enthalpies and entropies of mixing, which reflect the extent of deviations from non-ideality. Distillation, the most widespread

technique for separating liquid mixtures, is in particular the chief separation method used in the chemical industries. Experimental measurements of density and other property for binary and ternary mixtures have gained much importance in many chemical industries and engineering disciplines. The study of excess volume is the first step to a fundamental understanding of the thermodynamics of an important class of molecules.

We have presented in this paper experimental densities for the four binary mixtures (acetic acid with water, or benzene, or *n*-hexane, or *n*-heptane) at several temperatures (T = 296.15, 302.15, 308.15, 314.15, 319.15 K) at atmospheric pressure for the whole range of compositions. Using these data, excess molar volume, V^E_m have been calculated. In general, the sign of V^E_m depends upon the relative magnitude of contractive and expansive effects that arise on mixing of the components.

The factors that cause contraction on mixing are strong specific and physical interactions (dipole–dipole or dipole–induced dipole interactions), favorable geometrical fitting of component molecules and occupation of void spaces of one

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component by the other. A special type of interaction is hydrophobic hydration which occurs in water-rich regions when an organic solute molecule is surrounded by a network of highly ordered water molecules. The factors that cause expansion of volume on mixing of the components are dissociation of one component or both of the components, steric hindrance and geometrical mismatch of the molecules and formation of weaker solute–solvent bonds than solute–solute and solvent–solvent bonds.

The experimental results are analyzed by the Redlich-Kister polynomial equation to derive the binary coefficients and estimate the standard errors. The calculated results are discussed in terms of intermolecular interactions.

EXPERIMENTAL

The liquids involved in the experiments, acetic acid, water, benzene, *n*-hexane and *n*-heptane were purchased from Fluka and Aldrich, and were of maximum purity. Before use all substances were degassed with ultrasounds for several days and then stored in the dark on molecular sieves (Fluka, 0.3 nm) to remove the possible moisture. In order to characterize the quality of substances, the physical properties of pure compounds, density ρ, dynamic viscosity η and the refractive index n_D, were measured at 298.15 K. The values obtained are shown in Table 1 together with the values reported in literature at the same conditions; their comparison is acceptable in all cases. Densities for pure compounds and mixtures were measured with a digital vibrating-tube densimeter Anton Paar, model DMA 4500, with a reading error of ± 0.02 kg m^{-3}. The precision in the temperature control by a Peltier effect was of ± 0.01 K. From density measurements and know the composition, x, of the samples prepared with an uncertainty better than $\pm 5 \cdot 10^{-5}$, the V^E_m where indirectly calculated with an uncertainty of $\pm 2 \cdot 10^{-9}$ m^{3}mol^{-1}.

Table 1

Physical properties of pure substances measured at T = 298.15 K and atmospheric pressure, where ρ, η and n_D denote the density, viscosity and refractive index, respectively

Compound	$\overline{kg \cdot m^{-3}}$		$\dfrac{10^{3}}{Pa\ s}$		n_D	
	Exp.	Lit.	Exp.	Lit.	Exp.	Lit.
acetic acid	1043.50	1043.66[a]	1.1306[c]	1.1310[*]	1.3644	1.3698[a]
benzene	873.46	873.70[a] 873.60[b]	0.6015[c]	0.6028[a]	1.4980	1.4979[a,b]
n – hexane	654.42	654.81[a]	0.2951[c]	0.2985[a]	1.3750	1.3723[a]
n – heptane	679.43	679.51[a] 679.46[b]	0.3922[c]	0.3967[a]	1.3853	1.3851[a,b]

[a] Ref. [16]; [b]Ref. [17]; [*]Values interpolated from Ref. [16]; [c]Ref. [3].

RESULTS AND DISCUSSION

The values of excess molar volumes, V^E_m, were correlated with a following equation:

$$V^E_m = V_m - \sum_{i=1}^{2} V_i x_i \qquad (1)$$

where x_i, and V_i, represent the mole fraction and molar volume of the i pure component of the mixture respectively. The molar volume, V_m, of the mixture was calculated from the following equation:

$$V_m = \sum_{i=1}^{2} x_i M_i / \rho_m \qquad (2)$$

where ρ_m is the molecular weight of component i in the mixture. The experimental values of the excess volume V^E_m are fitted to the Redlich-Kister equation:

$$V^E_m = x_1 x_2 - \sum_{k=0}^{m} A_{ki} (2x_1 - 1)^k \qquad (3)$$

where A_k represents the parameters (Table 2).

The standard errors, σ, between the calculated and the experimental values have been estimated using:

$$\sigma = \left[\frac{\sum \left(Y_{exp} - Y_{cal} \right)^2}{(n - p)} \right]^{1/2} \qquad (4)$$

where n is the number of experimental points and p is the number of estimated parameters and Y represent the excess volume.

Fig. 1 shows the plots of densities as a function of mole fraction of water[18], benzene, *n*-hexane[18] and *n*-heptane[18] in acetic acid systems at T = (296.15, 302.15, 308.15, 314.15, 319.15) K.
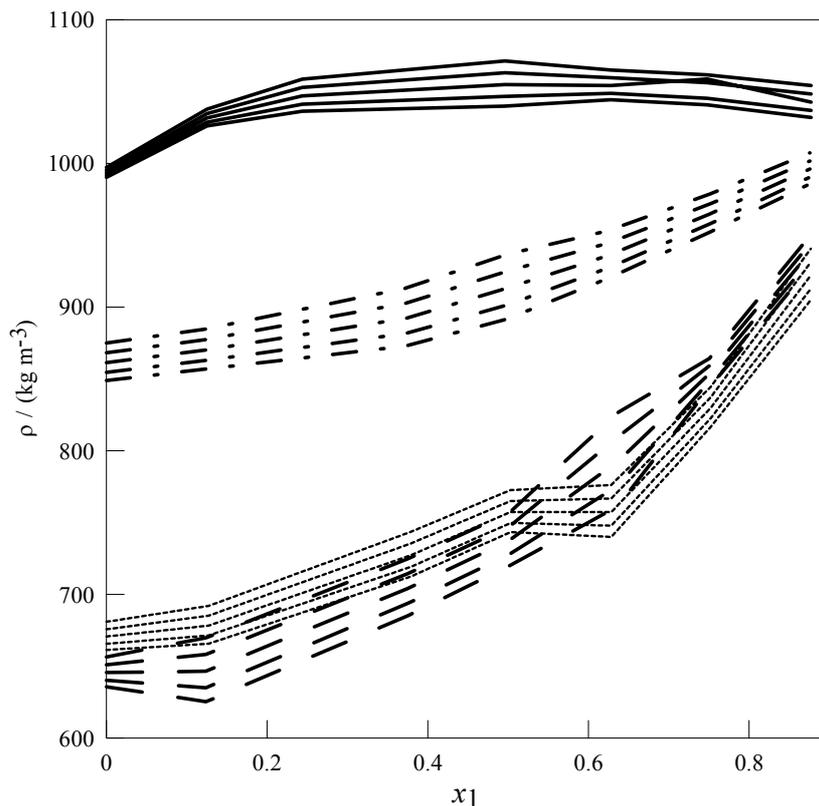
Fig. 1 – Plots of density (ρ) versus x_1 of water (-), benzene (-·-·-), n-hexane (---) and n-heptane (·····)
in acetic acid systems at T = (296.15, 302.15, 308.15, 314.15, 319.15) K.

Figs. 2-5 represent the excess volumes against the mole fraction and the Redlich-Kister fit, for the acetic acid + water, + benzene, + n-hexane, + n-heptane binary systems.
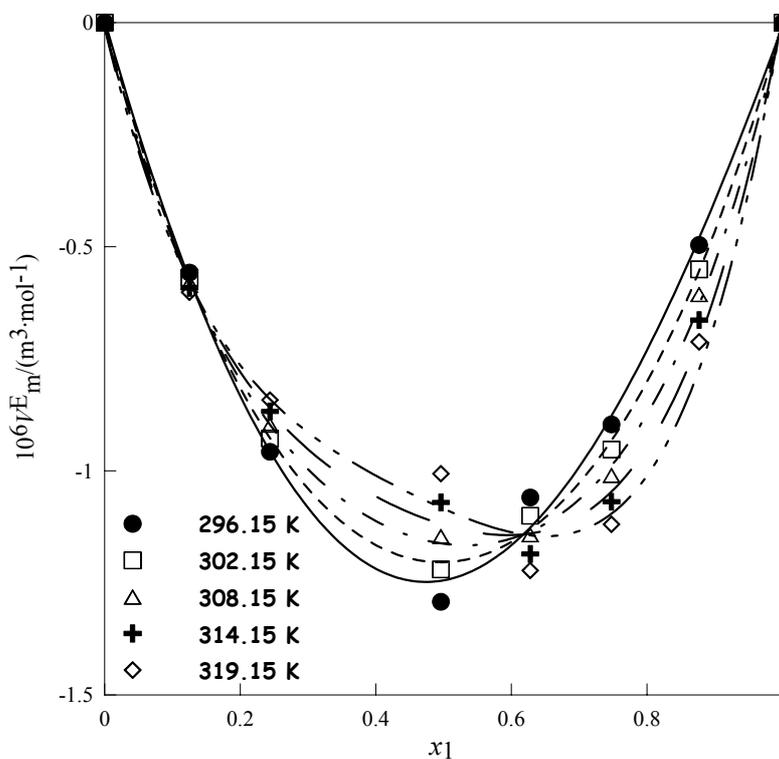

Fig. 2 – Excess molar volume for acetic acid-water mixtures.
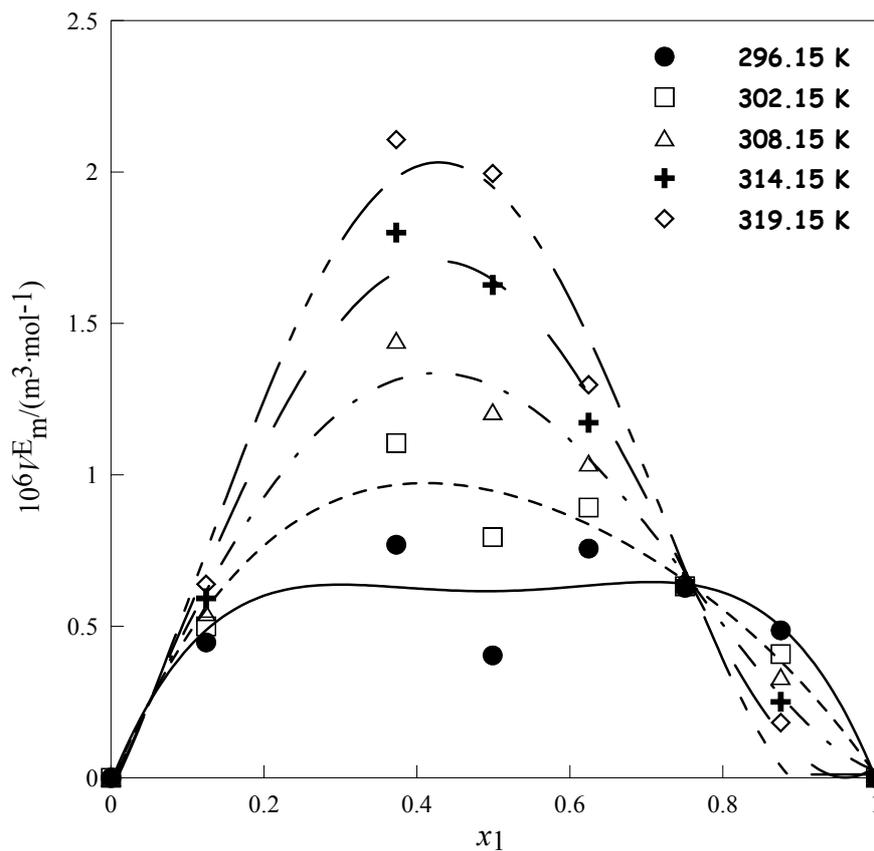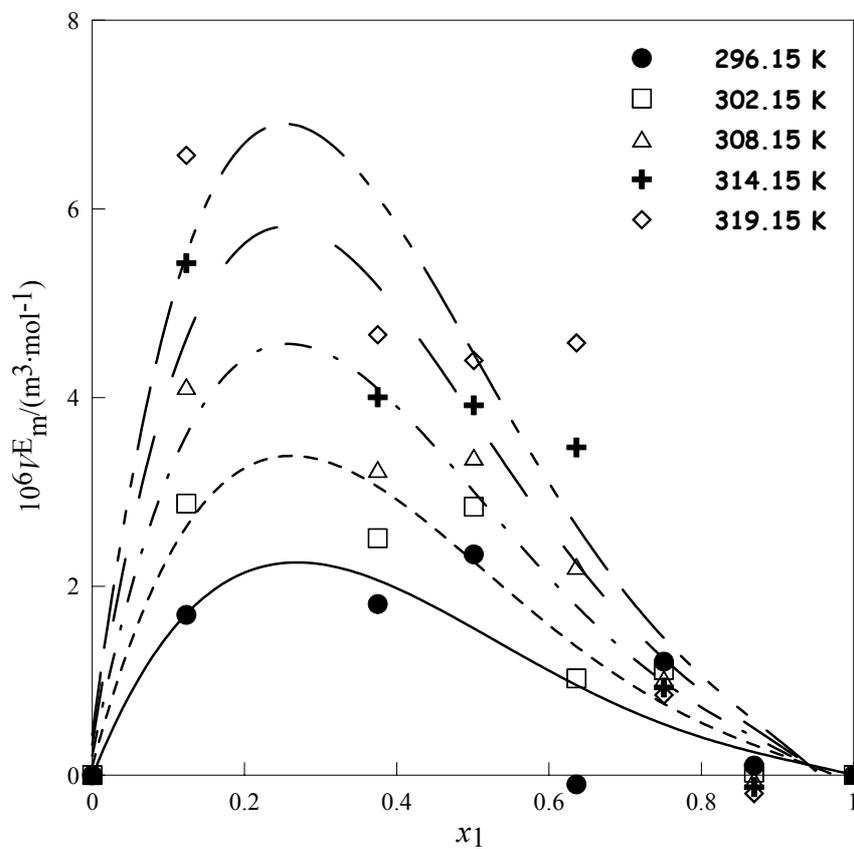
Fig. 3 – Excess molar volume for acetic acid-benzene mixtures.

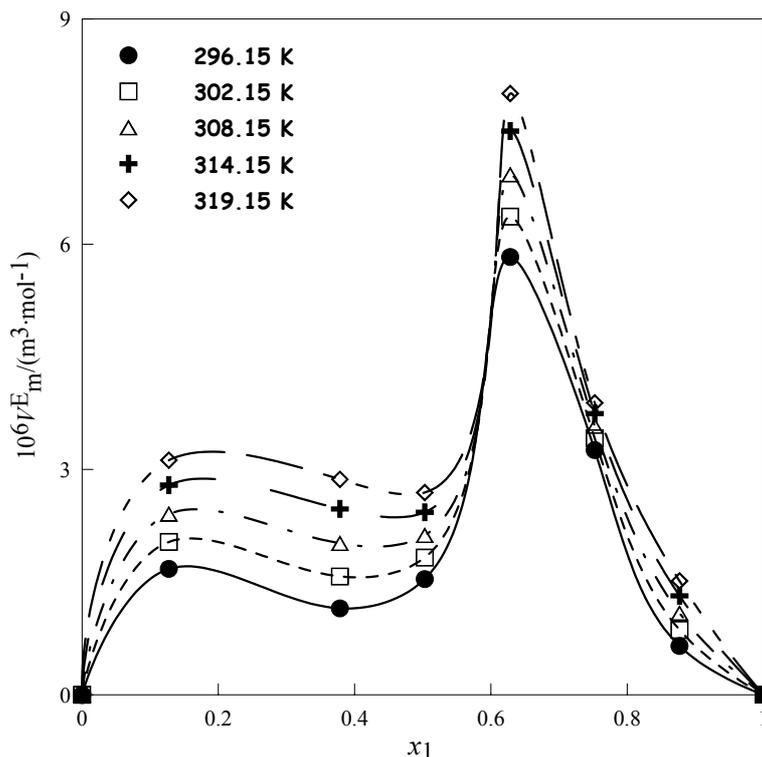Fig. 4 – Excess molar volume for acetic acid-*n*-hexane mixtures.

Fig. 5 – Excess molar volume for acetic acid-*n*-heptane mixtures.

Table 2 shows the A_i coefficients obtained were achieved by applying a least-squares procedure to each system, establishing as objective function the minimization of the standard deviation, σ, of the corresponding excess quantities.

The excess molar volume is related to the molecular interactions between the components of the mixture. Fig. 2 shows that, V^E_m is negative for acetic acid with water over the whole composition range. Excess molar volume decreases with increasing temperature up to $x_1 = 0.7$ and above this value it increases with temperature. In case of systems acetic acid with benzene, *n*-hexane and *n*-heptane V^E_m is positive. Looking at Fig. 3 we notice the excess molar volume increase with increasing temperature in the range 296.15-319.15 K, and at higher values of these acid molar fraction ($x_1 > 0.7$) decreases with increasing temperature. In the case of systems with *n*-hexane and *n*-heptane, excess molar volume shows the maximum for the first system at $x_1 = 0.3$ and for the second at $x_1 = 0.3$, $x_1 = 0.7$ respectively.

The excess volumes mainly depend on two effects: 1) variation of intermolecular forces when two components come into contact and 2) variation of molecular packing as a consequence of difference in the size and shape of the molecules of the components.[19] If the interactions between the molecules of two mixed components are weaker than in the pure component, the excess volume will be positive as it occurs for the compounds in this work (acetic acid with benzene, or *n*-hexane, or *n*-heptane). The interaction between these substances is probably due to kinds of interaction: the relatively strong interaction between aromatic π-electrons (π-π interactions), and the aromatic-hydrophilic group and aliphatic-hydrophilic group interactions. Interactions between acetic acid and water are extremely complex (acetic acid and water are self-associated liquids through H-bonding). Acetic acid posses hydrophilic –COOH group as well as hydrophobic group. The mode of interaction of these two groups toward water is completely different. The hydrophilic –COOH group of acetic acid an H-bond with water through hydrophilic interactions and disrupts normal water structure, while the alkyl group promotes the structure of water molecules surrounding this group through hydrophobic hydration. A better understanding of water–acid interaction is of vital importance in the field of solution chemistry, as it can provide important information regarding hydrophilic and hydrophobic interactions. It is believed that both these effects, hydrophilic and hydrophobic, take place in water-rich regions of aqueous acid solutions.

Table 2

Coefficients A_i (equation 3) and standard deviation σ (equation 4) obtained
in the correlations of experimental values

Mixture	T/K	A_0	A_1	A_2	A_3	A_4	σ
acetic acid-water	296.15	-0.206	-1.094	0.398	0.915	-5.010	0.766
	302.15	0.721	-0.108	-1.034	0.105	-4.797	0.797
	308.15	1.680	0.897	-2.509	-0.721	-4.579	0.999
	314.15	2.674	1.923	-4.026	-1.566	-4.356	0.992
	319.15	3.529	2.793	-5.324	-2.283	-4.167	0.983
acetic acid-benzene	296.15	-10.96	2.345	9.787	-1.139	2.224	0.786
	302.15	-8.492	3.686	5.758	-2.682	3.605	0.738
	308.15	-5.358	5.003	1.181	-4.133	5.066	0.975
	314.15	-2.785	6.648	-3.133	-5.840	6.524	0.999
	319.15	0.288	7.897	-7.334	-7.234	-7.824	0.998
acetic acid-*n*-hexane	296.15	-22.00	0.867	17.26	-10.04	5.666	0.744
	302.15	9.737	-17.52	1.830	-7.464	9.245	0.964
	308.15	43.16	-37.01	-14.39	-4.663	13.00	0.999
	314.15	70.39	-57.68	-31.47	-1.621	16.94	0.996
	319.15	109.2	-75.87	-46.39	1.113	20.39	0.989
acetic acid-*n*-heptane	296.15	-9.962	-78.62	5.382	37.67	10.81	0.796
	302.15	-0.340	-80.64	1.416	37.86	12.59	0.754
	308.15	9.653	-82.74	-2.716	38.05	14.44	0.714
	314.15	20.03	-84.91	-7.026	38.25	16.36	0.679
	319.15	29.00	-86.78	-10.75	38.43	18.02	0.653

CONCLUSIONS

This paper is focused on the study and measurement of physical properties of mixtures containing acetic acid with water, or benzene, or *n*-hexane, or *n*-heptane at several temperatures T = (296.15, 302.15, 308.15, 314.15, 319.15) K, as a continuation of a prevision work.

The experimental values of excess molar volumes, V^E_m, are fitted to the Redlich-Kister equation. There has been established the type of deviation from the ideal behavior for the binary systems and has been related to the molecular interactions between the components of the mixture.

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