Effect of temperature on some volumetric properties for ethanol + water mixtures

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Summary

The excess molar volumes and partial molar volumes of components were investigated from density measurements of the entire range of mole fractions for the ethanol + water system at 20.0, 25.0, 30.0, 35.0 and 40.0 °C. The results of excess molar volumes were fitted by Redlich-Kister equation using third degree polynomials and compared with those of literature for other systems. The systems exhibited large negative excess volumes (up to 1.09 cm^3 mol^{-1}) due to increased interactions like hydrogen bonding between unlike molecules or very large differences in the molar volumes of pure components. The effect of temperature on the different volumetric properties studied was also analyzed. Finally, the volume thermal expansion coefficients were also calculated founding values varying from 0.00025 K^{-1} for pure water up to 0.00112 K^{-1} for pure ethanol at 25.0 °C.

Key words: Ethanol – Water – Binary liquid mixtures – Excess volumes – Partial volumes

Resumen

Efecto de la temperatura sobre algunas propiedades volumétricas del sistema binario etanol-agua

A partir de medidas de densidad sobre todo el intervalo de composición, se evaluaron los volúmenes molares de exceso y molares parciales de los componentes en el sistema etanol-agua a 20.0, 25.0, 30.0, 35.0 y 40.0 °C. Los volúmenes de exceso se ajustaron al modelo de Redlich-Kister usando polinomios de tercer grado y los resultados fueron comparados con los presentados por otros sistemas líquidos. Este sistema presentó volúmenes de exceso altamente negativos (hasta 1.09 cm^3 mol^{-1}) debido a interacciones fuertes tales como enlaces de hidrógeno entre las moléculas de los dos compuestos y además, a la diferencia en volúmenes molares de los componentes puros. También se estudió el efecto de la temperatura sobre las diferentes propiedades volumétricas consideradas. Finalmente, también se calcularon los coeficientes de expansión térmico volumétricos encontrando valores entre 0.00025 K^{-1} para el agua pura y 0.00112 K^{-1} para el etanol puro a 25.0 °C.

Palabras clave: Etanol – Agua – Mezclas líquidas binarias – Volúmenes de exceso – Volúmenes parciales

Introduction

Water-cosolvent mixtures are used widely in pharmacy in order to increase the solubility of drugs poorly soluble in water during the design of homogeneous pharmaceutical dosage forms, such as syrups and elixirs, among others (1, 2). Ethanol is the cosolvent most used in design

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nowadays and especially for elaboration of peroral and parenteral medications (3).

The cosolvent mixtures obtained using this cosolvent and water are highly non-ideal due to increased interactions between unlike molecules and large differences in molar volumes of pure components, which conduce to non-additive volumes on mixing (4, 5). For this reason it is necessary to characterize the volumetric behavior of these binary mixtures as a function of temperature in order to extend the physicochemical information available for liquid mixtures. This information is useful in the pharmaceutical dosage forms design, and on the other hand, to inside in the intermolecular interactions present in these pharmaceutical systems (6).

In this report, the excess molar volumes and the partial molar volumes of the binary system of ethanol + water at various temperatures were calculated in addition to other volumetric properties according to procedures widely exposed in literature (7-10). Ethanol and water have proton-donor and proton-acceptor groups, which imply a significant degree of H-bonding, leading to self-association in the pure state, and on the other hand, leading to mutual association in their binary mixtures (11).

Experimental

Materials

In this investigation the following solvents were used: absolute ethanol A.R. (EtOH), obtained from Merck, which was maintained over molecular sieve to obtain a dry solvent (the dryness obtained was demonstrated by the density value obtained which is coincident with those presented in literature (10, 11)), and distilled water (W), conductivity < 2 μS, obtained from the Laboratory of Industrial Pharmacy, of the Universidad Nacional de Colombia.

Cosolvent mixtures preparation

All EtOH-W cosolvent mixtures were prepared in quantities of 40.00 g by weight using a Mettler AE 160 analytical balance with sensitivity ± 0.1 mg, in concentrations from 10 % w/w up to 90 % w/w varying in 10 % to study nine mixtures and the two pure solvents. Precautions were taken in order to prevent possible evaporation. The mixtures were allowed stand in Magni Whirl Blue M water baths at temperatures from 20.00 °C up to 40.00 °C varying in 5.00 ± 0.05 °C for at least 30 minutes previous to density determinations.

Density determination

This property was determined using a DMA 45 Anton Paar digital density meter connected to recirculation thermostatic water baths according to a procedure previously described (12). The equipment was calibrated according to Instruction Manual using air and water at the different temperatures studied (13). All preparations and measurements were repeated at least five times and the results were averaged. From density values all thermodynamic properties were calculated as it will be indicate in the next section.

Results and Discussion

In Table 1 the composition of EtOH-W mixtures in weight percent and mole fraction in addition to density values at several temperatures studied are presented. The mean standard deviation obtained in density measurements was 0.0001 g cm^{-3}. Our density values are in good agreement with those presented in literature, especially for 20.0 °C (14) and 25.0 °C (15). The differences were in general lower than 0.0002 g cm^{-3} although the differences found respect to those presented by Resa *et al.* for pure ethanol (10) and those presented by Belda *et al.* for binary mixtures (11) are higher. It should be kept in mind that the values reported by Belda *et al.* were determined using an immersion density meter while our data were determined by oscillatory digital density meter. In all cases the density decreases almost linearly as the temperature increases except for water (Table 1).

The density of a liquid binary mixture is expressed as

$$\rho = \frac{x_1 M_1 + x_2 M_2}{x_1 V_1 + x_2 V_2 + V^E} \qquad \text{(Eq. 1)}$$

Where, x_1 and x_2 are the mole fractions, M_1 and M_2 are the molar masses, V_1 and V_2 are the molar volumes, for both components respectively, and V^E is the molar excess volume. In Table 2 the molar volumes for binary mixtures at all temperatures are presented which were calculated from Eq. 2.

$$V = \frac{x_1 M_1 + x_2 M_2}{\rho} \qquad \text{(Eq. 2)}$$

On the other hand, the excess volumes calculated from Eq. 3 (where, ρ_1 and ρ_2 are the densities of pure components) at all temperatures studied are also presented in Table 2. This behavior is shown graphically in Figure 1 at 25.0 °C.

$$V^E = \frac{x_1 M_1 + x_2 M_2}{\rho} - \left(\frac{x_1 M_1}{\rho_1} + \frac{x_2 M_2}{\rho_2} \right) \qquad \text{(Eq. 3)}$$

Table 1. Densities for ethanol + water mixtures at various temperatures.

Ethanol		**Temperature / °C**				
% w/w	Mole fraction	20.00	25.00	30.00	35.00	40.00
0.00	0.0000	0.9982	0.9970	0.9957	0.9940	0.9920
10.00	0.0417	0.9818	0.9802	0.9787	0.9767	0.9747
20.00	0.0891	0.9686	0.9666	0.9639	0.9612	0.9585
30.00	0.1436	0.9538	0.9509	0.9474	0.9441	0.9407
40.00	0.2068	0.9352	0.9321	0.9277	0.9241	0.9202
50.00	0.2812	0.9138	0.9100	0.9059	0.9017	0.8977
60.00	0.3698	0.8911	0.8872	0.8829	0.8793	0.8744
70.00	0.4772	0.8677	0.8637	0.8592	0.8547	0.8505
80.00	0.6101	0.8435	0.8392	0.8347	0.8311	0.8261
90.00	0.7788	0.8180	0.8132	0.8094	0.8058	0.8007
100.00	1.0000	0.7895	0.7853	0.7811	0.7767	0.7720

Unit: g cm^{-3}

Table 2. Molar volumes, excess molar volumes, and partial molar volumes of components for ethanol + water mixtures at various temperatures.

T / °C	Ethanol		Molar volume (a)	Excess volume(a)	$\partial V/\partial x_{EtOH}$(a)	$\overline{V}_{EtOH}$(a)	$\overline{V}_{W}$(a)
	% w/w	Mole fraction					
20.00	0.00	0.0000	18.05	0.000	34.44	52.49	18.05
	10.00	0.0417	19.54	-0.187	35.14	53.22	18.08
	20.00	0.0891	21.18	-0.459	35.91	53.90	17.99
	30.00	0.1436	23.12	-0.723	36.74	54.58	17.84
	40.00	0.2068	25.47	-0.916	37.65	55.34	17.68
	50.00	0.2812	28.35	-1.033	38.63	56.12	17.49
	60.00	0.3698	31.86	-1.094	39.68	56.87	17.19
	70.00	0.4772	36.19	-1.091	40.77	57.51	16.74
	80.00	0.6101	41.65	-0.987	41.86	57.98	16.11
	90.00	0.7788	48.73	-0.704	42.82	58.21	15.39
	100.00	1.0000	58.35	0.000	43.36	58.36	14.99
25.00	0.00	0.0000	18.07	0.000	34.70	52.77	18.07
	10.00	0.0417	19.58	-0.189	35.42	53.52	18.10
	20.00	0.0891	21.23	-0.462	36.21	54.21	18.00
	30.00	0.1436	23.19	-0.716	37.06	54.92	17.86
	40.00	0.2068	25.56	-0.913	37.98	55.68	17.70
	50.00	0.2812	28.47	-1.018	38.98	56.49	17.51
	60.00	0.3698	32.00	-1.082	40.03	57.23	17.20
	70.00	0.4772	36.36	-1.083	41.12	57.86	16.74
	80.00	0.6101	41.86	-0.974	42.18	58.31	16.13
	90.00	0.7788	49.02	-0.664	43.07	58.55	15.48
	100.00	1.0000	58.67	0.000	43.47	58.67	15.20
30.00	0.00	0.0000	18.10	0.000	35.29	53.39	18.10
	10.00	0.0417	19.61	-0.195	35.96	54.07	18.11
	20.00	0.0891	21.29	-0.452	36.69	54.71	18.02
	30.00	0.1436	23.27	-0.696	37.48	55.37	17.89
	40.00	0.2068	25.68	-0.876	38.35	56.09	17.75
	50.00	0.2812	28.60	-0.995	39.28	56.83	17.55
	60.00	0.3698	32.16	-1.057	40.28	57.54	17.26
	70.00	0.4772	36.55	-1.055	41.33	58.16	16.83
	80.00	0.6101	42.09	-0.949	42.37	58.61	16.24
	90.00	0.7788	49.25	-0.684	43.31	58.83	15.53
	100.00	1.0000	58.98	0.000	43.85	58.98	15.13

Table 2. Continuation.

T / °C	Ethanol		Molar volume $^{(a)}$	Excess volume$^{(a)}$	$\partial V/\partial x_{EtOH}{}^{(a)}$	$\bar{V}_{EtOH}{}^{(a)}$	$\bar{V}_{W}{}^{(a)}$
	% w/w	Mole fraction					
35.00	0.00	0.0000	18.13	0.000	35.84	53.97	18.13
	10.00	0.0417	19.65	-0.198	36.45	54.58	18.13
	20.00	0.0891	21.35	-0.451	37.11	55.15	18.04
	30.00	0.1436	23.35	-0.689	37.84	55.76	17.92
	40.00	0.2068	25.78	-0.869	38.64	56.43	17.79
	50.00	0.2812	28.73	-0.978	39.52	57.14	17.62
	60.00	0.3698	32.29	-1.069	40.47	57.80	17.32
	70.00	0.4772	36.74	-1.038	41.50	58.44	16.94
	80.00	0.6101	42.27	-0.983	42.57	58.87	16.30
	90.00	0.7788	49.47	-0.731	43.62	59.12	15.50
	100.00	1.0000	59.32	0.000	44.46	59.32	14.85
40.00	0.00	0.0000	18.17	0.000	36.15	54.32	18.17
	10.00	0.0417	19.69	-0.208	36.77	54.93	18.15
	20.00	0.0891	21.41	-0.456	37.45	55.52	18.07
	30.00	0.1436	23.44	-0.688	38.19	56.15	17.95
	40.00	0.2068	25.89	-0.864	39.00	56.82	17.82
	50.00	0.2812	28.86	-0.978	39.89	57.53	17.64
	60.00	0.3698	32.47	-1.044	40.85	58.21	17.37
	70.00	0.4772	36.92	-1.048	41.87	58.82	16.95
	80.00	0.6101	42.53	-0.962	42.92	59.27	16.34
	90.00	0.7788	49.79	-0.706	43.92	59.50	15.58
	100.00	1.0000	59.68	0.000	44.66	59.68	15.02

(a)Units: $cm^3\ mol^{-1}$

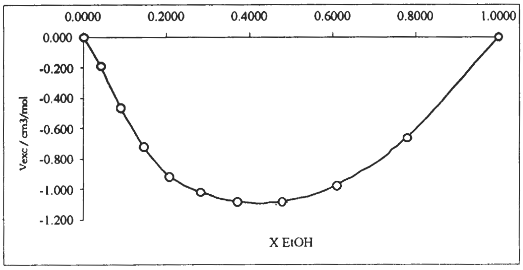

Figure 1. Excess molar volumes of ethanol + water mixtures at 25.00 °C

In all cases the excess volumes are largely negative (especially around 0.4 in mole fraction of ethanol, where is greater than 1 $cm^3\ mol^{-1}$) indicating contraction in volume. According to Fort and Moore (16), a negative excess volume is an indication of strong heteromolecular interactions in the liquid mixtures and is attributed to charge transfer, dipole-dipole, dipole-induced dipole interactions, and hydrogen bonding between the unlike components, while a positive sign indicates a weak interaction and is attributed to dispersion forces (London interactions) which are likely to be operative in every cases.

In the evaluated system, where the hydrogen bonding predominates, the contraction in volume has been interpreted basically in qualitative terms considering the following events: first: expansion due to depolymerization of ethanol and water by one another, second: contraction due to free volume difference of unlike molecules, and third: contraction due to hydrogen bond formation between ethanol and water through –OH •••OH bonding (5).

Thus, the large negative values of V^E over the free volume contribution indicate the presence of strong specific interactions with predominance of formation of hydrogen bonds between ethanol and water over the rupture of hydrogen bonding in ethanol-ethanol and water-water.

The excess molar volumes becomes less negative as the temperature is raised indicating volume expansion which points out the decrease in the interactions between ethanol and water molecules with increase in temperature.

The partial molar volumes for ethanol ($\bar{V}_{EtOH}$) and water ($\bar{V}_W$) were calculated by means of the classical Bakhuis-Roozeboom method by means Eqs. 4 and 5 (where x_{EtOH} is the mole fraction of ethanol) applied to variation of the respective molar volumes as a function of EtOH mole fraction (Table 2) and adjusting them to third degree polynomials by least squares regression analyses (6, 17, 18). The first derivatives were taken out on the polynomials obtained and solved at each composition point.

$$\bar{V}_{EtOH} = V + x_W \frac{dV}{dx_{EtOH}} \qquad \text{(Eq. 4)}$$

$$\bar{V}_W = V - x_{EtOH} \frac{dV}{dx_{EtOH}} \qquad \text{(Eq. 5)}$$

The $\bar{V}_{EtOH}$ $\bar{V}_W$ and values are also presented in Table 2 in addition to the slopes obtained at each composition (dV/dx_{EtOH}). Almost in all cases the partial molar volumes for ethanol and water in the mixtures are lower than those for the pure solvents. The partial volumes varied for ethanol from 53.52 cm^3 mol^{-1} (at 10 % w/w of EtOH) up to 58.55 cm^3 mol^{-1} (at 90 % w/w of EtOH), and varied for water from 18.10 cm^3 mol^{-1} (at 10 % w/w of EtOH) up to 15.48 cm^3 mol^{-1} (at 90 % w/w of EtOH). These results are coincident with the negative excess volumes obtained. The variation of this property is presented in Figure 2 as a function of EtOH mole fraction at 25.0 °C for ethanol and water respectively. These values were calculated as the difference between partial molar volumes and molar volumes presented in Table 2. For both solvents the partial molar volume diminishes as their proportion in the mixtures diminishes.

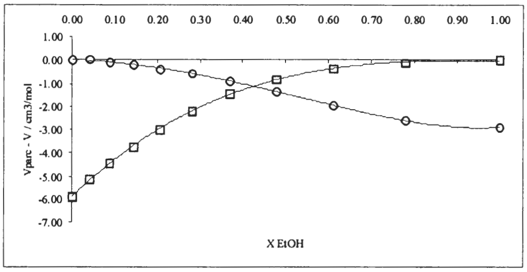

Figure 2. Partial molar volumes of ethanol (squares) and water (circles) in ethanol + water mixtures at 25.00 °C. Y-axis calculated as Vparc – V using data from Table 2.

Redlich and Kister (19) introduced in 1948 the general form of Eq. 6 to facilitate the representation of thermodynamic properties and the classification of solutions of multicomponent systems, especially those important in petroleum chemistry. The Redlich-Kister Equation (R-K Eq.) has been used for various decades for manipulating several kinds of physicochemical values of mixtures such as: excess volumes, excess viscosities, solubilities in cosolvent mixtures, among others.

$$V^E = x_1 x_2 \sum a_i \, (x_1 - x_2)^i \qquad \text{(Eq. 6)}$$

In the analysis of our data about excess volumes the Eq. 6 was used in the form of third degree polynomial equations using least square analyses, and therefore, obtaining four coefficients as presented in Eq. 7.

$$\frac{V^E}{x_1 x_2} = a_0 + a_1 (x_1 - x_2) + a_2 (x_1 - x_2)^2 + a_3 (x_3 - x_3)^3 \qquad \text{(Eq. 7)}$$

The R-K Eq. parameters for EtOH-W mixtures at all temperatures studied are presented in Table 3 in addition to determination coefficients and standard deviations calculated according to Eq. 8 (where *D* is the number of compositions studied and *N* is the number of terms used in the regression, that is 9 and 4 respectively in our cases). Eq. 8 has been widely used in literature. Figure 3 shows the R-K Eq. applied to EtOH-W data at 25.0 °C.

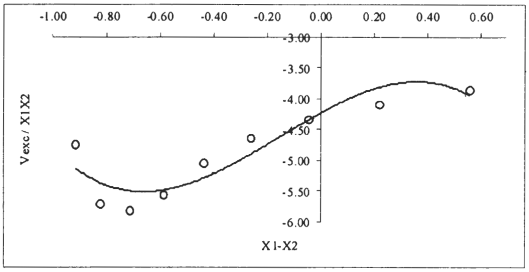

Figure 3. Regression adjusted to Redlich-Kister equation using four coefficients (third degree polynomial) for ethanol + water mixtures at 25.00 °C. (Mole fraction).

$$\sigma(V^E) = \left[\frac{\sum (V^E_{expt} - V^E_{calc})^2}{D - N} \right]^{0.5} \qquad \text{(Eq. 8)}$$

The r^2 values varies from 0.85 up to 0.93 which indicate that the obtained regular polynomials regressions do not describe adequately the excess volumes; nevertheless the standard deviations are similar to those presented in literature for other mixtures (7-10). According to that previously described, it is necessary to introduce some corrections or adjusts to R.K. Eq. in order to obtain more significant regression parameters. For this reason, the R-K Eq. was also used considering volume fractions instead of mole fractions. Volume fractions were calculated by means of:

$$\phi_2 = \frac{V_2 x_2}{V_2 x_2 + V_1 x_1} \qquad \text{(Eq. 9)}$$

Table 4 shows the respective a_i polynomial coefficients and determination coefficients at all temperatures studied for volume fractions, while Figure 4 shows the R-K Eq. at 25.0 °C

Table 3. Redlich-Kister regression results for the excess volumes of ethanol + water mixtures at various temperatures.

T / °C	a_0	a_1	a_2	a_3	r^2	σ / cm³ mol⁻¹
20.00	-4.2710	2.3837	-1.8455	-3.8204	0.8454	0.0431
25.00	-4.2332	2.3954	-1.5170	-3.3438	0.8555	0.0441
30.00	-4.1284	2.0352	-1.7285	-2.9482	0.9018	0.0320
35.00	-4.1585	1.6793	-1.9774	-2.7632	0.8936	0.0310
40.00	-4.1291	1.5896	-1.7458	-2.1064	0.9399	0.0251

Table 4. Redlich-Kister regression results for the excess volumes of ethanol + water mixtures at various temperatures in volume fraction.

T / °C	a_0	a_1	a_2	a_3	r^2
20.00	-3.7910	-2.2091	-2.0529	-3.8354	0.9978
25.00	-3.7846	-2.3446	-1.8266	-3.1733	0.9994
30.00	-3.6240	-2.1128	-2.1972	-3.6886	0.9970
35.00	-3.5415	-1.9234	-2.7046	-4.5313	0.9949
40.00	-3.5308	-1.9996	-2.6191	-4.0311	0.9962

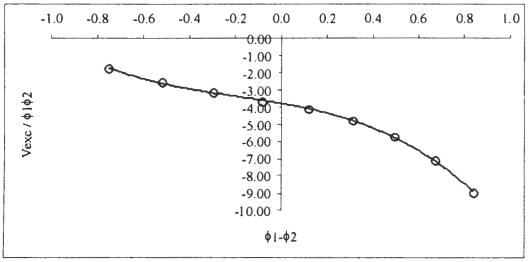

Figure 4. Regression adjusted to Redlich-Kister equation using four coefficients (third degree polynomial) for ethanol + water mixtures at 25.00 °C. (Volume fraction)

using the same concentration scale. It can be seen in Table 4 that the parameters obtained using volume fractions are better than those obtained using mole fraction because r^2 values are greater than 0.995 in all cases. Nevertheless, the physical meaning of this additional treatment using volume fractions is unclear.

In pharmaceutical preformulation studies is very important to predict the variation of properties presented in pharmaceutical dosage forms by effect of temperature; specially those properties which may affect the concentration of drugs in the formulations designed. For this reason the volume thermal expansion coefficients (α) were calculated by means of Eq. 10 (20) using the variation of molar volumes with temperature (Table 2).

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_{P,x} \qquad \text{(Eq. 10)}$$

Table 5 summarizes the ($\partial V/\partial T$) and α values for all mixtures and pure solvents whereas Figure 5 shows the volume thermal expansion coefficients at 25.0 °C. The α values varied from 0.00025 K^{-1} in water up to 0.00112 K^{-1} in pure ethanol. From 0 to 0.2 in mole fraction of EtOH the α values increases readily, while over 0.3 the value remains almost invariant up to 0.8.

An additional and important treatment is the evaluation of change of the excess molar volumes with temperature ($\partial V^E/\partial T$). Figure 6 shows this property at 25.00 °C which was obtained considering linear behavior of ($\partial V^E/\partial T$) in all mixtures studied (20). From Fig. 6 apparently, it follows that there are two tendencies according to compositions, that is, between 0.1 and 0.7 in mole fraction of EtOH, where this

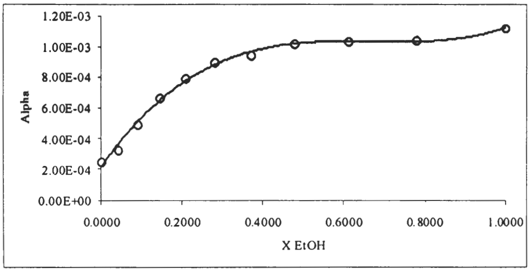

Figure 5. Volume thermal expansion coefficients (K^{-1}) for ethanol + water mixtures at 25.00 °C.

Table 5. Volume thermal expansion coefficients of ethanol + water mixtures at 25.00 °C.

Ethanol		$10^2\ (\partial V/\partial T)/$ cm^3 mol^{-1} K^{-1}	$10^4\ \alpha/\mathrm{K}^{-1}$
% w/w	Mole fraction		
0.00	0.0000	0.4549	2.517
10.00	0.0417	0.6328	3.232
20.00	0.0891	1.037	4.886
30.00	0.1436	1.547	6.671
40.00	0.2068	2.024	7.918
50.00	0.2812	2.558	8.985
60.00	0.3698	3.016	9.423
70.00	0.4772	3.699	10.17
80.00	0.6101	4.321	10.32
90.00	0.7788	5.112	10.43
100.00	1.0000	6.577	11.21

property is positive (excess volume diminishing with temperature arising) and outer this interval (0.0-0.1 and 0.7-1.0 in mole fraction of EtOH) where this property is negative (excess volume increases as temperature increases). Nevertheless, in order to verify fully this behavior, it is necessary to dispose density values with six, or at least, five decimals. These fine data would diminish the errors propagation in the calculated volumetric properties.

Finally, from the excess molar volumes presented in Table 2 was calculated the change of the excess molar enthalpies with pressure according to Eq. 11 (20):

$$\left(\frac{\partial H^E}{\partial p}\right)_T = V^E - T\left(\frac{\partial V^E}{\partial T}\right)_p \qquad \text{(Eq. 11)}$$

Figure 7 shows ($\partial H^E/\partial p$) values at 25.0 °C where it follows that this property is negative over 0.05 in mole fraction of EtOH, indicating an increase in the excess molar enthalpy as the pressure is increased.

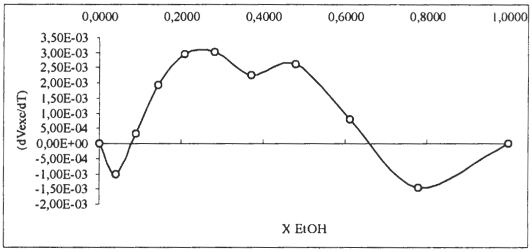

Figure 6. Change of the excess molar volumes with temperature (cm^3 mol^{-1} K^{-1}) for ethanol + water mixtures at 25.00 °C.

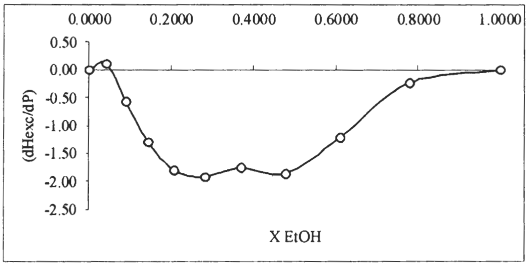

Figure 7. Change of the excess molar enthalpies with pressure (J mol^{-1} MPa^{-1}) obtained from the excess molar volumes for ethanol + water mixtures at 25.00 °C

In general terms it can be concluded that ethanol + water mixtures shows non ideal behavior. This result conduces to characterize systematically this important binary system in order to dispose complete information about the physical and chemical properties useful in design of liquid pharmaceutical dosage forms, especially those destined to parenteral administration of drugs.

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