Volumetric properties of 1,2-propanediol ethanol mixtures at different temperatures

Jackson Jiménez[a]; Fleming Martínez[a]

[a] Departamento de Farmacia, Universidad Nacional de Colombia, Bogotá, Colombia

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis
Taylor & Francis Group

Volumetric properties of 1,2-propanediol + ethanol mixtures at different temperatures

JACKSON JIMÉNEZ and FLEMING MARTÍNEZ*

Departamento de Farmacia, Universidad Nacional de Colombia,
A.A. 14490, Bogotá, Colombia

The excess molar volumes and partial molar volumes of components have been investigated from density measurements in the entire range of mole fractions for the 1,2-propanediol + ethanol system at 20.00, 25.00, 30.00, 35.00 and 40.00°C. The results of excess molar volumes were fitted by Redlich–Kister equation using third-degree polynomials and compared with those available in the literature for other systems. The system exhibited negative excess volumes (up to $0.39\,cm^3\,mol^{-1}$ at 25.00°C) due to increased interactions like hydrogen bonding between unlike molecules or large differences in the molar volumes of pure components. The effect of temperature on the different volumetric properties studied has also been analyzed. Finally, the thermal volume expansion coefficient has also been calculated, finding values varying from $0.00073\,K^{-1}$ for 1,2-propanediol up to $0.00112\,K^{-1}$ for ethanol at 25.00°C.

Keywords: Ethanol; 1,2-Propanediol; Binary liquid mixtures; Excess volumes; Partial volumes

1. Introduction

Water–cosolvent mixtures are widely used 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 (EtOH) and 1,2-propanediol (PD) are nowadays the most used cosolvents in the design and especially for the elaboration of parenteral medications [3].

The cosolvent mixtures obtained among these cosolvents 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 behaviour 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 PD + EtOH at various temperatures were calculated in addition to other

---

*Corresponding author. Email: fmartinezr@unal.edu.co

volumetric properties according to procedures widely exposed in the literature [7–10]. The present investigation is a continuation of those developed for EtOH + water [11] and for PD + water [12] cosolvent mixtures. PD and EtOH have proton-donor and proton-acceptor groups, which imply a significant degree of hydrogen bonding, leading to self-association in the pure state, and on the other hand, leading to mutual association in their binary mixtures [5].

2. Experimental

2.1. *Materials*

In this investigation propylene glycol USP [13] (Dow Chemical) and absolute EtOH A.R. (Merck) were used. The dehydrated propylene glycol (PD) and absolute EtOH employed were maintained over molecular sieve to obtain dry solvents before preparing the cosolvent mixtures. The quality of PD and EtOH obtained was demonstrated by the densities values obtained which coincide with those available in the literature [5,14].

2.2. *Cosolvent mixtures preparation*

All PD + EtOH cosolvent mixtures were prepared in quantities of 40.00 g by mass using a Mettler AE 160 analytical balance with sensitivity ±0.1 mg, in concentrations from 10 up to 90% in mass varying in 10% to study nine mixtures and the two pure solvents. The mixtures were allowed to stand in Magni Whirl Blue M water baths at temperatures from 20.00 up to 40.00°C varying in 5.00 ± 0.05°C for at least 30 min previous to density determinations.

2.3. *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 [15]. The equipment was calibrated according to Instruction Manual using air and water at the different temperatures studied [16]. All measurements were repeated at least 5 times and the results were averaged. From density values, all thermodynamic properties were calculated as it will be indicated in the next section.

3. Results and discussion

In table 1 the composition of EtOH + PD mixtures in mass percent and mole fraction in addition to density values at several temperatures studied are presented. Our density values for pure PD are in good agreement with those presented by Nakanishi *et al.* [17] at 25.00°C and those presented by Kapadi *et al.* [5] at 30.00, 35.00 and 40.00°C; while for EtOH, some differences were found with respect to those presented by Resa *et al.* [10] and by Belda *et al.* [18]. The differences found were in general lower than $0.0001 \, \text{g cm}^{-3}$ for PD and near to $0.0005 \, \text{g cm}^{-3}$ for EtOH. In all cases, the density decreases almost linearly as the temperature increases.

Table 1.   Densities[a,b] for PD + EtOH mixtures at various temperatures.

1,2-Propanediol		Temperature (°C)				
% in mass	Mole fraction	20.00	25.00	30.00	35.00	40.00
0.00	0.0000	0.7895	0.7853	0.7811	0.7767	0.7720
10.00	0.0630	0.8107	0.8065	0.8022	0.7980	0.7935
20.00	0.1315	0.8322	0.8282	0.8240	0.8197	0.8151
30.00	0.2060	0.8545	0.8506	0.8465	0.8422	0.8377
40.00	0.2876	0.8776	0.8737	0.8697	0.8654	0.8610
50.00	0.3771	0.9015	0.8977	0.8937	0.8896	0.8853
60.00	0.4759	0.9264	0.9227	0.9187	0.9148	0.9106
70.00	0.5855	0.9521	0.9485	0.9445	0.9406	0.9365
80.00	0.7078	0.9792	0.9756	0.9716	0.9678	0.9637
90.00	0.8449	1.0073	1.0037	0.9998	0.9960	0.9922
100.00	1.0000	1.0363	1.0328	1.0289	1.0251	1.0214

[a] Unit: $g\,cm^{-3}$.
[b] The mean standard deviation was $0.0001\,g\,cm^{-3}$.

The density of a liquid binary mixture is expressed as

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

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 equation (2).

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

On the other hand, the excess volumes calculated from equation (3) (where ρ_1 and ρ_2 are the densities of pure components) at all temperatures studied are also presented in table 2. This behaviour is shown graphically in figure 1 at 25.00°C.

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

In all cases, the excess volumes are largely negative (especially around 0.40 in mole fraction of PD, where it is near to $0.39\,cm^3\,mol^{-1}$ at 25.00°C) indicating contraction in volume. The behaviour obtained here is similar but lower with respect to that reported by Cratin and Gladden [19] for methanol + ethylene glycol mixtures. These authors found the largest excess volume near to 0.40 in mole fraction of ethylene glycol $(-0.654\,cm^3\,mol^{-1})$. According to Fort and Moore [20], 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 case.

In the system under study, where hydrogen bonding is very important, the contraction in volume has been interpreted basically in qualitative terms considering the following events: first: expansion due to depolymerization of PD and EtOH by

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

| | 1,2-Propanediol | | | | | | |
T (°C)	% in mass	Mole fraction	Molar volume[a,b]	Excess volume[a,b]	$\partial V/\partial x_{PD}$[a,b]	$\bar{V}_{PD}$[a,b]	$\bar{V}_{EtOH}$[a,b]
20.00	0.00	0.0000	58.35	0.000	13.13	71.48	58.35
	10.00	0.0630	59.16	−0.142	13.49	71.80	58.31
	20.00	0.1315	60.10	−0.233	13.86	72.14	58.28
	30.00	0.2060	61.15	−0.306	14.22	72.44	58.22
	40.00	0.2876	62.33	−0.355	14.58	72.72	58.14
	50.00	0.3771	63.66	−0.375	14.93	72.96	58.03
	60.00	0.4759	65.15	−0.373	15.26	73.15	57.89
	70.00	0.5855	66.85	−0.328	15.56	73.30	57.74
	80.00	0.7078	68.75	−0.273	15.80	73.36	57.56
	90.00	0.8449	70.92	−0.170	15.97	73.39	57.43
	100.00	1.0000	73.42	0.000	16.02	73.42	57.41
25.00	0.00	0.0000	58.67	0.000	12.94	71.61	58.67
	10.00	0.0630	59.47	−0.142	13.33	71.96	58.63
	20.00	0.1315	60.39	−0.247	13.72	72.31	58.59
	30.00	0.2060	61.43	−0.325	14.11	72.63	58.53
	40.00	0.2876	62.61	−0.371	14.49	72.93	58.44
	50.00	0.3771	63.93	−0.394	14.86	73.19	58.33
	60.00	0.4759	65.41	−0.394	15.21	73.39	58.18
	70.00	0.5855	67.10	−0.350	15.52	73.54	58.01
	80.00	0.7078	69.00	−0.287	15.78	73.61	57.83
	90.00	0.8449	71.17	−0.175	15.95	73.65	57.69
	100.00	1.0000	73.67	0.000	16.00	73.67	57.67
30.00	0.00	0.0000	58.98	0.000	12.80	71.78	58.98
	10.00	0.0630	59.79	−0.136	13.21	72.16	58.96
	20.00	0.1315	60.70	−0.249	13.62	72.53	58.91
	30.00	0.2060	61.73	−0.335	14.03	72.87	58.84
	40.00	0.2876	62.90	−0.388	14.43	73.18	58.75
	50.00	0.3771	64.22	−0.409	14.82	73.45	58.63
	60.00	0.4759	65.70	−0.407	15.18	73.66	58.47
	70.00	0.5855	67.39	−0.360	15.51	73.82	58.31
	80.00	0.7078	69.28	−0.293	15.77	73.89	58.12
	90.00	0.8449	71.45	−0.182	15.95	73.92	57.97
	100.00	1.0000	73.95	0.000	15.99	73.95	57.97
35.00	0.00	0.0000	59.32	0.000	12.74	72.05	59.32
	10.00	0.0630	60.10	−0.152	13.13	72.41	59.28
	20.00	0.1315	61.02	−0.257	13.53	72.77	59.24
	30.00	0.2060	62.05	−0.342	13.93	73.11	59.17
	40.00	0.2876	63.21	−0.392	14.33	73.42	59.09
	50.00	0.3771	64.51	−0.425	14.73	73.69	58.96
	60.00	0.4759	65.98	−0.433	15.10	73.89	58.79
	70.00	0.5855	67.67	−0.379	15.44	74.07	58.63
	80.00	0.7078	69.56	−0.312	15.74	74.16	58.42
	90.00	0.8449	71.72	−0.193	15.95	74.20	58.24
	100.00	1.0000	74.23	0.000	16.06	74.23	58.17
40.00	0.00	0.0000	59.68	0.000	12.59	72.26	59.68
	10.00	0.0630	60.44	−0.166	13.00	72.62	59.62
	20.00	0.1315	61.36	−0.262	13.41	73.01	59.60
	30.00	0.2060	62.38	−0.350	13.82	73.35	59.53
	40.00	0.2876	63.53	−0.404	14.24	73.68	59.44
	50.00	0.3771	64.83	−0.438	14.64	73.94	59.31
	60.00	0.4759	66.28	−0.446	15.02	74.15	59.13
	70.00	0.5855	67.96	−0.390	15.37	74.33	58.96
	80.00	0.7078	69.85	−0.312	15.67	74.43	58.77
	90.00	0.8449	72.00	−0.201	15.88	74.46	58.58
	100.00	1.0000	74.50	0.000	15.98	74.50	58.52

[a] Units: $cm^3\,mol^{-1}$.
[b] The mean standard deviation for V and V^E was $0.01\,cm^3\,mol^{-1}$ while for $\bar{V}_{PD}$ and $\bar{V}_{EtOH}$ was close to $0.03\,cm^3\,mol^{-1}$.
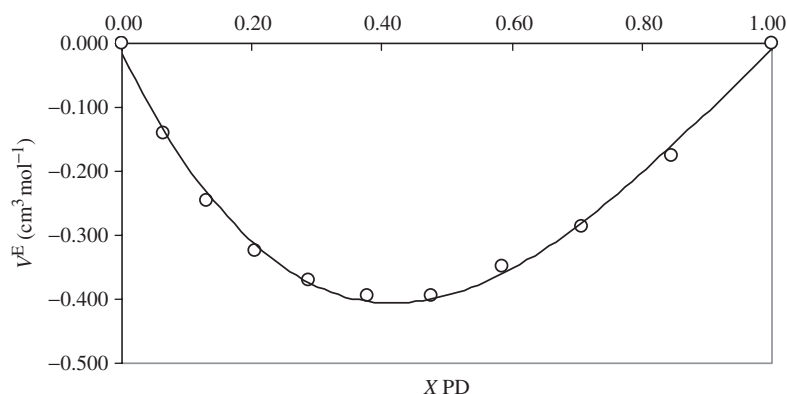
Figure 1.   Excess molar volumes of PD + EtOH mixtures at 25.00°C (XPD = mole fraction of PD).

one another, second: contraction due to free volume difference of unlike molecules and third: contraction due to hydrogen bond formation between EtOH and PD through –OH–OH bonding [5].

Thus, the 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 PD and EtOH over the rupture of hydrogen bonding in PD–PD and EtOH–EtOH.

The excess molar volumes becomes more negative as the temperature is raised indicating volume contraction which points out the increase in the interactions between PD and EtOH molecules with increase in temperature.

The partial molar volumes for PD ($\bar{V}_{PD}$) and EtOH ($\bar{V}_{EtOH}$) were calculated using the classical Bakhuis Roozeboom method by means equations (4) and (5) (where x_{PD} is the mole fraction of PD) applied to variation of the respective molar volumes as a function of PD mole fraction (table 2) and adjusting them to third-degree polynomials by least squares regression analyses [6,21,22]. The first derivatives were taken out on the polynomials obtained and solved at each composition point.

$$\bar{V}_{PD} = V + x_{EtOH}\frac{dV}{dx_{PD}} \tag{4}$$

$$\bar{V}_{EtOH} = V - x_{PD}\frac{dV}{dx_{PD}} \tag{5}$$

The $\bar{V}_{PD}$ and $\bar{V}_{EtOH}$ values are also presented in table 2 in addition to the slopes obtained at each composition (dV/dx_{PD}). Almost in all cases, the partial molar volumes for PD and EtOH in the mixtures are lower than those for the pure solvents. The partial volumes varied for PD from 71.96 cm^3 mol^{-1} (at 10% mm^{-1} of PD) up to 73.65 cm^3 mol^{-1} (at 90% in mass of PD), and varied for EtOH from 58.63 cm^3 mol^{-1} (at 10% in mass of PD) up to 57.69 cm^3 mol^{-1} (at 90% in mass of PD) at 25.00°C. The results obtained for $\bar{V}_{PD}$ and $\bar{V}_{EtOH}$ are in accordance with the negative excess volumes obtained. The variation of this property is presented in figure 2 as a function of PD mole fraction at 25.00°C for PD and EtOH respectively. These values were calculated as the difference between partial molar volumes and molar volumes presented in table 2.
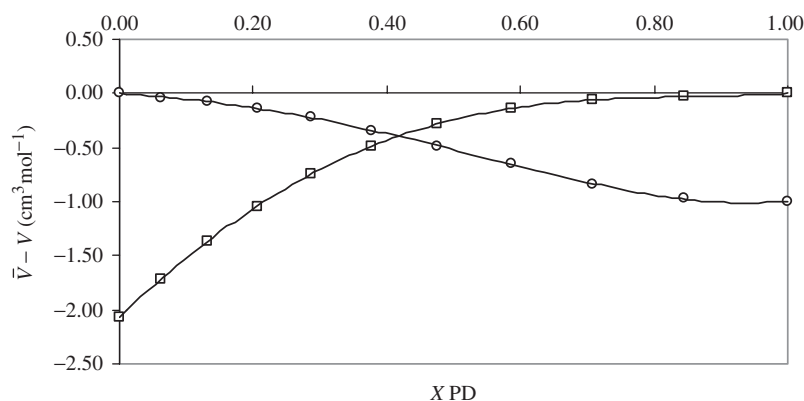
J. Jiménez and F. Martínez

Figure 2. Partial molar volumes of EtOH (circles) and PD (squares) in PD + EtOH mixtures at 25.00°C. Y-axis calculated as $\bar{V} - V$ using data from table 2.

Table 3. Redlich–Kister regression results for the excess volumes of PD + EtOH mixtures at various temperatures.

T (°C)	a_0	a_1	a_2	a_3	r^2	σ (cm^3 mol^{-1})
20.00	−1.4421	0.3831	−0.4603	0.3350	0.9894	0.0210
25.00	−1.5300	0.4619	−0.3999	0.2236	0.9984	0.0034
30.00	−1.5860	0.6010	−0.3707	−0.1257	0.9992	0.0024
35.00	−1.6588	0.4030	−0.3894	0.3373	0.9908	0.0074
40.00	−1.6894	0.3529	−0.4781	0.5364	0.9687	0.0130

For both solvents the partial molar volume diminishes as their proportion in the mixtures diminishes.

Redlich and Kister [23] introduced in 1948 the general form of equation (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 equation) 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.

$$V^E = x_1 x_2 \sum a_i (x_1 - x_2)^i \qquad (6)$$

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

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

The R–K equation parameters for PD–EtOH mixtures at all temperatures studied are presented in table 3 in addition to determination coefficients and standard deviations calculated according to equation (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
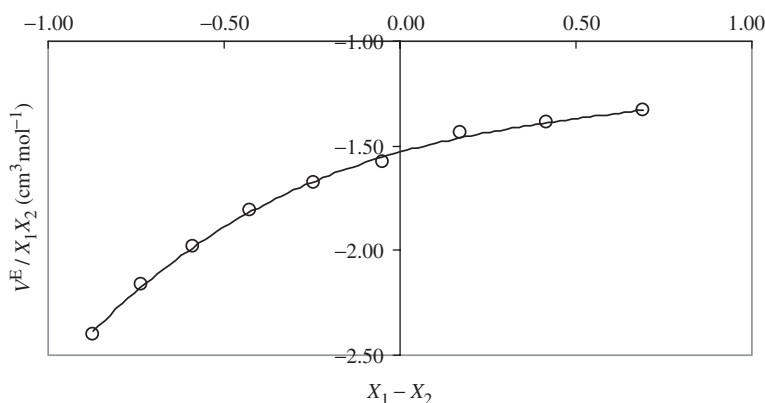
Figure 3.   Regression adjusted to R–K equation using four terms for PD + EtOH mixtures at 25.00°C.

in our cases). Equation (8) has been widely used in the literature [5,7,9]. Figure 3 shows the R–K equation applied to PD–EtOH data at 25.00°C.

$$\sigma\left(V^{E}\right) = \left[\sum \left(\frac{V_{\text{expt}}^{E} - V_{\text{calcd}}^{E})^{2}}{D - N}\right)\right]^{0.5} \tag{8}$$

The r^2 values vary from 0.97 up to 1.00, which indicates that the obtained regular polynomials regressions adequately describe the excess volumes, because the standard deviations are similar to those presented in the literature for other mixtures [7–10]. Nevertheless our σ values are almost 10 times lower than those presented by Kapadi *et al.* [5] for PD + water mixtures at temperatures from 30.00 to 45.00°C because they used polynomial models of second order, that is, using three coefficients.

In pharmaceutical preformulation studies, it is very important to predict the variation of properties presented in pharmaceutical dosage forms by effect of temperature; especially 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 equation (9) [24] using the variation of molar volumes with temperature (table 2).
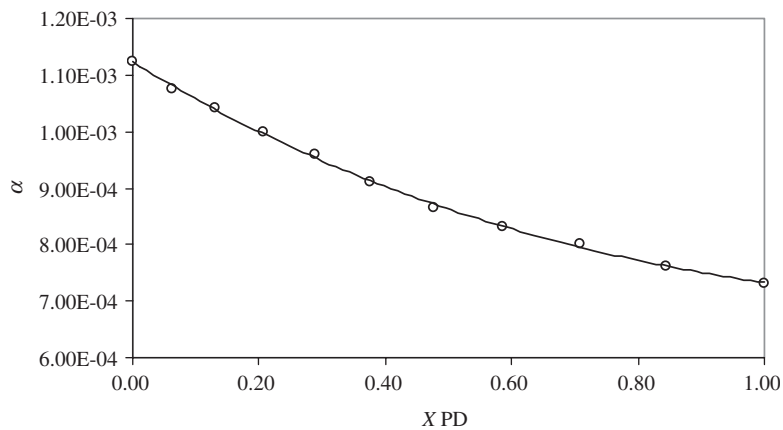
$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_{P,x} \tag{9}$$

Table 4 summarizes the $(\partial V/\partial T)$ and α values for all mixtures and pure solvents whereas figure 4 shows the volume thermal expansion coefficients at 25.00°C. The α values varied monotonically from 0.00073 K^{-1} in PD up to 0.00112 K^{-1} in pure EtOH.

An additional and important treatment is the evaluation of change of the excess molar volumes with temperature $(\partial V^{E}/\partial T)$. Figure 5 shows this property at 25.00°C which was obtained considering linear behaviour of $(\partial V^{E}/\partial T)$ in all mixtures studied [24]. From figure 5 it follows that there is only a tendency according to composition. This property is negative which reflect the fact that excess volume increases with increasing temperature. This behaviour is just opposite with respect to that found for EtOH + water and PD + water cosolvent mixtures [11,12].

Table 4.   Volume thermal expansion coefficients of PD + EtOH mixtures at 25.00°C.

1,2-Propanediol			
% in mass	Mole fraction	$10^2\ (\partial V/\partial T)$ $(\text{cm}^3\,\text{mol}^{-1}\,\text{K}^{-1})$	$10^4\ \alpha\ (\text{K}^{-1})$
0.00	0.0000	6.59	11.2
10.00	0.0630	6.40	10.8
20.00	0.1315	6.30	10.4
30.00	0.2060	6.13	9.98
40.00	0.2876	6.01	9.60
50.00	0.3771	5.82	9.11
60.00	0.4759	5.65	8.64
70.00	0.5855	5.58	8.32
80.00	0.7078	5.54	8.02
90.00	0.8449	5.42	7.61
100.00	1.0000	5.39	7.32

Figure 4.   Volume thermal expansion coefficients (K^{-1}) for PD + EtOH mixtures at 25.00°C.
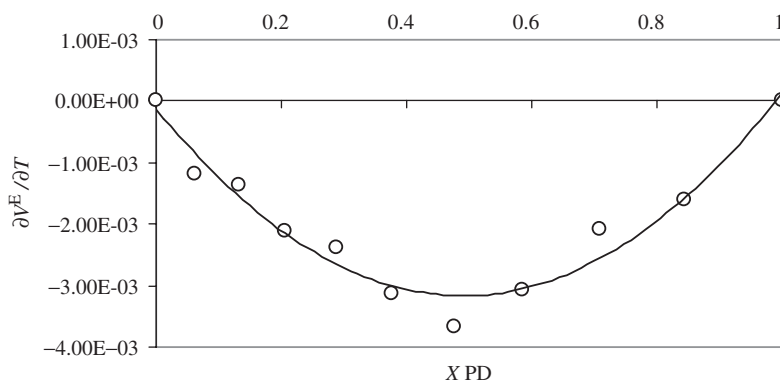
Figure 5.   Change of the excess molar volumes with temperature $(\text{cm}^3\,\text{mol}^{-1}\,\text{K}^{-1})$ for PD + EtOH mixtures at 25.00°C.
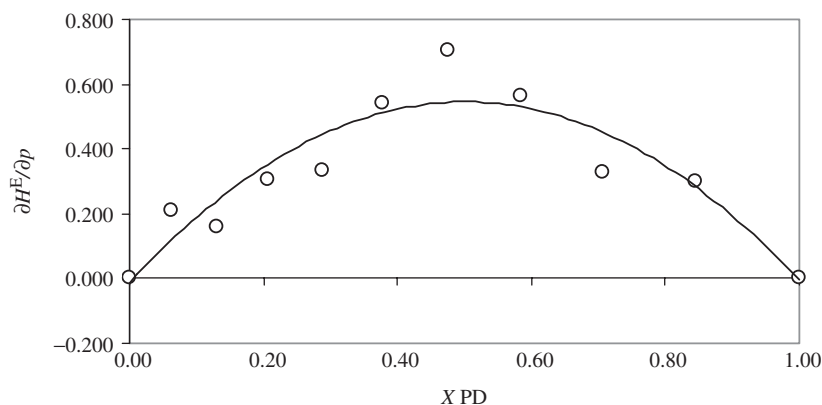
Figure 6. Change of the excess molar enthalpies with pressure ($J\,mol^{-1}\,MPa^{-1}$) obtained from the excess molar volumes for PD + EtOH mixtures at 25.00°C.

Finally, from the excess molar volumes presented in table 2 was calculated the change of the excess molar enthalpies with pressure according to equation (10) [24]:

$$\left(\frac{\partial H^{E}}{\partial p}\right)_{T} = V^{E} - T\left(\frac{\partial V^{E}}{\partial T}\right)_{p} \tag{10}$$

Figure 6 shows ($\partial H^{E}/\partial p$) values at 25.00°C where it follows that this property is positive in all compositions, indicating an increase in the excess molar enthalpy as the pressure is increased. Again, this behaviour is just opposite with respect to that found for EtOH + water and PD + water cosolvent mixtures [11,12].

In general terms, it can be considered that PD + EtOH mixtures show a non-ideal behaviour. These results 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, in those destined to parenteral administration of drugs in low volumes. On the other hand, these binary mixtures have been evaluated as possible solvents for acetaminophen in a recent study about solution thermodynamics of drugs [25].

Acknowledgements

References

[1] J.T. Rubino. In *Encyclopedia of Pharmaceutical Technology*, edited by J. Swarbrick, J.C. Boylan, Vol. 3, pp. 375–98, Marcel Dekker, Inc., New York (1988).
[2] S.H. Yalkowsky. *Solubility and Solubilization in Aqueous Media*, American Chemical Society and Oxford University Press, New York (1999).

[3] D.C. Pérez, C.C. Guevara, C.A. Cárdenas, J.A. Pinzón, H.J. Barbosa, F. Martínez. *Rev. Col. Cienc. Quím. Farm.*, **32**, 116 (2003).

[4] R. Battino. *Chem. Rev.*, **71**, 5 (1971).

[5] U.R. Kapadi, D.G. Hundiwale, N.B. Patil, M.K. Lande, P.R. Patil. *Fluid Phase Equilibria*, **192**, 63 (2001).

[6] S. Rodríguez, R.A. Vargas, J.A. Pinzón, H.J. Barbosa, F. Martínez. *Rev. Col. Cienc. Quím. Farm.*, **31**, 11 (2002).

[7] M.A. Wahab, M. Azhar, M.A. Mottaleb. *Bull. Korean Chem. Soc.*, **23**, 953 (2002).

[8] J.A. Salas, J.L. Zurita, M. Katz. *J. Arg. Chem. Soc.*, **90**, 61 (2002).

[9] R.D. Peralta, R. Infante, G. Cortez, R.R. Ramírez, J. Wisniak. *J. Chem. Thermodyn.*, **35**, 239 (2003).

[10] J.M. Resa, C. González, J.M. Goenaga, M. Iglesias. *J. Sol. Chem.*, **33**, 169 (2004).

[11] J. Jiménez, J. Manrique, F. Martínez. *Rev. Col. Cienc. Quím. Farm.*, **33**, 145 (2004).

[12] J. Jiménez, F. Martínez. *Rev. Col. Cienc. Quím. Farm.*, **34**, 46 (2005).

[13] USP23-NF18. *The United States Pharmacopeia*, 23rd Edn, The United States Pharmacopeial Convention, Rockville, MD (1994).

[14] D.R. Lide. *CRC Handbook of Chemistry and Physics*, 84th Edn, CRC Press LLC, Boca Raton (2003).

[15] F. Martínez, A. Gómez, C.M. Ávila. *Acta Farm. Bonaerense*, **21**, 107 (2002).

[16] K.G. Anton Paar. *DMA 45: Calculating Digital Density Meter Instruction Manual*, Graz, Austria (1980).

[17] K. Nakanishi, N. Kato, M. Maruyama. *J. Phys. Chem.*, **71**, 814 (1967).

[18] R. Belda, J.V. Herraez, O. Diez. *Phys. Chem. Liq.*, **42**, 467 (2004).

[19] P.D. Cratin, J.K. Gladden. *J. Phys. Chem.*, **67**, 1665 (1963).

[20] R.T. Fort, W.R. Moore. *Trans. Farad. Soc.*, **62**, 1112 (1966).

[21] J. Kestin. *A Course in Thermodynamics*, McGraw-Hill, New York (1979).

[22] P. Perrot. *A to Z of Thermodynamics*, Oxford University Press, Inc., New York (1998).

[23] O. Redlich, A.T. Kister. *Ind. Eng. Chem.*, **40**, 345 (1948).

[24] J.B. Ott, J. Boerio-Goates. *Chemical Thermodynamics: Advanced Applications*, Academic Press, London (2000).

[25] J. Jiménez, F. Martínez. *J. Sol. Chem.* (2005) (In press).