Study of some volumetric properties of 1,2-propanediol + water mixtures at several temperatures

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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 1,2-propanediol + 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 system exhibited large negative excess volumes (up to −0.70 cm³ 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 0.00073 K⁻¹ for pure 1,2-propanediol at 25.0 °C.

Key Words: 1,2-propanediol − Water − Binary liquid mixtures − Excess volumes − Partial volumes

Resumen
Estudio de algunas propiedades volumétricas de mezclas 1,2-propanodiol + agua a varias temperaturas

En este trabajo se calcularon los volúmenes molares de exceso y molares parciales a partir de medidas de densidad en el sistema 1,2-propanodiol + agua en todo el intervalo de composición a 20,0, 25,0, 30,0, 35,0 y 40,0 °C. Los resultados de volumen molar de exceso fueron modelados de acuerdo a la ecuación de Redlich-Kister usando polinomios regulares de tercer grado y comparados con otros presentados en la literatura para otros sistemas. El sistema estudiado presentó volúmenes de exceso altamente negativos (hasta −0,70 cm³ mol⁻¹) debido a las fuertes interacciones por unión de hidrógeno entre las moléculas de los dos compuestos y a la gran diferencia en los volúmenes molares de los dos componentes puros. También se analizó el efecto de la temperatura sobre las diferentes propiedades volumétricas estudiadas. Finalmente, también se calcularon los coeficientes térmicos de expansión volumétricos encontrado valores desde 0,00025 K⁻¹ para el agua pura hasta 0,00073 K⁻¹ para el 1,2-propanodiol puro a 25,0 °C.

Palabras clave: 1,2-propanodiol − Agua − Mezclas líquidas binarias − Volúmenes de exceso − Volúmenes parciales

Introduction

Water-cosolvent mixtures have been 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).

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1,2-propanediol (PD) and ethanol are the cosolvents most used in design nowadays and especially for elaboration of peroral and parenteral medications (3). Several examples of pharmaceutical formulations using these cosolvents have been presented by Rubino (1).

The cosolvent mixtures obtained using these cosolvents and water (W) 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 used in pharmacy. 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 1,2-propanediol + water at various temperatures in addition to other volumetric properties were calculated according to procedures widely exposed in literature (7-10). This report is a continuation of that presented previously about some volumetric properties of ethanol + water mixtures (11). 1,2-propanediol 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 (5).

Experimental

Materials

In this investigation dehydrated propylene glycol USP (12) (Dow Chemical) and Distilled

water (conductivity < 2 μS) obtained from Laboratory of Industrial Pharmacy, of the Universidad Nacional de Colombia were used. The dehydrated propylene glycol (1,2-propanediol) employed was maintained over molecular sieve to obtain a dry solvent previously to prepare the cosolvent mixtures. The dryness obtained for PD was demonstrated by the density and refractive index values obtained for it which were coincident with those presented in literature (5, 13).

Cosolvent mixtures preparation

All PD-W 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 % m/m up to 90 % m/m varying in 10 % m/m, to study nine mixtures and the two pure solvents. This procedure results imply an uncertainty of $\pm 2 \cdot 10^{-5}$ for the mole fraction. 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 (14). The equipment was calibrated according to Instruction Manual using air and water at the different temperatures studied (15). All mixture preparations and density 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 PD-W mixtures in weight percent and mole fraction in addition to density values at several temperatures studied are presented. Our density values are in good agreement with those presented by Nakanishi *et al.* (16) at 25.0 °C, those presented by Geyer *et al.* (17, 18) at 25.0 and 35.0 °C, and those presented by Kapady *et al.* (5) at 30.0, 35.0 and 40.0 °C. The differences found among all literature data were in general lower than 0.0003 g cm^{-3}. In all cases the density decreases almost linearly as the temperature increases except for water.

In Table 2 the molar volumes for binary mixtures at all temperatures are presented which were calculated from Eq. 1.

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

where, x_1 and x_2 are the mole fractions and M_1 and M_2 are the molar masses, for both components respectively, and ρ is the mixture density.

On the other hand, the excess volumes calculated from Eq. 2 (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.
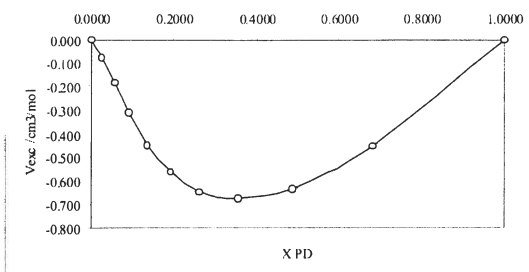

Figure 1. Excess molar volumes of 1,2-propanediol + water mixtures at 25.00 °C

Table 1. Densities [a, b] for 1,2-propanediol + water mixtures at various temperatures.

1,2-propanediol		Temperature / °C				
% m/m	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	0.0256	1.0059	1.0043	1.0026	1.0007	0.9986
20.00	0.0559	1.0147	1.0128	1.0106	1.0083	1.0059
30.00	0.0921	1.0235	1.0213	1.0187	1.0160	1.0131
40.00	0.1364	1.0316	1.0290	1.0257	1.0227	1.0195
50.00	0.1915	1.0380	1.0348	1.0316	1.0282	1.0245
60.00	0.2621	1.0422	1.0388	1.0348	1.0314	1.0278
70.00	0.3559	1.0439	1.0404	1.0368	1.0335	1.0290
80.00	0.4865	1.0436	1.0401	1.0358	1.0323	1.0283
90.00	0.6807	1.0411	1.0375	1.0335	1.0297	1.0258
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}

Table 2. Molar volumes, excess molar volumes, and partial molar volumes of components for 1,2-propanediol + water mixtures at various temperatures.

T / °C	1,2-propanediol		Molar volume [a,b]	Excess volume [a,b]	$\partial V/\partial x_{PD}$ [a]	$\bar{V}_{PD}$ [a,b]	$\bar{V}_W$ [a,b]
	% m/m	Mole fraction					
20.00	0.00	0.0000	18.05	0.000	51.02	69.07	18.05
	10.00	0.0256	19.39	-0.079	51.41	69.48	18.08
	20.00	0.0559	20.96	-0.189	51.85	69.91	18.06
	30.00	0.0921	22.83	-0.321	52.35	70.36	18.01
	40.00	0.1364	25.14	-0.459	52.92	70.85	17.93
	50.00	0.1915	28.07	-0.582	53.59	71.40	17.81
	60.00	0.2621	31.90	-0.671	54.35	72.00	17.65
	70.00	0.3559	37.06	-0.699	55.21	72.62	17.41
	80.00	0.4865	44.34	-0.653	56.11	73.15	17.04
	90.00	0.6807	55.28	-0.466	56.83	73.42	16.60
	100.00	1.0000	73.42	0.000	56.37	73.43	17.05
25.00	0.00	0.0000	18.07	0.000	51.39	69.46	18.07
	10.00	0.0256	19.43	-0.074	51.76	69.86	18.10
	20.00	0.0559	21.00	-0.185	52.19	70.27	18.08
	30.00	0.0921	22.88	-0.314	52.67	70.70	18.03
	40.00	0.1364	25.21	-0.448	53.23	71.18	17.95
	50.00	0.1915	28.16	-0.561	53.87	71.71	17.84
	60.00	0.2621	32.00	-0.648	54.61	72.29	17.69
	70.00	0.3559	37.19	-0.677	55.44	72.89	17.45
	80.00	0.4865	44.49	-0.636	56.31	73.40	17.09
	90.00	0.6807	55.47	-0.452	57.01	73.67	16.66
	100.00	1.0000	73.67	0.000	56.58	73.67	17.09
30.00	0.00	0.0000	18.10	0.000	51.80	69.90	18.10
	10.00	0.0256	19.46	-0.072	52.16	70.28	18.12
	20.00	0.0559	21.04	-0.177	52.57	70.67	18.10
	30.00	0.0921	22.94	-0.303	53.04	71.09	18.05
	40.00	0.1364	25.29	-0.426	53.57	71.56	17.98
	50.00	0.1915	28.25	-0.546	54.19	72.06	17.87
	60.00	0.2621	32.12	-0.615	54.91	72.64	17.73
	70.00	0.3559	37.31	-0.663	55.71	73.19	17.49
	80.00	0.4865	44.67	-0.599	56.55	73.71	17.16
	90.00	0.6807	55.68	-0.435	57.21	73.95	16.74
	100.00	1.0000	73.95	0.000	56.77	73.95	17.18

Table 2. Continuation

T / °C	1,2-propanediol % m/m	Mole fraction	Molar volume (a,b)	Excess volume (a,b)	$\partial V/\partial x_{PD}$ (a)	$\overline{V}_{PD}$ (a,b)	$\overline{V}_W$ (a,b)
35.00	0.00	0.0000	18.13	0.000	52.11	70.24	18.13
	10.00	0.0256	19.50	-0.072	52.46	70.61	18.15
	20.00	0.0559	21.09	-0.174	52.86	71.00	18.14
	30.00	0.0921	23.00	-0.295	53.32	71.41	18.09
	40.00	0.1364	25.36	-0.416	53.85	71.87	18.02
	50.00	0.1915	28.34	-0.530	54.45	72.37	17.91
	60.00	0.2621	32.23	-0.604	55.15	72.93	17.77
	70.00	0.3559	37.43	-0.661	55.94	73.46	17.52
	80.00	0.4865	44.82	-0.597	56.77	73.97	17.20
	90.00	0.6807	55.89	-0.426	57.43	74.23	16.79
	100.00	1.0000	74.23	0.000	57.03	74.23	17.19
40.00	0.00	0.0000	18.17	0.000	52.52	70.69	18.17
	10.00	0.0256	19.54	-0.073	52.86	71.04	18.18
	20.00	0.0559	21.14	-0.173	53.25	71.41	18.16
	30.00	0.0921	23.07	-0.287	53.69	71.81	18.12
	40.00	0.1364	25.44	-0.404	54.19	72.24	18.05
	50.00	0.1915	28.44	-0.509	54.77	72.73	17.95
	60.00	0.2621	32.34	-0.588	55.44	73.25	17.81
	70.00	0.3559	37.60	-0.617	56.19	73.79	17.60
	80.00	0.4865	45.00	-0.572	56.98	74.26	17.28
	90.00	0.6807	56.10	-0.409	57.61	74.50	16.89
	100.00	1.0000	74.50	0.000	57.20	74.50	17.29

(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 $\overline{V}_{PD}$ and $\overline{V}_W$ was close to 0.03 $cm^3\ mol^{-1}$

$$V^E = \frac{x_1 M_1 + x_2 M_2}{\rho} - \left(\frac{x_1 M_1}{\rho_1} + \frac{x_2 M_2}{\rho_2} \right) \quad \text{(Eq. 2)}$$

Analogous to the behavior obtained in other investigations (5, 11, 16-18), in all cases the excess volumes are largely negative (especially around 0.36 in mole fraction of 1,2-propanediol, where is near to 0.70 $cm^3\ mol^{-1}$) indicating contraction in volume. As was already said (11), according to Fort and Moore (19), 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.

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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 1,2-propanediol and water by one another, second: contraction due to free volume difference of unlike molecules, and third: contraction due to hydrogen bond formation between 1,2-propanediol 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 1,2-propanediol and water over the rupture of hydrogen bonding in 1,2-propanediol-1,2-propanediol 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 1,2-propanediol and water molecules with increase in temperature.

The partial molar volumes for 1,2-propanediol ($\bar{V}_{PD}$) and water ($\bar{V}_W$) were calculated using the classical Bakhuis- Roozeboom method by means Eqs. 3 and 4 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, 20, 21). Polynomials of third degree order are the most widely used in these cases based upon their good statistical parameters, specially their determination coefficients. The first derivatives were taken out on the polynomials obtained and solved at each composition point.

$$\bar{V}_{PD} = V + x_W \frac{dV}{dx_{PD}} \qquad \text{(Eq. 3)}$$

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

The $\bar{V}_{PD}$ and $\bar{V}_W$ 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 1,2-propanediol and water in the mixtures are lower than those for the pure solvents (except for water in mixtures up to 30% m/m of PD in some cases). The partial volumes varied for 1,2-propanediol from 69.86 cm³ mol⁻¹ (at 10 % m/m of PD) up to 73.42 cm³ mol⁻¹ (at 90 % m/m of PD), and varied for water from 18.08 cm³ mol⁻¹ (at 10 % m/m of PD) up to 17.05 cm³ mol⁻¹ (at 90 % m/m of PD) at 25.0°C. Our results for $\bar{V}_{PD}$ are coincident with those presented by Nakanishi *et al.* (16) at 25.0 °C. The results obtained for $\bar{V}_{PD}$ and $\bar{V}_W$ are in according with the negative excess volumes obtained. The variation of this property is presented in Figure 2 as a function of PD mole fraction at 25.0 °C for 1,2-propanediol 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.

As was already said (11), Redlich and Kister (22) introduced in 1948 the general form of
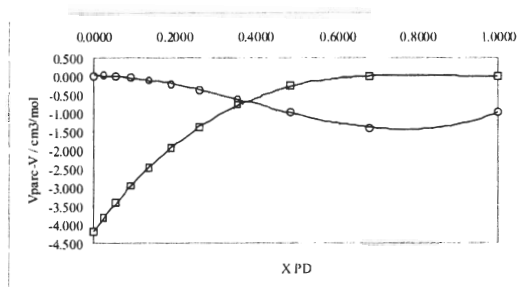

Figure 2. Partial molar volumes of water (circles) and 1,2-propanediol (squares) calculated as differences respect to pure solvent volumes in 1,2-propanediol + water mixtures at 25.00 °C.

Eq. 5 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.

$$V^E = x_1 x_2 \sum a_i (x_1 - x_2)^i \qquad \text{(Eq. 5)}$$

In the analysis of our data about excess volumes the Eq. 5 was used in the form of third degree polynomial equations using least square analyses, and therefore, obtaining four coefficients as presented in Eq. 6. Polynomials of third degree are the most widely used in this case again, because of their relevant statistic parameters such as determination coefficients and standard deviations.

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

$$\text{(Eq. 6)}$$

The R-K Eq. parameters for PD-W mixtures at all temperatures studied are presented in Table 3 in addition to determination coefficients and standard deviations calculated

according to Eq. 7 (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. 7 has been widely used in literature. Figure 3 shows the R-K Eq. applied to PD-W data at 25.0 °C.

$$\sigma(V^E) = \left[\frac{\sum \left(V_{expt}^E - V_{calc}^E \right)^2}{D - N} \right]^{0.5} \qquad \text{(Eq. 7)}$$

The r^2 values varies from 0.94 up to 0.97 which indicate that the obtained regular polynomials regressions describe adequately the excess volumes, because the standard deviations are
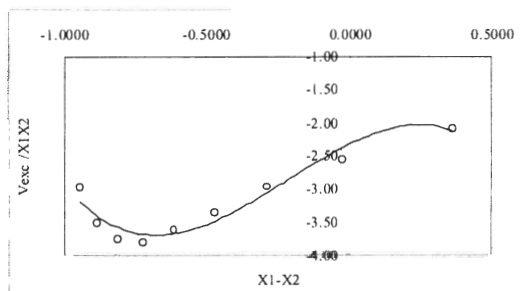

Figure 3. Regression adjusted to Redlich-Kister equation using four terms for 1,2-propanediol + water mixtures at 25.000 °C in mole fraction.

Table 3. Redlich-Kister regression results for the excess volumes of 1,2-propanediol + water mixtures at various temperatures in mole fraction.

$T / °C$	a_0	a_1	a_2	a_3	r^2	$\sigma / cm^3\ mol^{-1}$
20.00	-2.4090	2.1621	-2.6854	-4.1799	0.9616	0.0341
25.00	-2.3267	2.1144	-2.7239	-4.2090	0.9411	0.0355
30.00	-2.2207	2.0455	-2.7121	-4.1517	0.9489	0.0318
35.00	-2.2407	1.9618	-2.1872	-3.5502	0.9573	0.0277
40.00	-2.1369	1.8136	-2.0968	-3.1264	0.9707	0.0255

similar to those presented in literature for other mixtures (7-10). Nevertheless our σ values are almost ten fold lower than those presented by Kapadi *et al.* (5) at temperatures from 30.0 to 45.0 °C because they used polynomial models of second order and therefore, using three coefficients. On the other hand, some significant differences are found between our data and those presented by Geyer *et al.* (16, 17) at 25.0 and 35.0 °C, for the a_i coefficients and σ values. The σ values presented by these authors are almost three times lower than our data. For this reason, in order to improve the polynomial regressions, the R-K Eq. was also used considering volume and mass fractions instead of mole fractions. Volume fractions were calculated by means of:

$$\phi_2 = \frac{V_2 x_2}{V_2 x_2 + V_1 x_1}$$
(Eq. 8)

Tables 4 and 5 show the respective a_i polynomial coefficients, determination coefficients, and standard deviations at all temperatures studied, for mass and volume fractions, respectively, while Figure 4 shows the R-K Eq. at 25.0 °C using volume fraction. It can be seen in tables 4 and 5 that the parameters obtained using these concentration scales are better than those obtained using mole fraction because r^2 values are greater than 0.998 in all cases while σ values were minor than 0.0092 cm³ mol⁻¹ in all cases. A

similar behavior was found for ethanol + water mixtures (11). Nevertheless, the physical meaning of this additional treatment using mass and volume fractions is unclear.

On the other hand, 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. 9 (23) using the variation of molar volumes with temperature (Table 2).

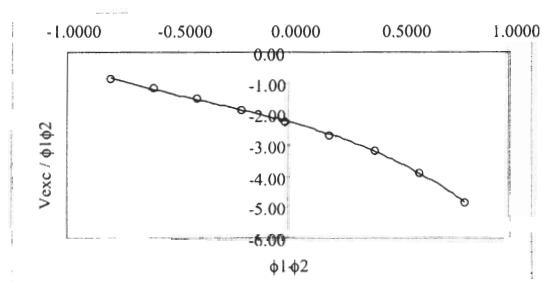$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_{P,A}$$
(Eq. 9)

Figure 4. Regression adjusted to Redlich-Kister equation using four terms for 1,2-propanediol + water mixtures at 25.00 °C in volume fraction.

Table 4. Redlich-Kister regression results for the excess volumes of 1,2-propanediol + water mixtures at various temperatures in volume fraction.

$T/°C$	a_0	a_1	a_2	a_3	r^2	$\sigma/$ cm³ mol⁻¹
20.00	-2.2835	-2.1067	-1.1057	-0.9061	0.9991	0.0083
25.00	-2.2169	-2.0115	-1.0694	-0.9566	0.9995	0.0062
30.00	-2.1299	-1.9253	-1.0151	-0.9185	0.9986	0.0092
35.00	-2.0923	-1.9878	-1.0193	-0.7270	0.9992	0.0072
40.00	-2.0090	-1.8253	-1.0036	-0.7759	0.9994	0.0059

Table 5. Redlich-Kister regression results for the excess volumes of 1,2-propanediol + water mixtures at various temperatures in mass fraction.

$T/°C$	a^0	a^1	a^2	a^3	r^2	σ / cm^3 mol^{-1}
20.00	-2.2835	-2.1067	-1.1057	-0.9061	0.9991	0.0083
25.00	-2.2169	-2.0115	-1.0694	-0.9566	0.9995	0.0062
30.00	-2.1299	-1.9253	-1.0151	-0.9185	0.9986	0.0092
35.00	-2.0923	-1.9878	-1.0193	-0.7270	0.9992	0.0072
40.00	-2.0090	-1.8253	-1.0036	-0.7759	0.9994	0.0059

Table 6 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. From pure water to 50% m/m of PD quadratic polynomials were used while from 60% m/m of PD to pure PD lineal models were used. In all cases, correlation coefficient values greater than 0.997 were obtained. The values varied from 0.00025 K^{-1} in water up to 0.00073 K^{-1} in pure 1,2-propanediol.

From 0 to 0.3 in mole fraction of PD the α values increase readily, while over this composition the value remains almost invariant up to 0.8. In a first approach this fact would be explained in terms of water-structure losing by addition of PD. It should be kept in mind that over 0.3 in mole fraction of PD the most contributing component to all mixture volume is PD which is also the less polar solvent in these mixtures (1, 2).

Table 6. Volume thermal expansion coefficients of 1,2-propanediol + water mixtures at 25.00 °C

1,2-propanediol		$10^2 (\partial V/\partial T)$ / cm^3 mol^{-1} K^{-1}	$10^4 \alpha$ / K^{-1}
% m/m	Mole faction		
0.00	0.0000	0.4549	2.517
10.00	0.0256	0.6461	3.326
20.00	0.0559	0.8424	4.012
30.00	0.0921	1.074	4.693
40.00	0.1364	1.430	5.671
50.00	0.1915	1.732	6.152
60.00	0.2621	2.244	7.012
70.00	0.3559	2.643	7.108
80.00	0.4865	3.309	7.439
90.00	0.6807	4.131	7.448
100.00	1.0000	5.388	7.313

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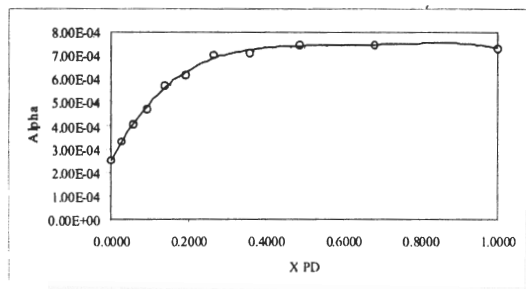
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Figure 5. Volume thermal expansion coefficients (K⁻¹) for 1,2-propanediol + water mixtures at 25.00 °C

An additional and important treatment is the evaluation of change of the excess molar volumes with temperature ($V \partial^E/\partial T$). Figura 6 shows this property at 25.00 °C (this value is constant over the entire temperature interval considered, that is, from 20.0 to 40.0 °C), which was obtained considering linear behavior of ($\partial V^E/\partial T$) in all mixtures studied (23). In almost all cases the determination coefficient values obtained were greater than 0.90, except for pure water. From Fig. 6 it follows that there is only a tendency according to composition. This property is positive which reflect the fact that excess volume decreases with increasing temperature.

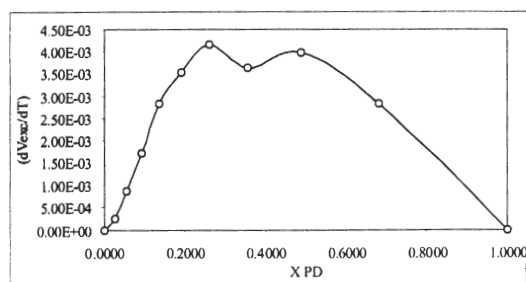Finally, from the excess molar volumes presented in Table 2 was calculated the change

of the excess molar enthalpies with pressure according to Eq. 10 (23):

$$\left(\frac{\partial H^E}{\partial p} \right)_T = V^E - T \left(\frac{\partial V^E}{\partial T} \right)_p \qquad \text{(Eq. 10)}$$

Figure 7 shows ($\partial H^E/\partial p$) values at 25.0 °C where it follows that this property is negative in all compositions, indicating an increase in the excess molar enthalpy as the pressure is increased. Unfortunately, there is not available experimental data in literature about this property for our system. Although, Kracht *et al.* (24) made a calorimetric study on heat of mixing of PD and W founding negative values for the excess molar enthalpies in all the temperatures studied. These values confirm fully the energetic nature of these mixing processes.

In general terms, based in our results and those presented in literature for other systems it can be concluded that 1,2-propanediol + water mixtures show non ideal behavior. These observations conduce 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.
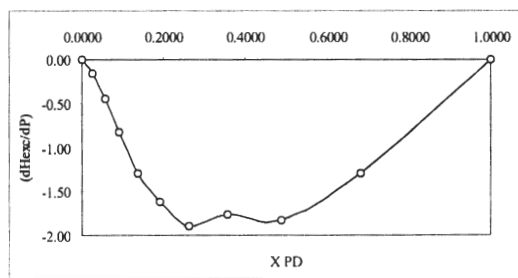

Figure 6. Change of the excess molar volumes with temperature (cm³ mol⁻¹ K⁻¹) for 1,2-propanediol + water mixtures at 25.00 °C (From 20.0 to 40.0 °C).

Figure 7. Change of the excess molar enthalpies with pressure (J mol⁻¹ MPa⁻¹) obtained from the excess molar volumes for 1,2-propanediol + water mixtures at 25.00 °C

Acknowledgments

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