

Volumetric properties of glycerol + water mixtures at several temperatures and correlation with the Jouyban-Acree model

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SUMMARY

Excess molar volumes and partial molar volumes were investigated from density values of the literature for glycerol + water mixtures at temperatures from (288.15 to 303.15) K. Excess molar volumes were fitted by Redlich-Kister equation and compared with values of literature for other similar systems. The system exhibits negative excess volumes probably due to increased interactions like hydrogen bonding and/or large differences in molar volumes of components. The effect of temperature on different volumetric properties studied is also analyzed. Besides, the volume thermal expansion coefficients are also calculated founding values from $2.51 \times 10^{-4} \text{ K}^{-1}$ for water to $7.24 \times 10^{-4} \text{ K}^{-1}$ for glycerol at 298.15 K. The Jouyban-Acree model was used for density and molar volume correlations of the studied mixtures at different temperatures. The mean relative deviations between experimental and calculated data were $0.19 \pm 0.11 \%$ and $0.32 \pm 0.25 \%$, respectively for density and molar volume data.

Key words: glycerol, water, binary liquid mixtures, density, excess volume, Jouyban-Acree model.

RESUMEN

Propiedades volumétricas de mezclas glicerol + agua a varias temperaturas y correlación con el modelo Jouyban-Acree

En este trabajo se calculan los volúmenes molares de exceso a partir de valores de densidad tomados de la literatura para el sistema glicerol + agua en todo el intervalo de composición a temperaturas entre 278,15 y 313,15 K. Los volúmenes molares de exceso se modelaron de acuerdo a la ecuación de Redlich-Kister usando polinomios regulares de segundo grado y se compararon con otros presentados en la literatura para otros sistemas. El sistema estudiado presenta volúmenes de exceso altamente negativos (hasta $-0,40 \text{ cm}^3 \text{ mol}^{-1}$) probablemente 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. Así mismo se calcularon los coeficientes térmicos de expansión volumétrica encontrado valores desde $2,51 \times 10^{-4} \text{ K}^{-1}$ para el agua pura hasta $4,38 \times 10^{-4} \text{ K}^{-1}$ para el glicerol puro a 298,15 K. Finalmente se usó el modelo Jouyban-Acree para correlacionar la densidad y el volumen molar de las diferentes mezclas encontrando desviaciones medias relativas de $0,19 \pm 0,11 \%$ y $0,32 \pm 0,25 \%$ para densidades y volúmenes molares respectivamente.

Palabras clave: glicerol, agua, mezclas líquidas binarias, volúmenes de exceso, modelo de Jouyban-Acree.

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). 1,2-Propanediol and ethanol are the cosolvents most used in design nowadays, especially those intended for elaboration of peroral and parenteral medications (3). Thus, several examples of pharmaceutical formulations using these cosolvents have been presented by Rubino (1). In similar way, glycerol has also been used in pharmaceutical and cosmetic sciences as cosolvent and evaporation regulator in several formulations (4, 5).

The mixtures obtained using these cosolvents and water show highly non-ideal behavior due to increased interactions between unlike molecules and large differences in

molar volumes of pure components, which leads to non-additive volumes on mixing (6, 7). 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 and cosmetics. This information is useful to understand the intermolecular interactions present in liquid pharmaceutical systems (8). Also, data related to density of solute free mixture of solvents might be useful in prediction of the density of pharmaceutical substances in mixture of solvents (9).

In this report, the excess molar volumes and the partial molar volumes of the binary system of glycerol + water at various temperatures in addition to other volumetric properties were calculated according to modified procedures widely exposed in the literature (10-12). This report is a continuation of those presented previously about some volumetric properties of ethanol + water (13), 1,2-propanediol + water mixtures (14), and glycerol formal + water (15).

DENSITIES AND CALCULATIONS

Density values of glycerol + water mixtures were taken from the literature (16). These values were determined in composition varying in 0.01 in mass fraction of glycerol to report 99 binary mixtures at temperatures of 288.15, 293.15, 298.15, and 303.15 K.

RESULTS AND DISCUSSION

In Table 1 the composition of glycerol + water mixtures, in mass percent and mole fraction, in addition to density values at several temperatures are presented (16). It is important to note that there are some other reports in the literature about density values of this binary system (17-20), but the more comprehensive and systematic is the one studied here. Moreover, some differences are found among the reported values. For this reason, the values compiled in the Ref. (16) are processed in this work. In all cases the density decreases almost linearly as the temperature increases except for water which is not linear. In the same way, density of mixtures increases almost linearly with the glycerol proportion.

Table 1. Densities (g cm^{-3}) for glycerol + water mixtures at various temperatures (16). μ_G and x_G represent mass and mole fraction of glycerol, respectively.

Glycerol		Temperature / K				Glycerol		Temperature / K			
μ_G	x_G	288.15	293.15	298.15	303.15	μ_G	x_G	288.15	293.15	298.15	303.15
0.0000	0.0000	0.99913	0.99823	0.99708	0.99658						
0.0100	0.0020	1.00155	1.00060	0.99945	0.99800	0.5100	0.1692	1.13150	1.12905	1.12650	1.12380
0.0200	0.0040	1.00395	1.00300	1.00180	1.00035	0.5200	0.1749	1.13425	1.13180	1.12920	1.12650
0.0300	0.0060	1.00635	1.00540	1.00415	1.00270	0.5300	0.1807	1.13705	1.13455	1.13195	1.12925
0.0400	0.0081	1.00875	1.00780	1.00655	1.00505	0.5400	0.1868	1.13980	1.13730	1.13465	1.13195
0.0500	0.0102	1.01120	1.01015	1.00890	1.00735	0.5500	0.1930	1.14260	1.14005	1.13740	1.13470
0.0600	0.0123	1.01360	1.01255	1.01125	1.00970	0.5600	0.1993	1.14535	1.14280	1.14015	1.13740
0.0700	0.0145	1.01600	1.01495	1.01360	1.01205	0.5700	0.2059	1.14815	1.14555	1.14285	1.14010
0.0800	0.0167	1.01840	1.01730	1.01600	1.01440	0.5800	0.2127	1.15095	1.14830	1.14560	1.14285
0.0900	0.0190	1.02085	1.01970	1.01835	1.01670	0.5900	0.2197	1.15370	1.15105	1.14835	1.14555
0.1000	0.0213	1.02325	1.02210	1.02070	1.01905	0.6000	0.2269	1.15650	1.15380	1.15105	1.14830
0.1100	0.0236	1.02575	1.02455	1.02315	1.02150	0.6100	0.2343	1.15925	1.15655	1.15380	1.15100
0.1200	0.0260	1.02830	1.02705	1.02560	1.02395	0.6200	0.2419	1.16200	1.15930	1.15655	1.15375
0.1300	0.0284	1.03080	1.02955	1.02805	1.02640	0.6300	0.2499	1.16480	1.16205	1.15925	1.15650
0.1400	0.0309	1.03330	1.03200	1.03055	1.02885	0.6400	0.2580	1.16755	1.16475	1.16200	1.15925
0.1500	0.0334	1.03580	1.03450	1.03300	1.03130	0.6500	0.2665	1.17030	1.16750	1.16475	1.16195
0.1600	0.0359	1.03835	1.03695	1.03545	1.03370	0.6600	0.2752	1.17305	1.17025	1.16745	1.16470
0.1700	0.0385	1.04085	1.03945	1.03790	1.03615	0.6700	0.2843	1.17585	1.17300	1.17020	1.16745
0.1800	0.0412	1.04335	1.04195	1.04035	1.03860	0.6800	0.2936	1.17860	1.17575	1.17295	1.17020
0.1900	0.0439	1.04590	1.04440	1.04280	1.04105	0.6900	0.3033	1.18135	1.17850	1.17565	1.17290
0.2000	0.0466	1.04840	1.04690	1.04525	1.04350	0.7000	0.3134	1.18415	1.18125	1.17840	1.17565
0.2100	0.0494	1.05100	1.04950	1.04780	1.04600	0.7100	0.3238	1.18690	1.18395	1.18110	1.17830
0.2200	0.0523	1.05365	1.05205	1.05035	1.04850	0.7200	0.3347	1.18965	1.18670	1.18380	1.18100
0.2300	0.0552	1.05625	1.05465	1.05290	1.05100	0.7300	0.3459	1.19235	1.18940	1.18650	1.18365
0.2400	0.0582	1.05885	1.05720	1.05545	1.05350	0.7400	0.3576	1.19510	1.19215	1.18925	1.18635
0.2500	0.0612	1.06150	1.05980	1.05800	1.05605	0.7500	0.3698	1.19785	1.19485	1.19195	1.18900
0.2600	0.0643	1.06410	1.06240	1.06055	1.05855	0.7600	0.3825	1.20060	1.19760	1.19465	1.19170
0.2700	0.0675	1.06670	1.06495	1.06305	1.06105	0.7700	0.3957	1.20335	1.20030	1.19735	1.19435
0.2800	0.0707	1.06935	1.06755	1.06560	1.06355	0.7800	0.4095	1.20610	1.20305	1.20005	1.19705

(Continued)

Table 1. Densities (g cm^{-3}) for glycerol + water mixtures at various temperatures (16). μ_G and x_G represent mass and mole fraction of glycerol, respectively (*continuation*).

Glycerol		Temperature / K				Glycerol		Temperature / K			
μ_G	x_G	288.15	293.15	298.15	303.15	μ_G	x_G	288.15	293.15	298.15	303.15
0.2900	0.0740	1.07195	1.07010	1.06815	1.06605	0.7900	0.4239	1.20885	1.20575	1.20275	1.19970
0.3000	0.0774	1.07455	1.07270	1.07070	1.06855	0.8000	0.4390	1.21160	1.20850	1.20545	1.20240
0.3100	0.0808	1.07725	1.07535	1.07335	1.07120	0.8100	0.4547	1.21425	1.21115	1.20810	1.20505
0.3200	0.0843	1.07995	1.07800	1.07600	1.07380	0.8200	0.4712	1.21690	1.21380	1.21075	1.20770
0.3300	0.0879	1.08265	1.08070	1.07860	1.07645	0.8300	0.4885	1.21955	1.21650	1.21340	1.21035
0.3400	0.0915	1.08530	1.08335	1.08125	1.07905	0.8400	0.5067	1.22220	1.21915	1.21605	1.21300
0.3500	0.0953	1.08800	1.08600	1.08390	1.08165	0.8500	0.5257	1.22485	1.22180	1.21870	1.21565
0.3600	0.0991	1.09070	1.08865	1.08655	1.08430	0.8600	0.5458	1.22750	1.22445	1.22135	1.21830
0.3700	0.1030	1.09340	1.09135	1.08915	1.08690	0.8700	0.5669	1.23015	1.22710	1.22400	1.22095
0.3800	0.1071	1.09605	1.09400	1.09180	1.08955	0.8800	0.5892	1.23280	1.22975	1.22665	1.22360
0.3900	0.1112	1.09875	1.09665	1.09445	1.09215	0.8900	0.6128	1.23545	1.23245	1.22935	1.22625
0.4000	0.1154	1.10145	1.09930	1.09710	1.09475	0.9000	0.6378	1.23810	1.23510	1.23200	1.22890
0.4100	0.1197	1.10415	1.10200	1.09975	1.09740	0.9100	0.6642	1.24075	1.23770	1.23460	1.23150
0.4200	0.1241	1.10690	1.10470	1.10240	1.10005	0.9200	0.6923	1.24340	1.24035	1.23725	1.23410
0.4300	0.1286	1.10960	1.10740	1.10510	1.10265	0.9300	0.7221	1.24600	1.24300	1.23985	1.23670
0.4400	0.1332	1.11235	1.11010	1.10775	1.10530	0.9400	0.7540	1.24865	1.24560	1.24250	1.23930
0.4500	0.1380	1.11510	1.11280	1.11040	1.10795	0.9500	0.7880	1.25130	1.24825	1.24515	1.24190
0.4600	0.1428	1.11780	1.11550	1.11310	1.11055	0.9600	0.8244	1.25385	1.25080	1.24770	1.24450
0.4700	0.1478	1.12055	1.11820	1.11575	1.11320	0.9700	0.8635	1.25645	1.25335	1.25030	1.24710
0.4800	0.1530	1.12325	1.12090	1.11840	1.11580	0.9800	0.9055	1.25900	1.25590	1.25290	1.24975
0.4900	0.1582	1.12600	1.12360	1.12110	1.11845	0.9900	0.9509	1.26160	1.25850	1.25545	1.25235
0.5000	0.1636	1.12870	1.12630	1.12375	1.12110	1.0000	1.0000	1.26415	1.26108	1.25802	1.25495

Molar volumes and excess molar volumes

Table 2 summarizes the molar volumes (V^0) for the binary mixtures at all temperatures. V^0 values were calculated from Eq. 1.

$$V^0 = \frac{x_1 M_1 + x_2 M_2}{\rho} \quad (\text{Eq. 1})$$

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.

Table 2. Molar volumes ($\text{cm}^3 \text{mol}^{-1}$) for glycerol + water mixtures at various temperatures.

Glycerol		Temperature / K				Glycerol		Temperature / K			
μ_G	x_G	288.15	293.15	298.15	303.15	μ_G	x_G	288.15	293.15	298.15	303.15
0.0000	0.0000	18.031	18.047	18.068	18.077						
0.0100	0.0020	18.133	18.150	18.171	18.198	0.5100	0.1692	26.996	27.055	27.116	27.181
0.0200	0.0040	18.238	18.255	18.277	18.303	0.5200	0.1749	27.303	27.363	27.426	27.491
0.0300	0.0060	18.344	18.362	18.384	18.411	0.5300	0.1807	27.618	27.679	27.743	27.809
0.0400	0.0081	18.453	18.470	18.493	18.521	0.5400	0.1868	27.943	28.005	28.070	28.137
0.0500	0.0102	18.562	18.582	18.605	18.633	0.5500	0.1930	28.277	28.340	28.406	28.474
0.0600	0.0123	18.675	18.694	18.718	18.747	0.5600	0.1993	28.622	28.686	28.752	28.822
0.0700	0.0145	18.790	18.809	18.834	18.863	0.5700	0.2059	28.976	29.042	29.111	29.181
0.0800	0.0167	18.906	18.927	18.951	18.981	0.5800	0.2127	29.342	29.409	29.479	29.550
0.0900	0.0190	19.025	19.046	19.071	19.102	0.5900	0.2197	29.720	29.788	29.858	29.931
0.1000	0.0213	19.146	19.168	19.194	19.225	0.6000	0.2269	30.109	30.179	30.251	30.324
0.1100	0.0236	19.268	19.290	19.317	19.348	0.6100	0.2343	30.512	30.583	30.656	30.730
0.1200	0.0260	19.391	19.415	19.442	19.474	0.6200	0.2419	30.928	31.000	31.074	31.149
0.1300	0.0284	19.518	19.542	19.570	19.602	0.6300	0.2499	31.357	31.431	31.507	31.582
0.1400	0.0309	19.647	19.672	19.700	19.732	0.6400	0.2580	31.802	31.878	31.953	32.029
0.1500	0.0334	19.779	19.804	19.833	19.865	0.6500	0.2665	32.262	32.339	32.415	32.494
0.1600	0.0359	19.913	19.940	19.968	20.002	0.6600	0.2752	32.738	32.816	32.895	32.973
0.1700	0.0385	20.050	20.077	20.107	20.141	0.6700	0.2843	33.230	33.311	33.390	33.469
0.1800	0.0412	20.190	20.217	20.248	20.282	0.6800	0.2936	33.741	33.823	33.903	33.983
0.1900	0.0439	20.332	20.361	20.393	20.427	0.6900	0.3033	34.271	34.354	34.437	34.518
0.2000	0.0466	20.478	20.507	20.540	20.574	0.7000	0.3134	34.819	34.905	34.989	35.071
0.2100	0.0494	20.625	20.655	20.688	20.724	0.7100	0.3238	35.390	35.478	35.564	35.648
0.2200	0.0523	20.774	20.806	20.840	20.876	0.7200	0.3347	35.983	36.073	36.161	36.247
0.2300	0.0552	20.928	20.959	20.994	21.032	0.7300	0.3459	36.601	36.692	36.782	36.870
0.2400	0.0582	21.084	21.117	21.152	21.191	0.7400	0.3576	37.243	37.335	37.426	37.517
0.2500	0.0612	21.243	21.278	21.314	21.353	0.7500	0.3698	37.911	38.006	38.098	38.193
0.2600	0.0643	21.407	21.441	21.479	21.519	0.7600	0.3825	38.607	38.703	38.799	38.895

(Continued)

Table 2. Molar volumes ($\text{cm}^3 \text{mol}^{-1}$) for glycerol + water mixtures at various temperatures (*continuation*).

Glycerol		Temperature / K				Glycerol		Temperature / K			
μ_G	x_G	288.15	293.15	298.15	303.15	μ_G	x_G	288.15	293.15	298.15	303.15
0.2700	0.0675	21.574	21.610	21.648	21.689	0.7700	0.3957	39.332	39.432	39.529	39.629
0.2800	0.0707	21.744	21.781	21.821	21.863	0.7800	0.4095	40.090	40.192	40.292	40.393
0.2900	0.0740	21.919	21.957	21.997	22.040	0.7900	0.4239	40.881	40.986	41.089	41.193
0.3000	0.0774	22.098	22.136	22.177	22.222	0.8000	0.4390	41.709	41.816	41.922	42.028
0.3100	0.0808	22.279	22.318	22.360	22.405	0.8100	0.4547	42.579	42.688	42.795	42.904
0.3200	0.0843	22.464	22.504	22.546	22.592	0.8200	0.4712	43.490	43.601	43.711	43.821
0.3300	0.0879	22.653	22.694	22.738	22.784	0.8300	0.4885	44.446	44.557	44.671	44.783
0.3400	0.0915	22.848	22.889	22.934	22.980	0.8400	0.5067	45.449	45.563	45.679	45.794
0.3500	0.0953	23.047	23.089	23.134	23.182	0.8500	0.5257	46.504	46.620	46.739	46.856
0.3600	0.0991	23.250	23.294	23.339	23.387	0.8600	0.5458	47.615	47.733	47.855	47.974
0.3700	0.1030	23.458	23.502	23.550	23.598	0.8700	0.5669	48.785	48.907	49.030	49.153
0.3800	0.1071	23.672	23.717	23.765	23.814	0.8800	0.5892	50.021	50.145	50.272	50.397
0.3900	0.1112	23.891	23.937	23.985	24.035	0.8900	0.6128	51.327	51.452	51.581	51.712
0.4000	0.1154	24.115	24.162	24.211	24.263	0.9000	0.6378	52.709	52.837	52.970	53.104
0.4100	0.1197	24.345	24.392	24.442	24.495	0.9100	0.6642	54.175	54.309	54.445	54.582
0.4200	0.1241	24.579	24.628	24.680	24.732	0.9200	0.6923	55.732	55.869	56.009	56.152
0.4300	0.1286	24.821	24.870	24.922	24.977	0.9300	0.7221	57.392	57.530	57.677	57.824
0.4400	0.1332	25.068	25.119	25.172	25.228	0.9400	0.7540	59.159	59.304	59.452	59.605
0.4500	0.1380	25.321	25.374	25.429	25.485	0.9500	0.7880	61.047	61.196	61.349	61.509
0.4600	0.1428	25.583	25.635	25.691	25.750	0.9600	0.8244	63.074	63.228	63.385	63.548
0.4700	0.1478	25.850	25.904	25.961	26.021	0.9700	0.8635	65.248	65.409	65.569	65.737
0.4800	0.1530	26.126	26.181	26.239	26.300	0.9800	0.9055	67.590	67.757	67.919	68.090
0.4900	0.1582	26.408	26.464	26.523	26.586	0.9900	0.9509	70.115	70.287	70.458	70.632
0.5000	0.1636	26.699	26.756	26.817	26.880	1.0000	1.0000	72.850	73.028	73.205	73.384

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 presented in Table 3. This behavior is shown graphically in Figure 1 at all temperatures.

$$V^{0-\text{Exc}} = \frac{x_1 M_1 + x_2 M_2}{\rho} - \left(\frac{x_1 M_1}{\rho_1} + \frac{x_2 M_2}{\rho_2} \right) \quad (\text{Eq. 2})$$

Table 3. Excess molar volumes ($\text{cm}^3 \text{mol}^{-1}$) for glycerol + water mixtures at various temperatures.

Glycerol		Temperature / K				Glycerol		Temperature / K			
μ_G	x_G	288.15	293.15	298.15	303.15	μ_G	x_G	288.15	293.15	298.15	303.15
0.0000	0.0000	0.000	0.000	0.000	0.000						
0.0100	0.0020	-0.006	-0.005	-0.005	0.012	0.5100	0.1692	-0.308	-0.293	-0.279	-0.252
0.0200	0.0040	-0.011	-0.011	-0.010	0.006	0.5200	0.1749	-0.313	-0.299	-0.284	-0.257
0.0300	0.0060	-0.016	-0.016	-0.015	0.001	0.5300	0.1807	-0.320	-0.305	-0.290	-0.264
0.0400	0.0081	-0.021	-0.022	-0.021	-0.004	0.5400	0.1868	-0.325	-0.310	-0.295	-0.269
0.0500	0.0102	-0.027	-0.026	-0.025	-0.007	0.5500	0.1930	-0.332	-0.316	-0.301	-0.275
0.0600	0.0123	-0.032	-0.031	-0.030	-0.012	0.5600	0.1993	-0.337	-0.321	-0.307	-0.280
0.0700	0.0145	-0.037	-0.036	-0.034	-0.017	0.5700	0.2059	-0.343	-0.326	-0.311	-0.285
0.0800	0.0167	-0.041	-0.040	-0.039	-0.021	0.5800	0.2127	-0.349	-0.331	-0.316	-0.291
0.0900	0.0190	-0.047	-0.045	-0.043	-0.025	0.5900	0.2197	-0.353	-0.336	-0.322	-0.295
0.1000	0.0213	-0.051	-0.049	-0.047	-0.029	0.6000	0.2269	-0.359	-0.341	-0.325	-0.300
0.1100	0.0236	-0.057	-0.055	-0.053	-0.035	0.6100	0.2343	-0.363	-0.345	-0.330	-0.304
0.1200	0.0260	-0.064	-0.061	-0.058	-0.040	0.6200	0.2419	-0.366	-0.350	-0.335	-0.309
0.1300	0.0284	-0.070	-0.067	-0.064	-0.046	0.6300	0.2499	-0.371	-0.354	-0.338	-0.314
0.1400	0.0309	-0.076	-0.072	-0.070	-0.052	0.6400	0.2580	-0.375	-0.356	-0.342	-0.319
0.1500	0.0334	-0.081	-0.078	-0.075	-0.057	0.6500	0.2665	-0.378	-0.359	-0.346	-0.322
0.1600	0.0359	-0.088	-0.083	-0.080	-0.062	0.6600	0.2752	-0.380	-0.363	-0.348	-0.326
0.1700	0.0385	-0.093	-0.088	-0.085	-0.067	0.6700	0.2843	-0.384	-0.366	-0.351	-0.330
0.1800	0.0412	-0.098	-0.094	-0.090	-0.072	0.6800	0.2936	-0.387	-0.369	-0.355	-0.334
0.1900	0.0439	-0.104	-0.098	-0.095	-0.077	0.6900	0.3033	-0.389	-0.371	-0.356	-0.336
0.2000	0.0466	-0.109	-0.103	-0.099	-0.082	0.7000	0.3134	-0.392	-0.373	-0.359	-0.339
0.2100	0.0494	-0.116	-0.110	-0.105	-0.087	0.7100	0.3238	-0.393	-0.374	-0.360	-0.339
0.2200	0.0523	-0.123	-0.116	-0.112	-0.093	0.7200	0.3347	-0.394	-0.375	-0.360	-0.340
0.2300	0.0552	-0.130	-0.123	-0.118	-0.098	0.7300	0.3459	-0.394	-0.375	-0.360	-0.339
0.2400	0.0582	-0.136	-0.129	-0.124	-0.103	0.7400	0.3576	-0.394	-0.376	-0.361	-0.340
0.2500	0.0612	-0.143	-0.135	-0.129	-0.110	0.7500	0.3698	-0.394	-0.374	-0.361	-0.338
0.2600	0.0643	-0.149	-0.142	-0.135	-0.115	0.7600	0.3825	-0.393	-0.375	-0.360	-0.338
0.2700	0.0675	-0.155	-0.147	-0.140	-0.119	0.7700	0.3957	-0.392	-0.373	-0.358	-0.335
0.2800	0.0707	-0.162	-0.153	-0.145	-0.124	0.7800	0.4095	-0.391	-0.372	-0.356	-0.334
0.2900	0.0740	-0.168	-0.158	-0.150	-0.129	0.7900	0.4239	-0.389	-0.369	-0.354	-0.330

(Continued)

Table 3. Excess molar volumes ($\text{cm}^3 \text{mol}^{-1}$) for glycerol + water mixtures at various temperatures (*continuation*).

Glycerol		Temperature / K				Glycerol		Temperature / K			
μ_G	x_G	288.15	293.15	298.15	303.15	μ_G	x_G	288.15	293.15	298.15	303.15
0.3000	0.0774	-0.173	-0.164	-0.156	-0.133	0.8000	0.4390	-0.387	-0.367	-0.351	-0.328
0.3100	0.0808	-0.181	-0.171	-0.163	-0.141	0.8100	0.4547	-0.380	-0.361	-0.345	-0.323
0.3200	0.0843	-0.188	-0.177	-0.170	-0.147	0.8200	0.4712	-0.373	-0.354	-0.339	-0.318
0.3300	0.0879	-0.195	-0.185	-0.175	-0.154	0.8300	0.4885	-0.365	-0.349	-0.332	-0.312
0.3400	0.0915	-0.201	-0.191	-0.182	-0.160	0.8400	0.5067	-0.357	-0.341	-0.325	-0.305
0.3500	0.0953	-0.208	-0.198	-0.189	-0.166	0.8500	0.5257	-0.347	-0.332	-0.317	-0.298
0.3600	0.0991	-0.215	-0.204	-0.195	-0.173	0.8600	0.5458	-0.336	-0.322	-0.307	-0.289
0.3700	0.1030	-0.222	-0.211	-0.200	-0.178	0.8700	0.5669	-0.325	-0.311	-0.297	-0.280
0.3800	0.1071	-0.228	-0.217	-0.207	-0.185	0.8800	0.5892	-0.312	-0.299	-0.286	-0.270
0.3900	0.1112	-0.234	-0.222	-0.213	-0.190	0.8900	0.6128	-0.298	-0.288	-0.276	-0.258
0.4000	0.1154	-0.240	-0.228	-0.218	-0.195	0.9000	0.6378	-0.283	-0.274	-0.262	-0.246
0.4100	0.1197	-0.246	-0.234	-0.224	-0.201	0.9100	0.6642	-0.267	-0.256	-0.245	-0.230
0.4200	0.1241	-0.254	-0.241	-0.230	-0.207	0.9200	0.6923	-0.248	-0.239	-0.229	-0.212
0.4300	0.1286	-0.259	-0.247	-0.236	-0.212	0.9300	0.7221	-0.226	-0.220	-0.208	-0.193
0.4400	0.1332	-0.266	-0.253	-0.242	-0.218	0.9400	0.7540	-0.205	-0.197	-0.189	-0.172
0.4500	0.1380	-0.273	-0.259	-0.247	-0.223	0.9500	0.7880	-0.181	-0.175	-0.167	-0.149
0.4600	0.1428	-0.278	-0.265	-0.253	-0.227	0.9600	0.8244	-0.150	-0.145	-0.138	-0.124
0.4700	0.1478	-0.285	-0.271	-0.258	-0.232	0.9700	0.8635	-0.119	-0.113	-0.109	-0.097
0.4800	0.1530	-0.290	-0.276	-0.262	-0.236	0.9800	0.9055	-0.082	-0.077	-0.078	-0.069
0.4900	0.1582	-0.296	-0.281	-0.268	-0.241	0.9900	0.9509	-0.044	-0.041	-0.040	-0.036
0.5000	0.1636	-0.301	-0.287	-0.272	-0.246	1.0000	1.0000	0.000	0.000	0.000	0.000

Analogous to the behavior obtained in other investigations (13-15), in almost all cases the excess volumes are largely negative (especially around 0.38 in mole fraction of glycerol, where it is near to $-0.38 \text{ cm}^3 \text{ mol}^{-1}$) indicating contraction in volume. As mentioned before (13-15), according to Fort and Moore (21), 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 all cases.

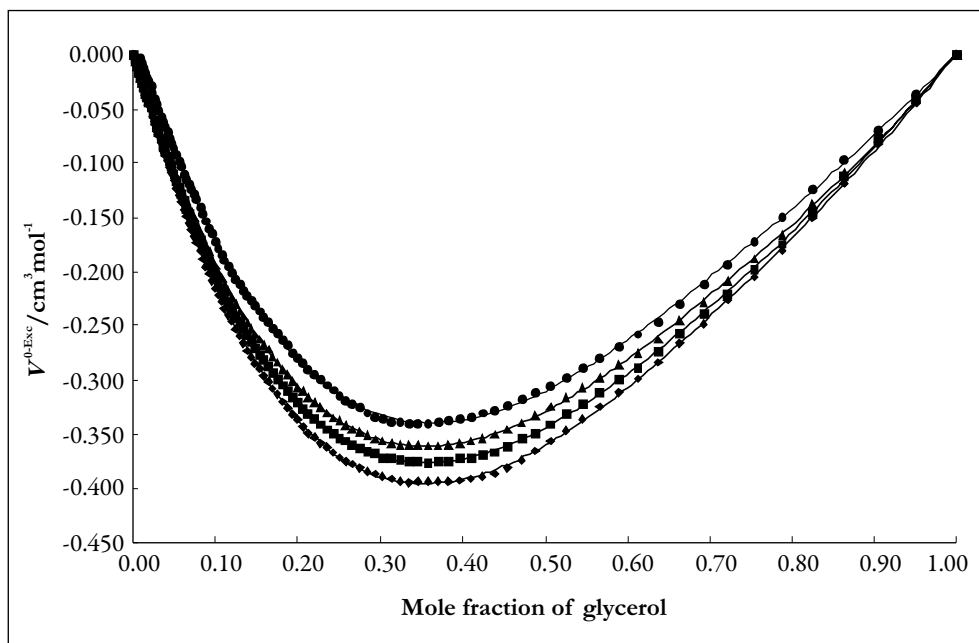


Figure 1. Excess molar volumes of glycerol + water mixtures at several temperatures. (◆): 288.15 K; (■): 293.15 K; (▲): 298.15 K; (●): 303.15 K.

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 water by addition of glycerol; second: contraction due to free volume difference of unlike molecules; and third: contraction due to hydrogen bond formation between glycerol and water through -OH--OH bonding (21).

Thus, the large negative values of $V^{0\text{-Exc}}$ over the free volume contribution indicate the presence of strong specific interactions with predominance of formation of hydrogen bonds between glycerol and water over the rupture of hydrogen bonding in 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 glycerol and water molecules with increase in temperature.

With the aim to compare the effect of the mixtures polarity on the maximum excess molar volumes, Table 4 shows the values obtained for ethanol + water (13), 1,2-propanediol + water (14), and glycerol + water. Mixtures compositions are expressed in

mass, mole, and volume fractions, respectively. Volume fractions were calculated by assuming additive behavior according to $f = V_{\text{cosolv}} / (V_{\text{cosolv}} + V_{\text{water}})$ with V equal to volume of each component (22). Dielectric constant (relative dielectric permittivity) and Hildebrand solubility parameter of mixtures have been chosen as polarity indexes (23, 24). These properties have been calculated by considering additive behavior when the mixtures compositions are expressed in volume fractions (2), except for the dielectric constant of ethanol + water and glycerol + water mixtures, where a model developed by Jouyban *et al.* was employed (25). It is remarkable that maximum negative excess molar volumes are linearly correlated with both polarity indexes as can be seen in Figures 2 and 3 in which the greater the absolute excess volume is, the lower the polarity of cosolvent is. Besides, better correlation was found with solubility parameter.

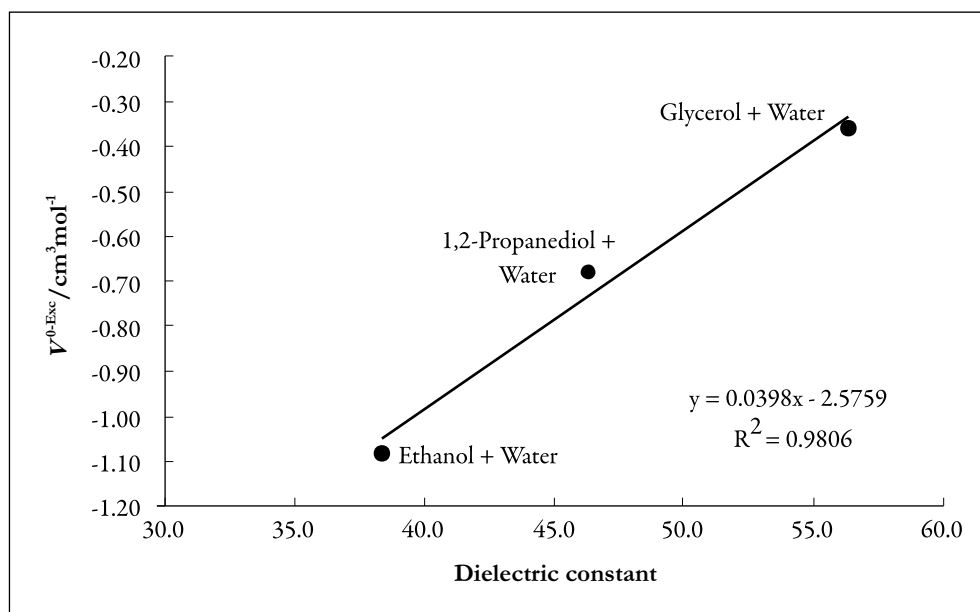


Figure 2. Maximum excess volume for cosolvent + water mixtures as function of mixtures dielectric constant at 298.15 K

Table 4. Composition of cosolvent mixtures where maximum excess volume for cosolvent + water mixtures were obtained as function of mixtures dielectric constant (ϵ) and Hildebrand solubility parameter (δ) at 298.15 K

Cosolvent	Mass fraction	Mole fraction	Volume fraction	ϵ		$\delta / \text{MPa}^{1/2}$		$V^{0-\text{Exc}} / \text{cm}^3 \text{mol}^{-1}$
				Mix	Pure	Mix	Pure	
Ethanol	0.7000	0.4772	0.7476	38.4	24.5	31.9	26.5	-1.082
1,2-Propanediol	0.7000	0.3559	0.6925	46.3	32.0	35.6	30.2	-0.677
Glycerol	0.7400	0.3576	0.6928	56.4	42.5	39.7	36.1	-0.361

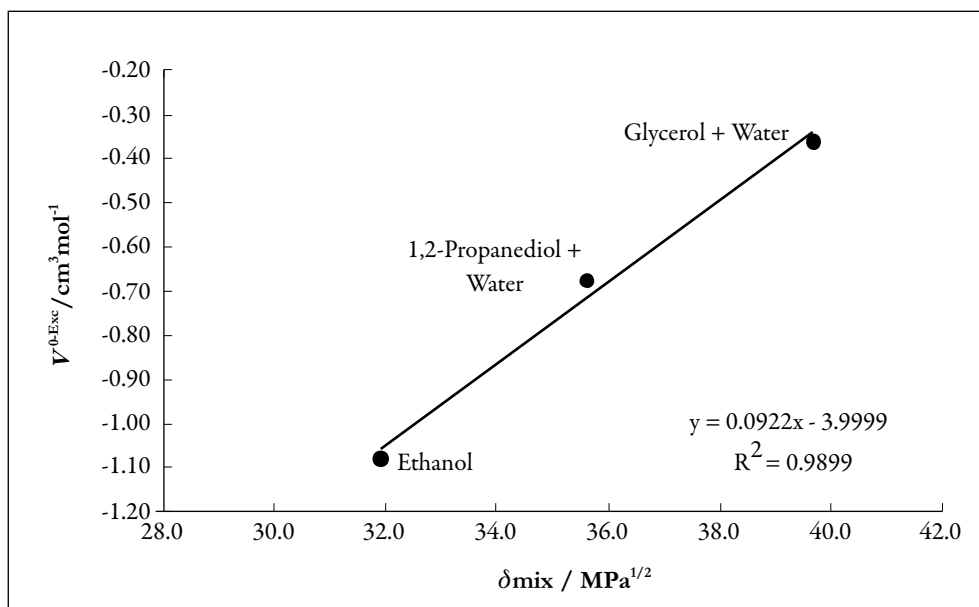


Figure 3. Maximum excess volume for cosolvent + water mixtures as function of mixtures Hildebrand solubility parameter at 298.15 K.

Redlich-Kister equation

Redlich and Kister (26) introduced in 1948 the general form of Eq. 3 to facilitate the representation of thermodynamic properties and the classification of solutions in multicomponent systems, especially those important in petroleum chemistry. The Redlich-Kister equation has been used in recent decades for manipulating several kinds of physicochemical values of mixtures such as: excess volumes, excess viscosities, solubilities in cosolvent mixtures, among others.

$$V^{0-\text{Exc}} = x_1 x_2 \sum a_i (x_1 - x_2)^i \quad (\text{Eq. 3})$$

In the analysis of excess volume data, Eq. 3 was used in the form of second degree polynomial equations using least square analyses, and therefore, obtaining three coefficients as presented in Eq. 4. Polynomials of second and third degrees are the most widely used in this case again, based on their relevant statistic parameters such as determination coefficients and standard deviations.

$$\frac{V^{0-\text{Exc}}}{x_1 x_2} = a_0 + a_1 (x_1 - x_2) + a_2 (x_1 - x_2)^2 \quad (\text{Eq. 4})$$

The Redlich-Kister parameters for glycerol + water mixtures at all temperatures studied are presented in Table 5 in addition to determination coefficients and standard deviations calculated according to Eq. 5 (where D is the number of compositions studied and N is the number of terms used in the regression, that is 99 and 3 respectively in this case). Eq. 5 has been widely used in the literature (8, 10-15). Figure 4 shows the Redlich-Kister equation applied to glycerol + water excess molar volume data at all temperatures studied.

$$\sigma(V^{0-\text{Exc}}) = \sqrt{\frac{\sum (V_{\text{expt}}^{0-\text{Exc}} - V_{\text{calc}}^{0-\text{Exc}})^2}{D - N}} \quad (\text{Eq. 5})$$

Table 5. Redlich-Kister regression results for the excess molar volumes of glycerol + water mixtures at various temperatures.

T / K	a_0	a_1	a_2	r^2	$\sigma / \text{cm}^3 \text{mol}^{-1}$
288.15	-1.4506	0.8771	-0.3428	0.9907	0.0021
293.15	-1.3816	0.8304	-0.3329	0.9910	0.0019
298.15	-1.3169	0.7854	-0.3449	0.9881	0.0015
303.15	-1.1954	0.7598	-0.2085	0.9981	0.0089

The variation coefficients are greater than 0.99 which indicate that the obtained regular polynomials regressions describe adequately the excess volumes, because the standard deviations are similar to those presented in the literature for other mixtures (8, 10-15). It is important to note that the different behavior observed at 303.15 K could be due to the low negative excess molar volumes and even positive values obtained in water-rich mixtures. On the other hand, σ values obtained for glycerol + water mixtures were

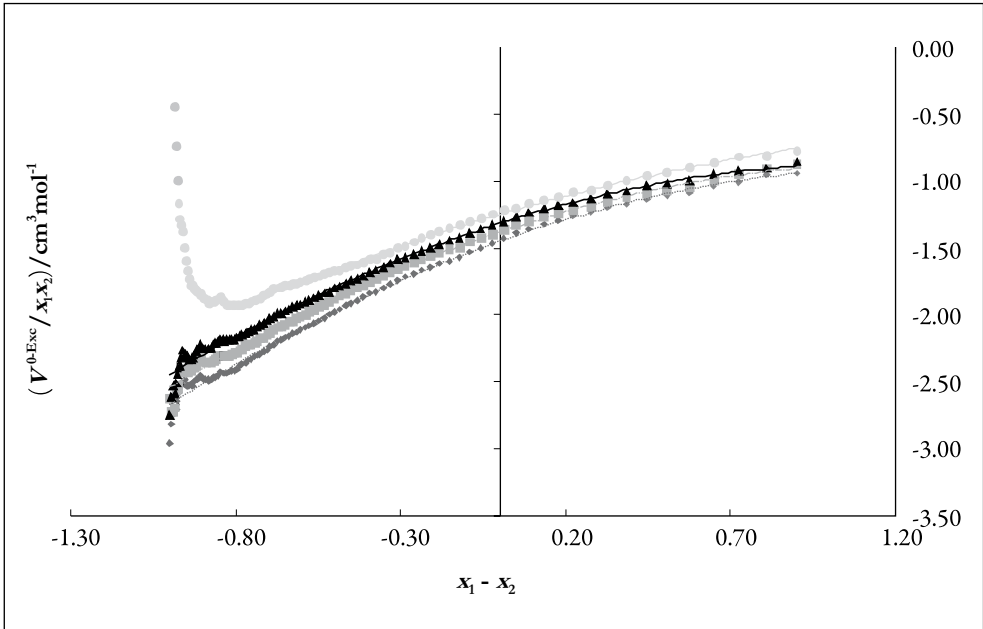


Figure 4. Regression adjusted to Redlich-Kister equation using three terms for glycerol + water mixtures at several temperatures. (\diamond): 288.15 K; (\square): 293.15 K; (Δ): 298.15 K; (\circ): 303.15 K.

in general lower than those obtained for ethanol + water (13) and 1,2-propanediol + water (14) although third degree regular polynomials were used to describe these systems.

Volume thermal expansion

On the other hand, in pharmaceutical and chemical pre-formulation studies, it is very important to predict the variation of physicochemical properties related to pharmaceutical dosage forms, with respect to temperature changes; especially those properties which affect the concentration of active ingredients in the formulations developed. For this reason, the volume thermal expansion coefficients (α) were calculated by means of Eq. 6 (27) using the variation of molar volumes with temperature (Table 2).

$$\alpha = \frac{1}{V^0} \left(\frac{\partial V^0}{\partial T} \right)_{p,x} \quad (\text{Eq. 6})$$

Table 6 summarizes the $(\partial V^0 / \partial T)$ and α values for pure solvents and binary mixtures varying in mole fractions near to 0.05, whereas Figure 5 shows the volume thermal expansion coefficients at 298.15 K. For all mixtures and pure solvents, linear models

were used, in which obtained determination coefficients are greater than 0.999, except for water where quadratic model has been obtained. The α values varied from $2.51 \times 10^{-4} \text{ K}^{-1}$ in water up to $4.86 \times 10^{-4} \text{ K}^{-1}$ in pure glycerol. From 0 to 0.20 in mole fraction of glycerol the α values increase readily. In a first approach this fact would be explained in terms of water-structure loosing by addition of glycerol. It should be kept in mind that over 0.3 in mole fraction of glycerol the most contributing component in mass to all mixtures is glycerol, which is also the less polar solvent in these mixtures (2, 3).

Table 6. Variation of molar volumes with temperature ($\partial V^0/\partial T$), volume thermal expansion coefficients (α), excess molar volumes with temperature ($\partial V^{0-\text{Exc}}/\partial T$), and excess molar enthalpies with pressure ($\partial H^{0-\text{Exc}}/\partial p$) of glycerol + water mixtures at 298.15 K.

Glycerol		$10^2 (\partial V^0/\partial T) / \text{cm}^3 \text{ mol}^{-1} \text{ K}^{-1}$	$10^4 \alpha / \text{K}^{-1}$	$10^3 (\partial V^{0-\text{Exc}}/\partial T) / \text{cm}^3 \text{ mol}^{-1} \text{ K}^{-1}$	$(\partial H^{0-\text{Exc}}/\partial p) / \text{J mol}^{-1} \text{ MPa}^{-1}$
μ_G	x_G				
0.0000	0.0000	0.454	2.510	0.000	0.000
0.2100	0.0494	0.659	3.183	2.444	-0.834
0.3600	0.0991	0.913	3.914	3.284	-1.174
0.4700	0.1478	1.138	4.383	3.952	-1.436
0.5600	0.1993	1.334	4.639	4.245	-1.572
0.6300	0.2499	1.502	4.768	4.021	-1.537
0.6900	0.3033	1.648	4.786	3.582	-1.424
0.7300	0.3459	1.794	4.876	3.633	-1.443
0.7700	0.3957	1.973	4.990	3.865	-1.511
0.8100	0.4547	2.166	5.061	3.860	-1.496
0.8400	0.5067	2.301	5.036	3.590	-1.395
0.8600	0.5458	2.400	5.015	3.297	-1.290
0.8800	0.5892	2.510	4.993	2.976	-1.173
0.9000	0.6378	2.634	4.972	2.834	-1.107
0.9200	0.6923	2.800	4.999	2.723	-1.040
0.9400	0.7540	2.974	5.002	2.572	-0.955
0.9500	0.7880	3.077	5.016	2.625	-0.950
0.9600	0.8244	3.158	4.981	2.120	-0.770
0.9700	0.8635	3.254	4.963	1.688	-0.613
0.9800	0.9055	3.326	4.897	0.726	-0.294
0.9900	0.9509	3.449	4.895	0.483	-0.184
1.0000	1.0000	3.560	4.862	0.000	0.000

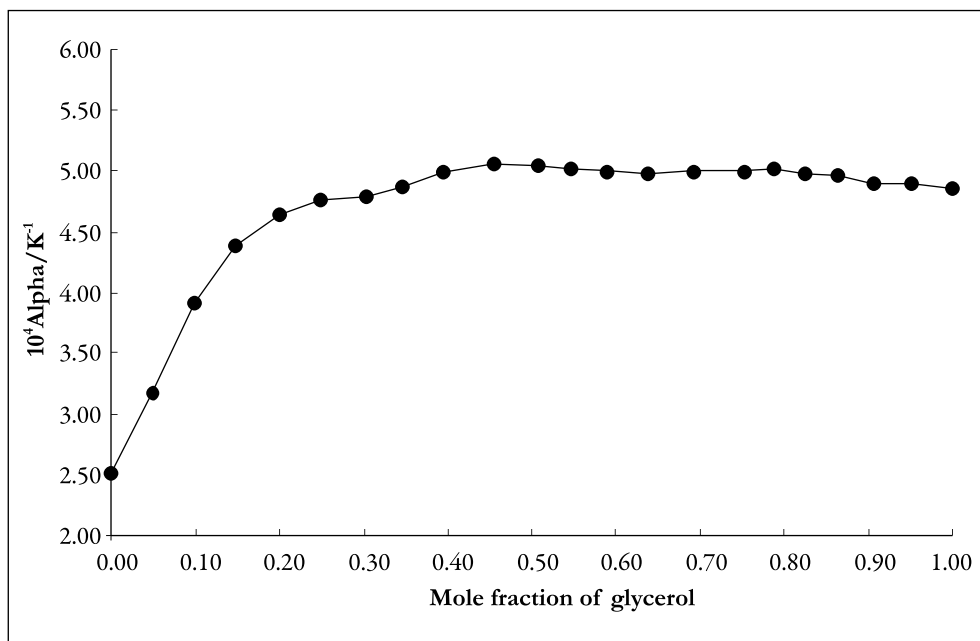


Figure 5. Volume thermal expansion coefficients for glycerol + water mixtures at 298.15 K

To correlate volume thermal expansion coefficients with solvent polarity Figures 6 and 7 show the variation of this property with the dielectric constant and Hildebrand solubility parameter of each pure solvent for ethanol, 1,2-propanediol and glycerol, respectively. It is clear that inverse relation is found between α and polarity indexes because bigger molar expansivities correspond to lesser polar cosolvents.

Variation of excess molar volume with temperature

An additional and important treatment is the evaluation of change of the excess molar volumes with temperature ($\partial V^{\text{Exc}} / \partial T$). Table 6 and Figure 8 show this property at 298.15 K (this value is constant over the entire temperature interval considered, that is, from 288.15 K to 303.15 K), which was obtained considering parabolic behavior of ($\partial V^{\text{Exc}} / \partial T$) in almost all mixtures studied, except the last two. In almost all cases the determination coefficient values obtained were greater than 0.98. From Figure 8 it follows that there is only a tendency according to composition, that is, this property is always positive, which reflects the fact that excess volume decreases with increasing temperature. This result could be due to weakening of hydrogen-bonding as the temperature increases which could lead to solvent structure loosing, and thus, leading to more ideal mixing behavior.

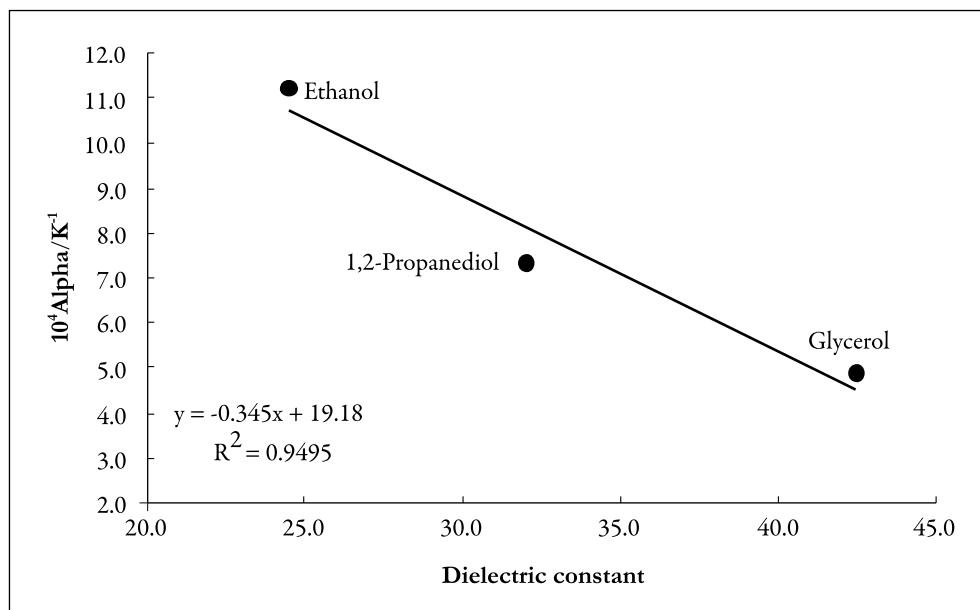


Figure 6. Volume thermal expansion coefficients for ethanol, 1,2-propanediol and glycerol as pure solvents as function of dielectric constant at 298.15 K

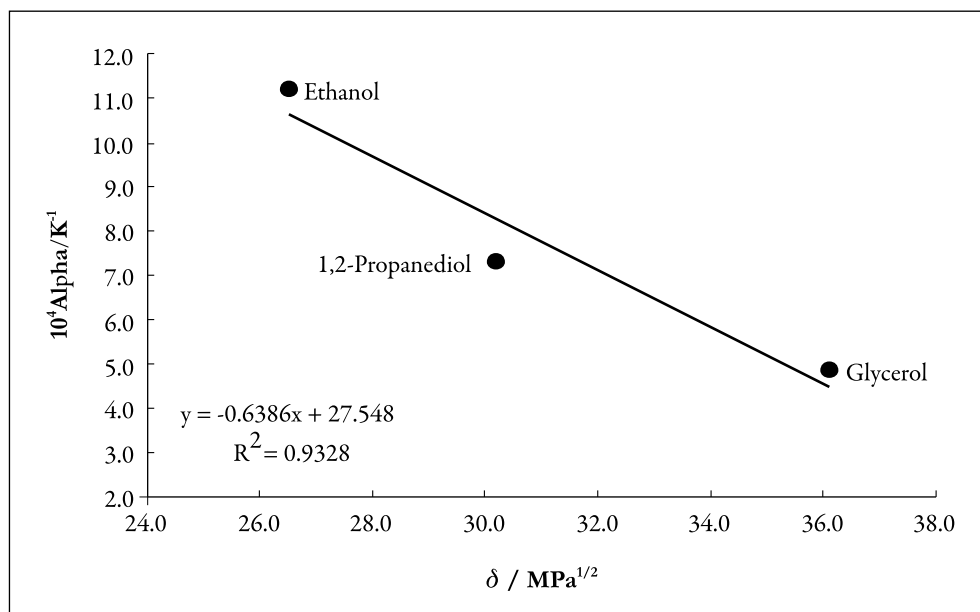


Figure 7. Volume thermal expansion coefficients for ethanol, 1,2-propanediol, and glycerol, as pure solvents as function of Hildebrand solubility parameter at 298.15 K

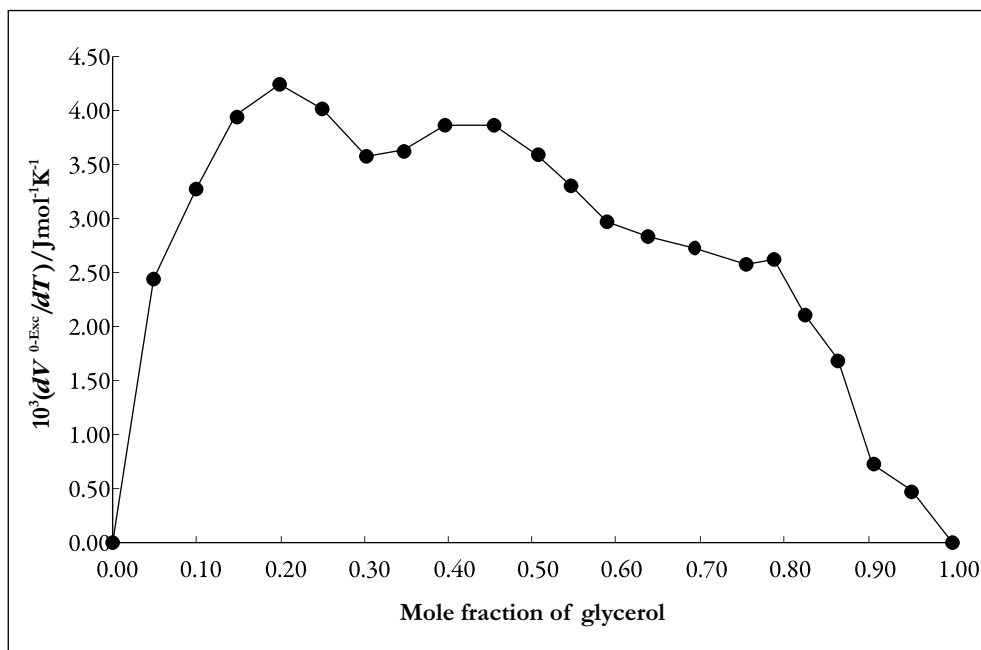


Figure 8. Variation of excess molar volumes with temperature for glycerol + water mixtures at 298.15 K (Considering the interval from 288.15 to 303.15 K).

Variation of excess molar enthalpy with pressure

From the excess molar volumes presented in Table 3, the change of the excess molar enthalpies with pressure according to Eq. 7 was calculated (27):

$$\left(\frac{\partial H^{0-Exc}}{\partial p}\right)_T = V^E - T\left(\frac{\partial V^{0-Exc}}{\partial T}\right)_p \quad (\text{Eq. 7})$$

Table 6 and Figure 9 show $(\partial H^{0-Exc}/\partial p)$ values at 298.15 K. 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 the literature about this property for this system. Although, Batov *et al.* (28) made a calorimetric study on heat of mixing of glycerol and water founding excess molar enthalpies negative in all the mixtures studied at 298.15 K (from 298.15 K to 338.15 K).

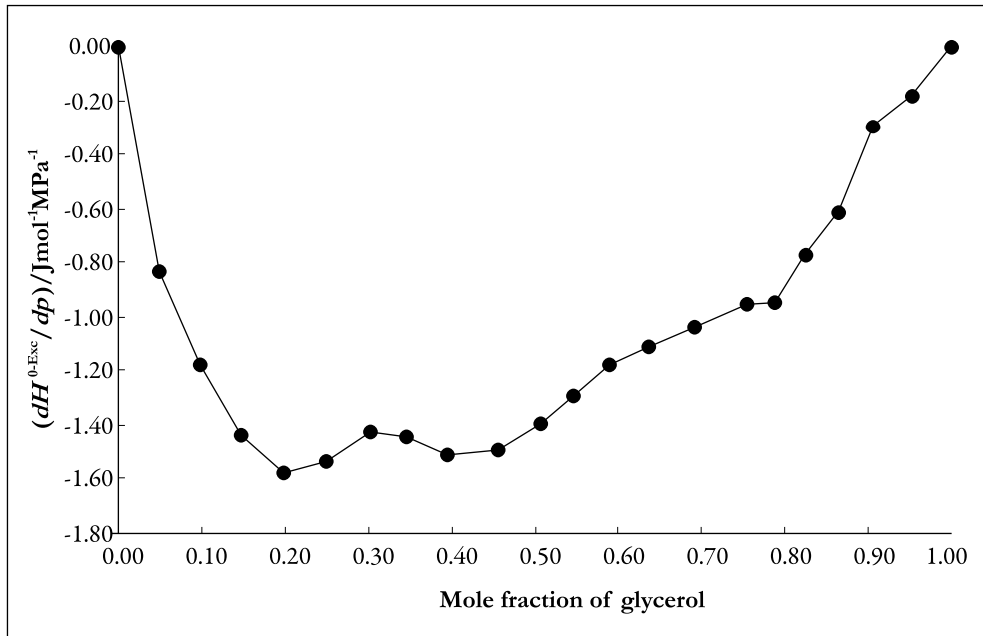


Figure 9. Variation of excess molar enthalpies with pressure obtained from the excess molar volumes for glycerol + water mixtures at 298.15 K.

On the other hand, some other theoretical and experimental techniques have been used to investigate the nanoscopic structure of these mixtures. In particular, molecular dynamics simulation and infra-red spectra analysis have been developed on glycerol + water mixtures to determine the hydrogen bond patterns of glycerol and its mixtures with water (29). This study was performed to verify that the ability of glycerol/water mixtures to inhibit ice crystallization is linked to the concentration of glycerol and the hydrogen bonding patterns formed by these solutions (29).

Data correlation using the Jouyban-Acree model

For binary data analyses, the Jouyban-Acree model was used to correlate the experimental density data of mixed solvents (15, 30):

$$\ln \rho_{m,T} = x_1 \ln \rho_{1,T} + x_2 \ln \rho_{2,T} + \frac{x_1 x_2}{T} \cdot \sum_{i=0}^2 J_i (x_1 - x_2)^i \quad (\text{Eq. 8})$$

where $\rho_{m,T}$, $\rho_{1,T}$, $\rho_{2,T}$ are densities of mixed solvents, cosolvent, and water at different temperatures (T), respectively. The x_1 , x_2 are mole fractions of cosolvent and water, respectively. The methodology to find the J_i terms was described in previous works

(15, 30). The following equation was obtained for density correlation of mixtures of glycerol and water at different temperatures:

$$\ln \rho_{m,T} = x_1 \ln \rho_{1,T} + x_2 \ln \rho_{2,T} + 93.766 \frac{x_1 x_2}{T} - 77.285 \frac{x_1 x_2 (x_1 - x_2)}{T} + 73.028 \frac{x_1 x_2 (x_1 - x_2)^2}{T} \quad (\text{Eq. 9})$$

The main advantage of the Jouyban-Acree model over Redlich-Kister equation is that it includes the effects of temperature in the model constants and provides the possibility of density predictions at other temperatures using interpolation technique, whereas the constants of the Redlich-Kister equation is only valid for one temperature. As noted in Introduction, Eq. 9 could be used to predict the density of saturated solutions of a drug dissolved in glycerol + water mixtures employing the experimental densities of saturated solutions in glycerol and water as described in more details for other systems in a previous paper (9).

The calculated density values using Eq. 8 against the experimental values are presented in Figure 10.

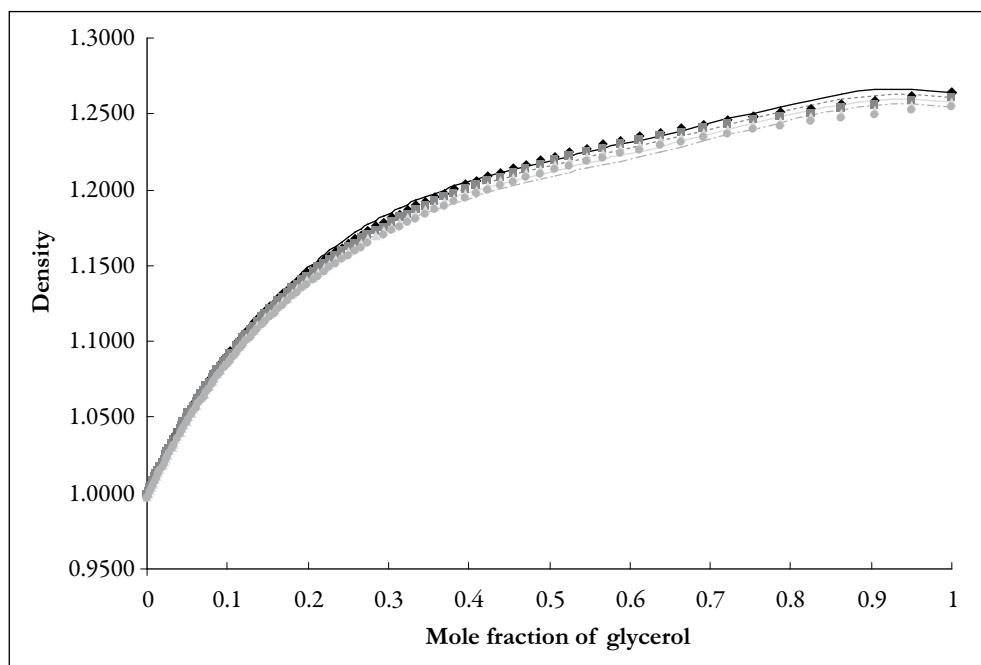


Figure 10. The calculated density values (g cm^{-3}) using Eq. 9 against the corresponding experimental values. (\blacklozenge): 288.15 K; (\blacksquare): 293.15 K; (\blacktriangle): 298.15 K; (\bullet): 303.15 K.

An adopted version of Eq. 9 could be used for representing the molar volume data of mixed solvents. The trained version of the model for glycerol + water mixtures at various temperatures is:

$$\ln V_{m,T}^0 = x_1 \ln V_{1,T}^0 + x_2 \ln V_{2,T}^0 + 257.510 \frac{x_1 x_2}{T} - 109.243 \frac{x_1 x_2 (x_1 - x_2)}{T} + 60.556 \frac{x_1 x_2 (x_1 - x_2)^2}{T} \quad (\text{Eq. 10})$$

where $V_{m,T}^0$, $V_{1,T}^0$, $V_{2,T}^0$ are molar volumes of mixed solvents, cosolvent, and water at different temperatures.

The model fits very well to the experimental data. This is the second report of application of the Jouyban-Acree model for representing the molar volume data of solvent mixtures at various temperatures.

The mean relative deviation (MRD) between experimental and calculated data was calculated using:

$$MRD = \frac{100}{N} \left(\frac{|Calculated - Experimental|}{Experimental} \right) \quad (\text{Eq. 11})$$

and were 0.19 ± 0.11 % and 0.32 ± 0.25 % for Eq. 9 and Eq. 10, respectively. The N in Eq. 11 is the number of data points in the data set.

CONCLUSIONS

This report expands widely the experimental volumetric information about the glycerol + water cosolvent system available nowadays because it includes the behavior at four temperatures commonly found in technological conditions. As mentioned earlier, this information could be employed in several engineering processes and for the theoretical understanding of the behavior of cosolvent mixtures used in the chemical and pharmaceutical industries. In general terms, based on our results and those presented in the literature for other experimental and theoretical procedures, it can be concluded that glycerol + water mixtures clearly show non ideal behavior. Nevertheless, the observed deviations are lower than those observed earlier for aqueous mixtures containing ethanol and 1,2-propanediol as cosolvents. These observations demonstrate clearly that it is

necessary to characterize systematically this important binary system in order to have complete experimental information about the physical and chemical properties useful in the understanding of liquid pharmaceutical systems.

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