Volumetric properties of the glycerol formal+water cosolvent system and correlation with the Jouyban–Acree model

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Excess molar volumes and partial molar volumes were investigated from
density measurements for glycerol formal + water mixtures at temperatures
from 278.15 to 313.15 K. Excess molar volumes are fitted using Redlich–
Kister equation and compared with literature values for other systems. The
system exhibits negative excess volumes, probably due to increased
interactions like hydrogen bonding or large differences in molar volumes
of components. The effect of temperature on different volumetric proper-
ties studied is also analysed. Besides, the volume thermal expansion
coefficients are also calculated as $2.51 \times 10^{-4}\,K^{-1}$ for water and $7.24 \times 10^{-4}\,K^{-1}$ for glycerol formal at 298.15 K. Finally, 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 $0.24 \pm 0.14\%$ and $0.71 \pm 0.62\%$,
respectively, for density and molar volume data.

Keywords: glycerol formal; water; binary liquid mixtures; excess volumes;
partial volumes; Jouyban–Acree model

1. Introduction

Water–cosolvent mixtures have been widely used in pharmacy in order to increase
the solubility of drugs that are poorly soluble in water during the design of
homogeneous pharmaceutical dosage forms, such as syrups and elixirs, among
others [1]. 1,2-Propanediol and ethanol are the cosolvents mostly used in design
nowadays, especially those intended for elaboration of per oral and parenteral
medications [2]. Otherwise, glycerol formal is a non-toxic and environmentally
friendly organic solvent [3], miscible with water in all possible compositions and has
been widely used as a cosolvent for veterinarian formulations such as those
containing the antinematodal drug, ivermectin [4–6]. Glycerol formal is available as
a mixture of 5-hydroxy-1,3-dioxane and 4-hydroxymethyl-1,3-dioxolane (60:40) and
as individual isomers [3,7].

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The mixtures obtained using 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 leads to non-additive volumes on mixing [8,9]. For this reason, it is necessary to characterise the volumetric behaviour 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 to represent the intermolecular interactions present in liquid pharmaceutical systems [10].

In this article, the excess molar volumes and the partial molar volumes of the binary system of glycerol formal + water at various temperatures in addition to other volumetric properties are calculated according to modified procedures widely reported in literature [11–13]. This study is a continuation of those presented previously about some volumetric properties of ethanol + water [14], 1,2-propane-diol + water mixtures [15] and 1,4-dioxane + water mixtures [16].

2. Experimental

2.1. *Materials*

In this investigation, glycerol formal (5-hydroxy-1,3-dioxane isomer) from Lambiotte & Cie S.A. was used and is in agreement with the quality requirements indicated for veterinarian medicinal products. Density and refractive index of glycerol formal ($\rho = 1.2214 \, \text{g cm}^{-3}$ and $n_D = 1.4535$ at 298.15 K, respectively) were in good agreement with the values reported for the single 5-hydroxy-1,3-dioxane isomer ($\rho_4^{25} = 1.2200$ and $n_D^{25} = 1.4527$) [17]. The dehydrated glycerol formal used in this study was maintained over a molecular sieve to obtain a dry solvent prior to the preparation of the cosolvent mixtures. Distilled water (conductivity $< 2 \, \mu\text{S cm}^{-1}$) was also used. Prior to preparation of the mixtures, distilled water was treated in an Elmasonic E 60 H ultrasonic bath at room temperature for 10 min to remove the dissolved air.

2.2. *Cosolvent mixture preparation*

All glycerol formal + water mixtures were prepared in quantities of 40.00 g by mass using a Ohaus Pioneer TM PA214 analytical balance with a sensitivity of ±0.1 mg, in concentrations from 0.05 to 0.95 varying 0.05 in mass fraction of glycerol formal, to study 19 mixtures and the two pure solvents. This procedure implies an uncertainty of $\pm 2 \times 10^{-5}$ in mole fraction. The mixtures were maintained in Magni Whirl Blue M or Neslab RTE 10 Digital Plus (Thermo Electron Company) water baths at temperatures from 278.15 to 313.15 K varying in 5.00 ± 0.05 K for at least 30 min prior to density determinations.

2.3. *Density determination*

This property was determined using a DMA 45 Anton Paar digital density meter connected to a Neslab RTE 10 Digital Plus (Thermo Electron Company) recirculating thermostatic water bath according to a procedure previously described [18]. The equipment was calibrated according to the instruction manual using air and

water at the different temperatures studied [19]. From density values, all thermo-dynamic properties were calculated as indicated in the following section.

3. Results and discussion

In Table 1, the composition of glycerol formal + water mixtures, in mass (μ_{GF}) and mole (x_{GF}) fraction, in addition to density values at several temperatures studied, is presented. Our density values of mixtures are similar but slightly greater to those reported by Pineda *et al.* at 298.15 K [20]. It is important to note that these authors used glycerol formal directly without any dehydration process (0.31% in mass of water) just as it is used in the pharmaceutical industries for production purposes [20]. No other literature values are available and therefore no direct comparison possible. In all cases, the density increases as the proportion of glycerol formal increases in the mixtures and decreases linearly as the temperature increases, except for the systems with $0 \leq \mu_{GF} \leq 0.20$, where parabolic tendencies were obtained.

3.1. *Molar volumes and excess molar volumes*

In Table 2, the molar volumes for binary mixtures at all temperatures studied are presented, which were calculated from Equation (1).

$$V^0 = \frac{x_1 M_1 + x_2 M_2}{\rho} \tag{1}$$

where M_1 and M_2 are the molar masses, for both components, respectively, (104.10 g mol^{-1} for glycerol formal and 18.02 g mol^{-1} for water [3]), x_1 and x_2 the respective mole fraction of components and ρ the mixture density.

On the other hand, the excess molar volumes calculated from Equation (2) (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 298.15 K.

$$V^{0-E} = \frac{x_1 M_1 + x_2 M_2}{\rho} - \left(\frac{x_1 M_1}{\rho_1} + \frac{x_2 M_2}{\rho_2} \right) \tag{2}$$

Analogous to the behaviour obtained in other investigations [14–16], in all cases, the excess volumes are largely negative (especially around 0.24 in mole fraction of glycerol formal, where it is near 0.52 cm^3 mol^{-1} at 278.15 K), indicating contraction in volume. In this mixture composition, there are three molecules of water for each glycerol formal. As was already said [14–16], 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.

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 depolymerisation of water by the addition of glycerol formal; second, contraction due to free volume difference of

Table 1. Densities ($g\,cm^{-3}$) for glycerol formal + water mixtures at various temperatures.

Glycerol formal		Temperature (K)							
		278.15		283.15		288.15		293.15	
μ_{GF}	x_{GF}	Exp.	Cal.	Exp.	Cal.	Exp.	Cal.	Exp.	Cal.
0.0000	0.0000	1.0000	1.0000	0.9997	0.9997	0.9991	0.9991	0.9982	0.9982
0.0500	0.0090	1.0119	1.0104	1.0114	1.0099	1.0106	1.0091	1.0095	1.0080
0.1000	0.0189	1.0241	1.0214	1.0231	1.0207	1.0219	1.0197	1.0207	1.0185
0.1500	0.0296	1.0367	1.0327	1.0353	1.0319	1.0340	1.0307	1.0324	1.0292
0.2000	0.0415	1.0495	1.0448	1.0477	1.0437	1.0465	1.0423	1.0442	1.0407
0.2500	0.0545	1.0623	1.0572	1.0600	1.0559	1.0582	1.0543	1.0562	1.0524
0.3000	0.0690	1.0747	1.0702	1.0719	1.0686	1.0699	1.0668	1.0678	1.0647
0.3500	0.0852	1.0877	1.0836	1.0851	1.0818	1.0822	1.0798	1.0804	1.0774
0.4000	0.1034	1.1004	1.0974	1.0971	1.0954	1.0945	1.0931	1.0922	1.0905
0.4500	0.1240	1.1125	1.1115	1.1097	1.1092	1.1064	1.1066	1.1041	1.1038
0.5000	0.1475	1.1252	1.1256	1.1220	1.1230	1.1184	1.1203	1.1159	1.1172
0.5500	0.1746	1.1372	1.1396	1.1337	1.1367	1.1302	1.1337	1.1276	1.1304
0.6000	0.2061	1.1495	1.1530	1.1456	1.1499	1.1419	1.1466	1.1388	1.1431
0.6500	0.2432	1.1611	1.1654	1.1574	1.1621	1.1535	1.1586	1.1501	1.1549
0.7000	0.2876	1.1722	1.1764	1.1686	1.1728	1.1647	1.1692	1.1614	1.1653
0.7500	0.3417	1.1831	1.1855	1.1798	1.1818	1.1757	1.1781	1.1722	1.1740
0.8000	0.4091	1.1939	1.1930	1.1899	1.1891	1.1862	1.1854	1.1825	1.1812
0.8500	0.4951	1.2049	1.2000	1.2005	1.1961	1.1965	1.1923	1.1925	1.1881
0.9000	0.6090	1.2157	1.2110	1.2114	1.2070	1.2068	1.2031	1.2026	1.1987
0.9500	0.7668	1.2269	1.2327	1.2223	1.2283	1.2183	1.2242	1.2139	1.2195
1.0000	1.0000	1.2393	1.2393	1.2349	1.2349	1.2309	1.2309	1.2263	1.2263
		298.15		303.15		308.15		313.15	
μ_{GF}	x_{GF}	Exp.	Cal.	Exp.	Cal.	Exp.	Cal.	Exp.	Cal.
0.0000	0.0000	0.9970	0.9970	0.9956	0.9956	0.9940	0.9940	0.9922	0.9922
0.0500	0.0090	1.0081	1.0067	1.0065	1.0051	1.0048	1.0034	1.0028	1.0014
0.1000	0.0189	1.0192	1.0169	1.0175	1.0152	1.0156	1.0133	1.0135	1.0111
0.1500	0.0296	1.0305	1.0275	1.0287	1.0256	1.0265	1.0235	1.0241	1.0212
0.2000	0.0415	1.0420	1.0387	1.0400	1.0366	1.0379	1.0343	1.0352	1.0318
0.2500	0.0545	1.0538	1.0503	1.0514	1.0479	1.0492	1.0455	1.0467	1.0428
0.3000	0.0690	1.0655	1.0623	1.0633	1.0598	1.0607	1.0572	1.0579	1.0543
0.3500	0.0852	1.0777	1.0748	1.0753	1.0721	1.0725	1.0692	1.0692	1.0661
0.4000	0.1034	1.0895	1.0877	1.0871	1.0847	1.0836	1.0816	1.0806	1.0783
0.4500	0.1240	1.1007	1.1007	1.0980	1.0975	1.0949	1.0943	1.0914	1.0907
0.5000	0.1475	1.1125	1.1138	1.1096	1.1104	1.1063	1.1070	1.1030	1.1032
0.5500	0.1746	1.1243	1.1268	1.1211	1.1231	1.1180	1.1195	1.1139	1.1155
0.6000	0.2061	1.1353	1.1393	1.1321	1.1354	1.1289	1.1316	1.1253	1.1274
0.6500	0.2432	1.1465	1.1508	1.1429	1.1467	1.1398	1.1428	1.1359	1.1384
0.7000	0.2876	1.1573	1.1611	1.1534	1.1568	1.1504	1.1528	1.1463	1.1483
0.7500	0.3417	1.1681	1.1697	1.1639	1.1653	1.1607	1.1613	1.1563	1.1566
0.8000	0.4091	1.1783	1.1768	1.1742	1.1723	1.1706	1.1682	1.1662	1.1635
0.8500	0.4951	1.1881	1.1835	1.1839	1.1791	1.1805	1.1751	1.1760	1.1703
0.9000	0.6090	1.1981	1.1941	1.1938	1.1895	1.1903	1.1855	1.1855	1.1807
0.9500	0.7668	1.2092	1.2146	1.2047	1.2098	1.2012	1.2058	1.1963	1.2007
1.0000	1.0000	1.2214	1.2214	1.2167	1.2167	1.2131	1.2131	1.2081	1.2081

Note: The mean standard deviation was $0.0001\,g\,cm^{-3}$. Exp., experimental; Cal., calculated.

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

	Glycerol formal		V^0	V^{0-E}	$\left(\frac{\partial V}{\partial \mu_{GF}}\right)$	$\bar{V}^0_{GF}$	$\bar{V}^0_W$
T (K)	μ_{GF}	x_{GF}	($cm^3\,mol^{-1}$)	($cm^3\,mol^{-1}$)	($cm^3\,g^{-1}$)	($cm^3\,mol^{-1}$)	($cm^3\,mol^{-1}$)
278.15	0.0000	0.0000	18.02	0.000	−0.2535	77.71	18.02
	0.0500	0.0090	18.57	−0.040	−0.2474	78.41	18.03
	0.1000	0.0189	19.18	−0.083	−0.2413	79.04	18.03
	0.1500	0.0296	19.84	−0.132	−0.2352	79.60	18.01
	0.2000	0.0415	20.57	−0.184	−0.2292	80.11	17.99
	0.2500	0.0545	21.38	−0.236	−0.2231	80.58	17.96
	0.3000	0.0690	22.29	−0.277	−0.2170	81.06	17.94
	0.3500	0.0852	23.31	−0.331	−0.2109	81.44	17.89
	0.4000	0.1034	24.46	−0.377	−0.2048	81.81	17.85
	0.4500	0.1240	25.79	−0.408	−0.1987	82.20	17.80
	0.5000	0.1475	27.30	−0.452	−0.1926	82.49	17.75
	0.5500	0.1746	29.06	−0.477	−0.1865	82.81	17.69
	0.6000	0.2061	31.11	−0.508	−0.1805	83.05	17.62
	0.6500	0.2432	33.55	−0.516	−0.1744	83.31	17.56
	0.7000	0.2876	36.49	−0.502	−0.1683	83.56	17.49
	0.7500	0.3417	40.09	−0.472	−0.1622	83.77	17.42
	0.8000	0.4091	44.59	−0.422	−0.1561	83.95	17.34
	0.8500	0.4951	50.33	−0.359	−0.1500	84.06	17.25
	0.9000	0.6090	57.94	−0.257	−0.1439	84.13	17.15
	0.9500	0.7668	68.49	−0.126	−0.1379	84.13	17.04
	1.0000	1.0000	84.00	0.000	−0.1318	84.00	16.91
283.15	0.0000	0.0000	18.02	0.000	−0.2470	78.42	18.02
	0.0500	0.0090	18.58	−0.038	−0.2413	79.06	18.03
	0.1000	0.0189	19.20	−0.075	−0.2357	79.67	18.03
	0.1500	0.0296	19.87	−0.120	−0.2300	80.20	18.02
	0.2000	0.0415	20.60	−0.167	−0.2243	80.68	18.00
	0.2500	0.0545	21.42	−0.211	−0.2187	81.14	17.98
	0.3000	0.0690	22.35	−0.245	−0.2130	81.60	17.96
	0.3500	0.0852	23.37	−0.305	−0.2073	81.91	17.91
	0.4000	0.1034	24.54	−0.339	−0.2017	82.29	17.87
	0.4500	0.1240	25.86	−0.385	−0.1960	82.59	17.82
	0.5000	0.1475	27.38	−0.423	−0.1903	82.88	17.77
	0.5500	0.1746	29.15	−0.444	−0.1847	83.18	17.72
	0.6000	0.2061	31.21	−0.468	−0.1790	83.42	17.66
	0.6500	0.2432	33.66	−0.485	−0.1733	83.63	17.59
	0.7000	0.2876	36.61	−0.480	−0.1677	83.85	17.53
	0.7500	0.3417	40.21	−0.465	−0.1620	84.02	17.46
	0.8000	0.4091	44.74	−0.398	−0.1563	84.24	17.39
	0.8500	0.4951	50.51	−0.326	−0.1506	84.37	17.31
	0.9000	0.6090	58.15	−0.235	−0.1450	84.43	17.22
	0.9500	0.7668	68.75	−0.099	−0.1393	84.45	17.12
	1.0000	1.0000	84.30	0.000	−0.1336	84.30	17.00
288.15	0.0000	0.0000	18.03	0.000	−0.2405	79.16	18.03
	0.0500	0.0090	18.60	−0.037	−0.2353	79.74	18.04
	0.1000	0.0189	19.22	−0.068	−0.2300	80.32	18.04
	0.1500	0.0296	19.89	−0.113	−0.2248	80.79	18.03
	0.2000	0.0415	20.63	−0.165	−0.2195	81.20	18.01

Table 2. Continued.

T (K)	Glycerol formal μ_{GF}	x_{GF}	V^0 (cm^3 mol^{-1})	V^{0-E} (cm^3 mol^{-1})	$\left(\frac{\partial V}{\partial \mu_{GF}}\right)$ (cm^3 g^{-1})	$\bar{V}^0_{GF}$ (cm^3 mol^{-1})	$\bar{V}^0_{W}$ (cm^3 mol^{-1})
	0.2500	0.0545	21.46	−0.199	−0.2143	81.65	17.99
	0.3000	0.0690	22.39	−0.232	−0.2090	82.07	17.97
	0.3500	0.0852	23.43	−0.276	−0.2038	82.41	17.93
	0.4000	0.1034	24.60	−0.319	−0.1985	82.71	17.89
	0.4500	0.1240	25.93	−0.351	−0.1933	83.03	17.85
	0.5000	0.1475	27.46	−0.385	−0.1881	83.29	17.80
	0.5500	0.1746	29.24	−0.411	−0.1828	83.55	17.75
	0.6000	0.2061	31.31	−0.432	−0.1776	83.77	17.70
	0.6500	0.2432	33.77	−0.446	−0.1723	83.97	17.64
	0.7000	0.2876	36.73	−0.444	−0.1671	84.17	17.57
	0.7500	0.3417	40.35	−0.426	−0.1618	84.34	17.51
	0.8000	0.4091	44.87	−0.377	−0.1566	84.50	17.44
	0.8500	0.4951	50.68	−0.298	−0.1513	84.64	17.37
	0.9000	0.6090	58.37	−0.185	−0.1461	84.74	17.30
	0.9500	0.7668	68.97	−0.086	−0.1408	84.72	17.20
	1.0000	1.0000	84.58	0.000	−0.1356	84.58	17.08
293.15	0.0000	0.0000	18.05	0.000	−0.2383	79.49	18.05
	0.0500	0.0090	18.62	−0.036	−0.2331	80.07	18.06
	0.1000	0.0189	19.24	−0.068	−0.2278	80.65	18.06
	0.1500	0.0296	19.92	−0.108	−0.2226	81.14	18.05
	0.2000	0.0415	20.67	−0.148	−0.2174	81.59	18.04
	0.2500	0.0545	21.50	−0.191	−0.2122	82.00	18.01
	0.3000	0.0690	22.44	−0.225	−0.2070	82.41	17.99
	0.3500	0.0852	23.47	−0.279	−0.2018	82.70	17.95
	0.4000	0.1034	24.65	−0.315	−0.1965	83.04	17.91
	0.4500	0.1240	25.99	−0.351	−0.1913	83.33	17.87
	0.5000	0.1475	27.53	−0.384	−0.1861	83.60	17.82
	0.5500	0.1746	29.31	−0.412	−0.1809	83.85	17.77
	0.6000	0.2061	31.40	−0.425	−0.1757	84.10	17.72
	0.6500	0.2432	33.87	−0.436	−0.1704	84.31	17.66
	0.7000	0.2876	36.83	−0.442	−0.1652	84.48	17.60
	0.7500	0.3417	40.47	−0.425	−0.1600	84.65	17.53
	0.8000	0.4091	45.02	−0.376	−0.1548	84.81	17.47
	0.8500	0.4951	50.85	−0.293	−0.1496	84.96	17.40
	0.9000	0.6090	58.58	−0.181	−0.1444	85.06	17.32
	0.9500	0.7668	69.22	−0.083	−0.1391	85.04	17.22
	1.0000	1.0000	84.89	0.000	−0.1339	84.89	17.10
298.15	0.0000	0.0000	18.07	0.000	−0.2347	79.99	18.07
	0.0500	0.0090	18.64	−0.034	−0.2296	80.56	18.08
	0.1000	0.0189	19.27	−0.067	−0.2246	81.10	18.08
	0.1500	0.0296	19.96	−0.102	−0.2195	81.60	18.08
	0.2000	0.0415	20.72	−0.139	−0.2145	82.05	18.06
	0.2500	0.0545	21.55	−0.182	−0.2094	82.44	18.04
	0.3000	0.0690	22.49	−0.220	−0.2043	82.81	18.01
	0.3500	0.0852	23.53	−0.269	−0.1993	83.11	17.97
	0.4000	0.1034	24.71	−0.308	−0.1942	83.42	17.94
	0.4500	0.1240	26.07	−0.332	−0.1892	83.75	17.90
	0.5000	0.1475	27.61	−0.368	−0.1841	83.99	17.85

(*Continued*)

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Table 2. Continued.

T (K)	Glycerol formal μ_{GF}	x_{GF}	V^0 (cm^{3}mol^{-1})	V^{0-E} (cm^{3}mol^{-1})	$\left(\frac{\partial V}{\partial \mu_{GF}}\right)$ (cm^{3}g^{-1})	$\bar{V}^0_{GF}$ (cm^{3}mol^{-1})	$\bar{V}^0_{W}$ (cm^{3}mol^{-1})
	0.5500	0.1746	29.39	−0.404	−0.1791	84.21	17.80
	0.6000	0.2061	31.50	−0.415	−0.1740	84.45	17.75
	0.6500	0.2432	33.98	−0.429	−0.1690	84.65	17.69
	0.7000	0.2876	36.96	−0.425	−0.1639	84.84	17.63
	0.7500	0.3417	40.61	−0.413	−0.1589	84.99	17.57
	0.8000	0.4091	45.18	−0.368	−0.1538	85.15	17.51
	0.8500	0.4951	51.04	−0.285	−0.1487	85.30	17.44
	0.9000	0.6090	58.80	−0.176	−0.1437	85.40	17.37
	0.9500	0.7668	69.49	−0.080	−0.1386	85.37	17.27
	1.0000	1.0000	85.23	0.000	−0.1336	85.23	17.16
303.15	0.0000	0.0000	18.09	0.000	−0.2325	80.36	18.09
	0.0500	0.0090	18.67	−0.033	−0.2275	80.94	18.10
	0.1000	0.0189	19.30	−0.066	−0.2225	81.47	18.11
	0.1500	0.0296	19.99	−0.102	−0.2174	81.96	18.10
	0.2000	0.0415	20.76	−0.138	−0.2124	82.41	18.09
	0.2500	0.0545	21.60	−0.174	−0.2074	82.82	18.07
	0.3000	0.0690	22.53	−0.220	−0.2024	83.16	18.04
	0.3500	0.0852	23.58	−0.268	−0.1974	83.46	18.00
	0.4000	0.1034	24.76	−0.310	−0.1924	83.75	17.96
	0.4500	0.1240	26.13	−0.331	−0.1873	84.09	17.93
	0.5000	0.1475	27.68	−0.366	−0.1823	84.33	17.88
	0.5500	0.1746	29.48	−0.398	−0.1773	84.55	17.83
	0.6000	0.2061	31.58	−0.414	−0.1723	84.78	17.78
	0.6500	0.2432	34.08	−0.421	−0.1673	84.99	17.72
	0.7000	0.2876	37.09	−0.413	−0.1623	85.19	17.67
	0.7500	0.3417	40.76	−0.396	−0.1572	85.35	17.60
	0.8000	0.4091	45.33	−0.360	−0.1522	85.49	17.54
	0.8500	0.4951	51.22	−0.279	−0.1472	85.63	17.47
	0.9000	0.6090	59.01	−0.175	−0.1422	85.72	17.40
	0.9500	0.7668	69.75	−0.079	−0.1372	85.70	17.30
	1.0000	1.0000	85.56	0.000	−0.1322	85.56	17.19
308.15	0.0000	0.0000	18.12	0.000	−0.2302	80.77	18.12
	0.0500	0.0090	18.70	−0.032	−0.2254	81.36	18.14
	0.1000	0.0189	19.34	−0.063	−0.2205	81.88	18.14
	0.1500	0.0296	20.04	−0.095	−0.2157	82.33	18.13
	0.2000	0.0415	20.80	−0.134	−0.2108	82.74	18.12
	0.2500	0.0545	21.65	−0.170	−0.2060	83.14	18.10
	0.3000	0.0690	22.59	−0.210	−0.2012	83.49	18.07
	0.3500	0.0852	23.64	−0.255	−0.1963	83.78	18.04
	0.4000	0.1034	24.84	−0.283	−0.1915	84.11	18.01
	0.4500	0.1240	26.21	−0.314	−0.1866	84.39	17.97
	0.5000	0.1475	27.76	−0.346	−0.1818	84.64	17.92
	0.5500	0.1746	29.56	−0.385	−0.1770	84.83	17.87
	0.6000	0.2061	31.67	−0.400	−0.1721	85.05	17.82
	0.6500	0.2432	34.18	−0.412	−0.1673	85.24	17.76
	0.7000	0.2876	37.19	−0.410	−0.1624	85.42	17.71
	0.7500	0.3417	40.87	−0.389	−0.1576	85.59	17.65
	0.8000	0.4091	45.47	−0.341	−0.1528	85.75	17.59

(*Continued*)

Table 2. Continued.

T (K)	Glycerol formal		V^0	V^{0-E}	$\left(\frac{\partial V}{\partial \mu_{GF}}\right)$	$\bar{V}^0_{GF}$	$\bar{V}^0_{W}$
	μ_{GF}	x_{GF}	(cm^3 mol^{-1})	(cm^3 mol^{-1})	(cm^3 g^{-1})	(cm^3 mol^{-1})	(cm^3 mol^{-1})
	0.8500	0.4951	51.37	−0.272	−0.1479	85.88	17.53
	0.9000	0.6090	59.18	−0.168	−0.1431	85.97	17.45
	0.9500	0.7668	69.95	−0.077	−0.1382	85.95	17.36
	1.0000	1.0000	85.82	0.000	−0.1334	85.82	17.25
313.15	0.0000	0.0000	18.16	0.000	−0.2276	81.22	18.16
	0.0500	0.0090	18.74	−0.031	−0.2229	81.81	18.17
	0.1000	0.0189	19.38	−0.062	−0.2182	82.32	18.18
	0.1500	0.0296	20.08	−0.090	−0.2134	82.77	18.17
	0.2000	0.0415	20.85	−0.126	−0.2087	83.18	18.15
	0.2500	0.0545	21.70	−0.169	−0.2040	83.54	18.13
	0.3000	0.0690	22.65	−0.205	−0.1992	83.89	18.11
	0.3500	0.0852	23.71	−0.242	−0.1945	84.21	18.08
	0.4000	0.1034	24.91	−0.280	−0.1897	84.49	18.04
	0.4500	0.1240	26.29	−0.303	−0.1850	84.79	18.01
	0.5000	0.1475	27.85	−0.344	−0.1803	85.00	17.96
	0.5500	0.1746	29.67	−0.365	−0.1755	85.24	17.91
	0.6000	0.2061	31.78	−0.398	−0.1708	85.40	17.86
	0.6500	0.2432	34.29	−0.406	−0.1660	85.60	17.80
	0.7000	0.2876	37.32	−0.402	−0.1613	85.78	17.75
	0.7500	0.3417	41.02	−0.377	−0.1566	85.96	17.70
	0.8000	0.4091	45.64	−0.334	−0.1518	86.11	17.64
	0.8500	0.4951	51.56	−0.268	−0.1471	86.23	17.57
	0.9000	0.6090	59.42	−0.157	−0.1423	86.33	17.50
	0.9500	0.7668	70.24	−0.071	−0.1376	86.31	17.41
	1.0000	1.0000	86.17	0.000	−0.1329	86.17	17.31

Note: The mean standard deviation for V^0 and V^{0-E} was 0.01 cm^3 mol^{-1} while for $\bar{V}^0_{GF}$ and $\bar{V}^0_{W}$ close to 0.03 cm^3 mol^{-1}.

unlike molecules; and third, contraction due to hydrogen bond formation between glycerol formal and water through –OH $\cdots$ O< bonding, among others [9].

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

3.2. *Partial molar volumes*

The partial specific volumes of glycerol formal ($\bar{V}_{GF}$) and water ($\bar{V}_{W}$) were calculated using the classical Bakhuis–Roozeboom method from Equations (3) and (4) by applying the variation of the respective specific volumes as a function of glycerol
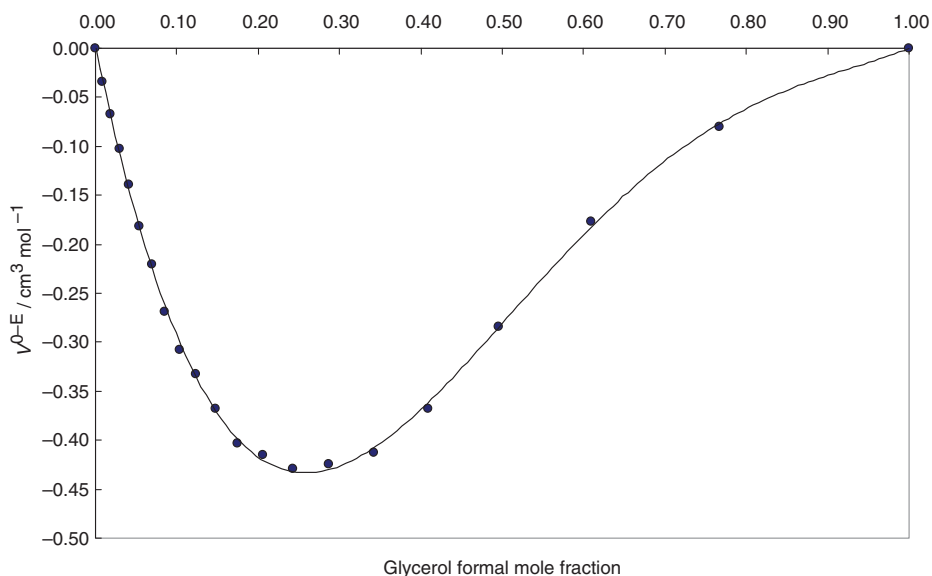
Figure 1. Excess molar volumes of glycerol formal + water mixtures at 298.15 K.
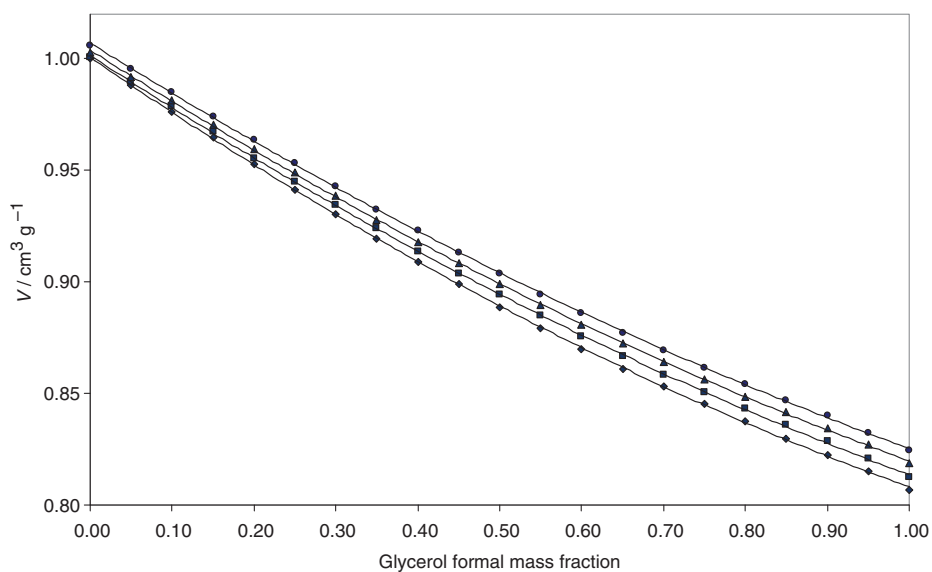

Figure 2. Specific volume of glycerol formal + water mixtures as a function of the mixture composition. ◆, 278.15 K; ■, 288.15; ▲, 298.15 K; and ●, 308.15.

formal mass fraction (Table 2, Figure 2) and adjusting them to second-degree polynomials by least squares regression analyses [22,23]. Polynomials of second- and third-degree order are the most widely used in these cases, based upon their good statistical parameters, especially their determination coefficients (Figure 2). The first

derivatives were taken out on the polynomials obtained and solved at each composition point.

$$\overline{V}_{GF} = V + \mu_W \frac{dV}{d\mu_{GF}} \tag{3}$$

$$\overline{V}_W = V - \mu_{GF} \frac{dV}{d\mu_{GF}} \tag{4}$$

The partial molar volumes were calculated from the respective product of partial specific volumes and molar masses. The values of $\bar{V}^0_{GF}$ and $\bar{V}^0_W$ are also presented in Table 2 in addition to the slopes obtained ($dV/d\mu_{GF}$) at each composition and temperature. In the vast majority of cases, the partial molar volumes for glycerol formal and water in the mixtures are lower than those for the pure solvents (except for water in mixtures of 0.05 and 0.10 in mass fraction of glycerol formal and for glycerol formal in mixtures of 0.85, 0.90 and 0.95 in mass fraction of glycerol formal at almost all temperatures). The partial volumes varied from $78.41\,cm^3\,mol^{-1}$ (for $\mu_{GF} = 0.10$ at 278.15 K) to $86.33\,cm^3\,mol^{-1}$ (for $\mu_{GF} = 0.90$ at 313.15 K) for glycerol formal and from $17.04\,cm^3\,mol^{-1}$ (for $\mu_{GF} = 0.95$ at 278.15 K) to $18.18\,cm^3\,mol^{-1}$ (for $\mu_{GF} = 0.10$ at 313.15 K) for water. These results are similar to those obtained for 1,4-dioxane + water mixtures [16]. The differences between glycerol formal and 1,4-dioxane are the positions of the ether–oxygen atoms and the presence of one hydroxyl group in glycerol formal [3]. The results obtained for $\bar{V}^0_{GF}$ and $\bar{V}^0_W$ are in agreement with the negative excess volumes obtained. The variation of this property is presented in Figure 3 as a function of glycerol formal mole fraction at 298.15 K for glycerol formal 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 respective proportion in the mixtures diminishes in those mixtures where they are predominating in proportion. This behaviour is also similar to that observed in 1,4-dioxane + water mixtures [16].

3.3. *Redlich–Kister equation*

As was already said [14–16], Redlich and Kister [24] introduced in 1948 the general form of Equation (5) 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 for various decades for manipulating several kinds of physicochemical values of mixtures such as excess volumes, excess viscosities, solubilities in cosolvent mixtures, among others.

$$V^{0-E} = x_1 x_2 \sum a_i (x_1 - x_2)^i \tag{5}$$

In the analysis of our data about excess volumes, Equation (5) was used in the form of second-degree polynomial equations using least squares analyses, and therefore, obtaining three coefficients as presented in Equation (6). Polynomials of second and third degree are the most widely used in this case again, because of their
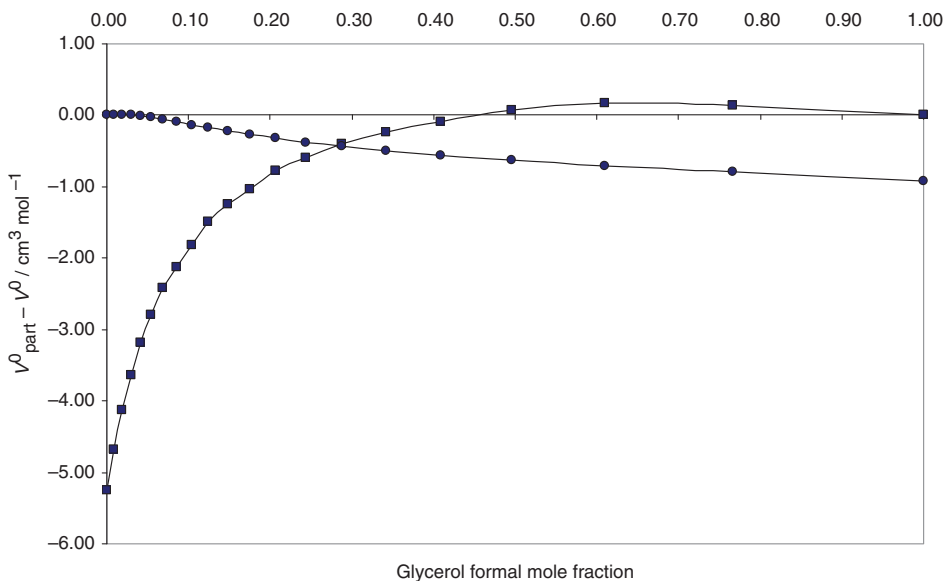
Figure 3. Partial molar volumes of water ($\bullet$) and glycerol formal ($\blacksquare$) calculated as differences with respect to pure solvent volumes in glycerol formal + water mixtures at 298.15 K.

Table 3. Redlich–Kister regression results for the excess volumes of glycerol formal + water mixtures at various temperatures.

T (K)	a_0	a_1	a_2	r^2	σ (cm^3 mol^{-1})
278.15	−1.3998	2.0627	−1.4152	0.9892	0.011
283.15	−1.3214	2.0290	−1.0885	0.9948	0.009
288.15	−1.1661	1.9103	−1.1183	0.9906	0.005
293.15	−1.1865	1.9363	−0.9115	0.9944	0.007
298.15	−1.1619	1.8834	−0.8349	0.9952	0.007
303.15	−1.1449	1.8674	−0.8089	0.9924	0.010
308.15	−1.1115	1.7886	−0.7541	0.9950	0.007
313.15	−1.0926	1.7881	−0.6419	0.9929	0.009

relevant statistic parameters such as determination coefficients and standard deviations.

$$\frac{V^{0-\mathrm{E}}}{x_1 x_2} = a_0 + a_1(x_1 - x_2) + a_2(x_1 - x_2)^2 \tag{6}$$

The Redlich–Kister parameters for glycerol formal + water mixtures at all temperatures studied are presented in Table 3 in addition to determination coefficients and standard deviations calculated according to Equation (7) (where D is the number of compositions studied and N the number of terms used in the
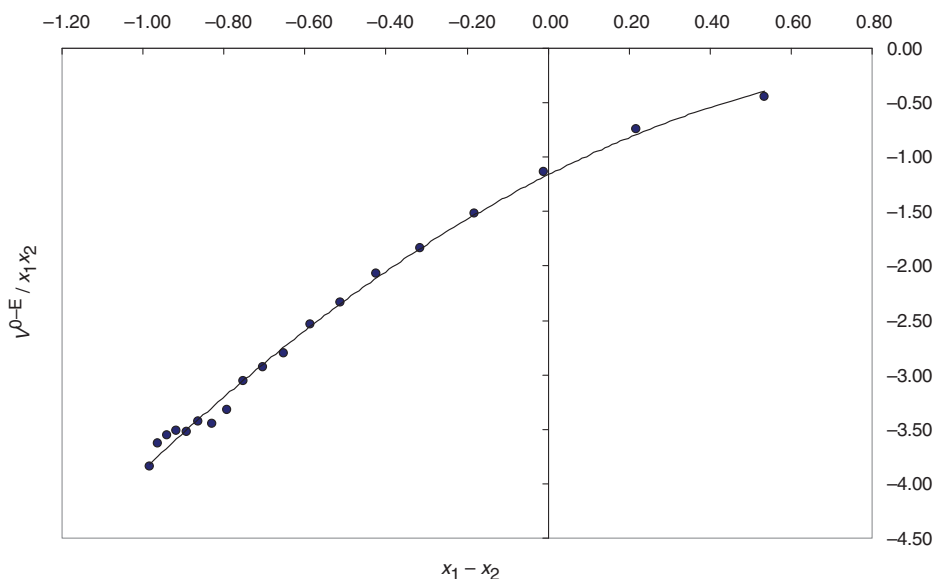
Figure 4. Regression adjusted to Redlich–Kister equation using four terms for glycerol formal + water mixtures in mole fraction at 298.15 K.

regression, i.e. 19 and 3, respectively, in this study). Figure 4 shows the Redlich–Kister equation applied to glycerol formal + water data at 298.15 K.

$$\sigma\left(V^{0-E}\right) = \sqrt{\frac{\sum \left(V^{0-E}_{\text{experimental}} - V^{0-E}_{\text{calculated}}\right)^2}{D-N}} \tag{7}$$

The variation coefficients greater than 0.99 (except at 278.15 K) indicate that the obtained regular polynomial regressions describe adequately the excess volumes, because the standard deviations are similar to those presented in literature for other mixtures [9–16]. On the other hand, σ values obtained for glycerol formal + water mixtures were, in general, lower than those obtained for ethanol + water (near 0.035 cm^3 mol^{-1} [14]), 1,2-propanediol + water (near 0.030 cm^3 mol^{-1} [15]) and 1,4-dioxane + water (near 0.020 cm^3 mol^{-1} [16]); although in those mixtures, third-degree regular polynomials were used.

3.4. *Volume thermal expansion*

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 from Equation (8) [25], using the variation of molar volumes with temperature (Table 2).

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_{p,x} \tag{8}$$

Table 4. Volume thermal expansion coefficients of glycerol formal + water mixtures at 298.15 K.

Glycerol formal		100 $(\partial V^0/\partial T)$ $(cm^3 \, mol^{-1} \, K^{-1})$	$10^4 \, \alpha \, (K^{-1})$
μ_{GF}	x_{GF}		
0.0000	0.0000	0.454	2.52
0.0500	0.0090	0.560	3.00
0.1000	0.0189	0.635	3.29
0.1500	0.0296	0.728	3.65
0.2000	0.0415	0.837	4.04
0.2500	0.0545	0.904	4.20
0.3000	0.0690	0.982	4.37
0.3500	0.0852	1.120	4.76
0.4000	0.1034	1.245	5.04
0.4500	0.1240	1.408	5.40
0.5000	0.1475	1.554	5.63
0.5500	0.1746	1.690	5.75
0.6000	0.2061	1.881	5.97
0.6500	0.2432	2.108	6.20
0.7000	0.2876	2.352	6.36
0.7500	0.3417	2.662	6.56
0.8000	0.4091	3.009	6.66
0.8500	0.4951	3.510	6.88
0.9000	0.6090	4.194	7.13
0.9500	0.7668	4.978	7.16
1.0000	1.0000	6.205	7.28

Table 4 summarises the $(\partial V^0/\partial T)$ and α values for all mixtures and pure solvents. For mixtures of $0.00 \leq \mu_{GF} \leq 0.20$, quadratic polynomial models were used, whereas for mixtures of $0.25 \leq \mu_{GF} \leq 1.00$, linear models were obtained. It is remarkable that in all cases the determination coefficients obtained were greater than 0.999. The values of α varied from $2.52 \times 10^{-4} \, K^{-1}$ in water up to $7.28 \times 10^{-4} \, K^{-1}$ in pure glycerol formal at 298.15 K. From 0.00 to 0.20 in mole fraction of glycerol formal, the values of α increase readily. In the first approach, this fact would be explained in terms of the loss of water structure by the addition of glycerol formal. It should be kept in mind that over 0.20 in mole fraction of glycerol formal, the most contributing component to all mixture volume is glycerol formal (glycerol formal volume fraction near 0.55 or mass fraction near 0.60), which is also the less polar solvent in these mixtures.

3.5. *Variation of excess molar volume with temperature*

An additional and important treatment is the evaluation of change of the excess molar volumes with temperature $(\partial V^{0-E}/\partial T)$. Figure 5 shows this property at 298.15 K (this value is constant over the entire temperature interval considered, i.e. from 278.15 to 313.15 K), which was obtained considering linear behaviour of $\partial V^{0-E}/\partial T$ in all mixtures studied [25]. Almost in all cases, the determination coefficient values obtained were greater than 0.97. From Figure 5, it follows that
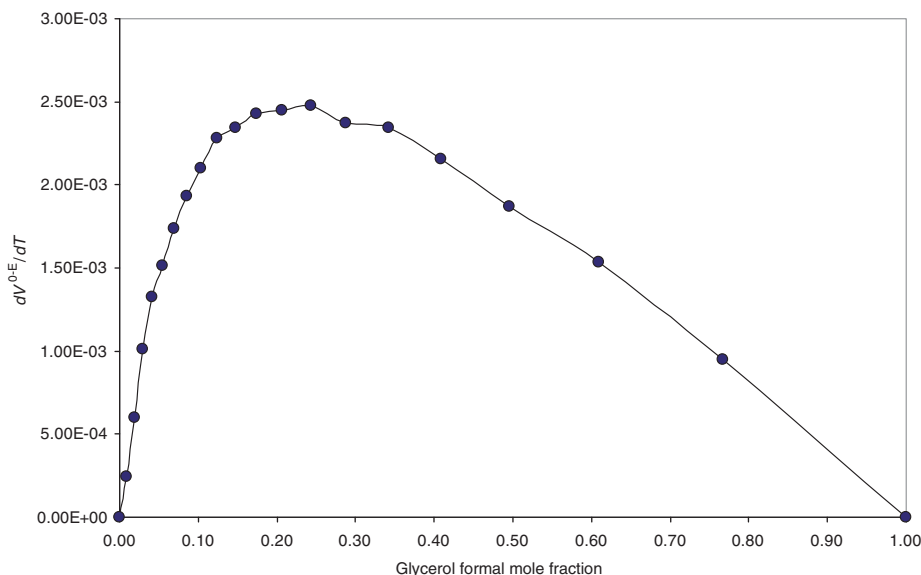
Figure 5. Change of the excess molar volumes with temperature ($cm^3\,mol^{-1}\,K^{-1}$) for glycerol formal + water mixtures at 298.15 K (from 278.15 to 313.15 K).

there is only a tendency according to composition, and this property is always positive, which reflects the fact that excess volume decreases with increase in temperature. This result could be due to weakening of hydrogen bonding as the temperature increases which could lead to loss of solvent structure and thus to a more ideal mixing behaviour.

3.6. *Variation of excess molar enthalpy with pressure*
From the excess molar volumes presented in Table 2, the change of the excess molar enthalpies with pressure was calculated according to Equation (9) [25]:

$$\left(\frac{\partial H^{0-E}}{\partial p}\right)_T = V^{0-E} - T\left(\frac{\partial V^{0-E}}{\partial T}\right)_p \tag{9}$$

Figure 6 shows the values of $\partial H^{0-E}/\partial p$ at 298.15 K, where it follows that the mentioned property is negative in all compositions, indicating an increase in the excess molar enthalpy as the pressure is increased. This behaviour is similar to that reported for 1,4-dioxane + water mixtures. Unfortunately, there is no experimental data in literature about this property for these systems. Nevertheless, Suzuki *et al.* [26] performed a calorimetric study on heat of mixing of 1,4-dioxane and water and found the excess molar enthalpies to be negative from 0 to 0.4 in mole fraction of 1,4-dioxane and positive for the remaining binary mixtures at all the temperatures studied (from 298.15 to 338.15 K).

According to Suzuki *et al.* [26], the exothermic behaviour shows that new strong hydrogen bonds might be formed in the water-rich region, probably due to hydrophobic hydration around ethyl moieties of 1,4-dioxane. It is probable that
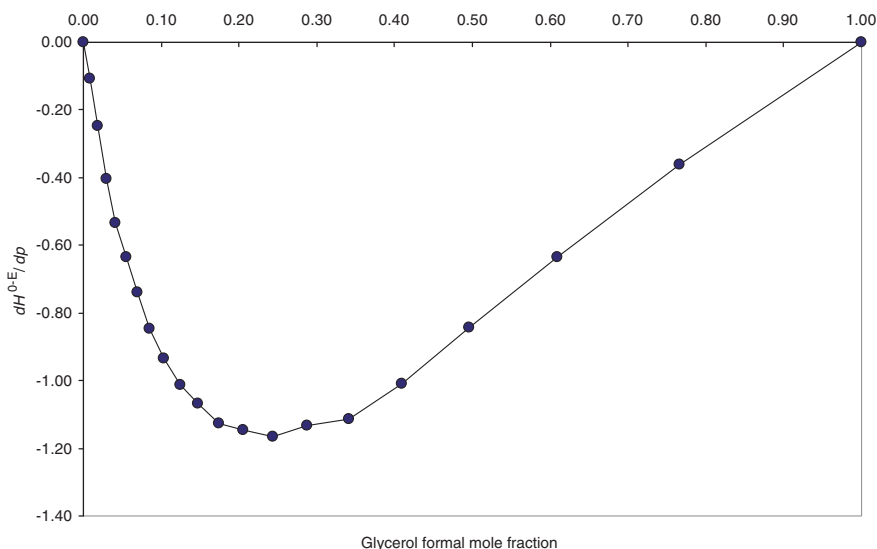
Figure 6. Change of the excess molar enthalpies with pressure $(J\,mol^{-1}\,MPa^{-1})$ obtained from the excess molar volumes for glycerol formal + water mixtures at 298.15 K.

similar events be present with glycerol formal instead of 1,4-dioxane in aqueous mixtures.

3.7. *Data correlation using the Jouyban–Acree model*

The Jouyban–Acree model was used to correlate the experimental density data of mixed solvents. The model is widely used for calculation of different physicochemical properties in mixture of solvents, including density [27]. The main form of the model is:

$$\ln \rho_{m,T} = x_1 \ln \rho_{1,T} + x_2 \ln \rho_{2,T} + \frac{x_1 x_2}{T} \cdot \sum_{i=0}^{2} J_i(x_1 - x_2)^i \quad (10)$$

where $\rho_{m,T}$, $\rho_{1,T}$, $\rho_{2,T}$ are densities of mixed solvent, cosolvent and water at different temperatures (T), respectively, x_1, x_2 the mole fractions of cosolvent and water, respectively, and J_i the coefficients of the model which can be derived using a no intercept regression of the following equation:

$$\ln \rho_{m,T} - \left(x_1 \ln \rho_{1,T} + x_2 \ln \rho_{2,T}\right) = J_0 \frac{x_1 x_2}{T} + J_1 \frac{x_1 x_2(x_1 - x_2)}{T} + J_2 \frac{x_1 x_2(x_1 - x_2)^2}{T} \quad (11)$$

The following equation was obtained for density correlation of mixtures of glycerol formal and water at different temperatures:

$$\ln \rho_{m,T} = x_1 \ln \rho_{1,T} + x_2 \ln \rho_{2,T} + 83.896 \frac{x_1 x_2}{T} - 81.181 \frac{x_1 x_2(x_1 - x_2)}{T}$$

$$+ 101.858 \frac{x_1 x_2(x_1 - x_2)^2}{T} \quad (12)$$
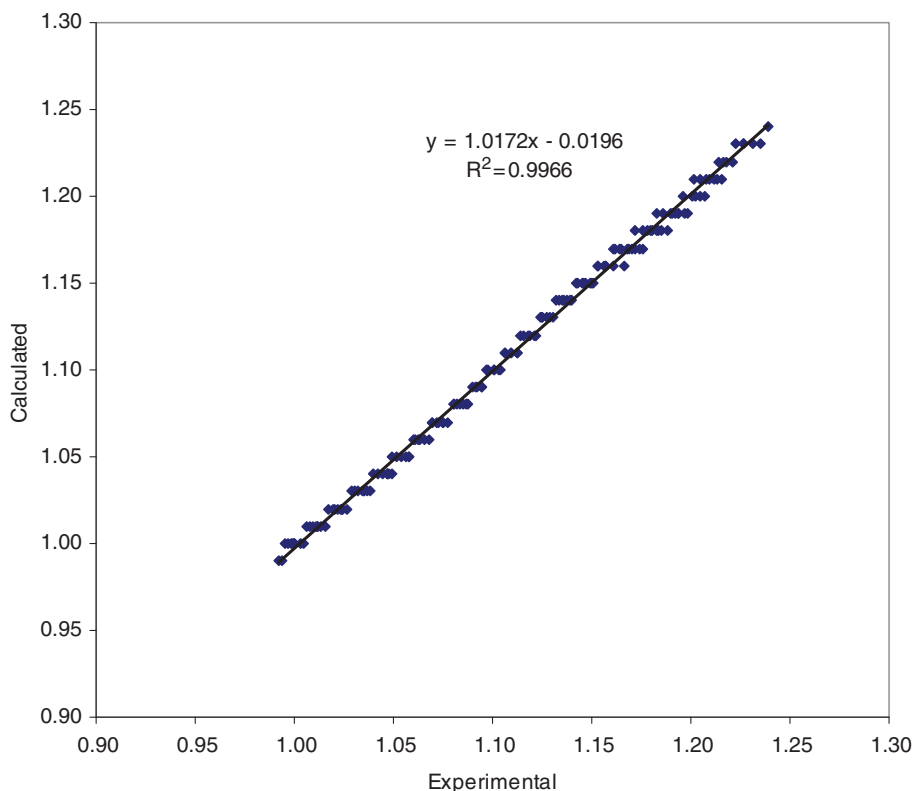
Figure 7. The density values calculated using Equation (12) against the corresponding experimental values.

The calculated density values using Equation (12) against the experimental values are presented in Figure 7. The mean relative deviation (MRD) between experimental and calculated data was calculated using

$$\text{MRD} = \frac{100}{N} \left(\frac{\left| \text{Calculated} - \text{Experimental} \right|}{\text{Experimental}} \right) \tag{13}$$

and was $0.24 \pm 0.14\%$ for Equation (12). The N in Equation (13) is the number of data points in the data set.

An adopted version of Equation (12) could be used for representing the molar volume data of mixed solvents. The trained version for this purpose is:

$$\ln V_{m,T} = x_1 \ln V_{1,T} + x_2 \ln V_{2,T} + 313.430 \frac{x_1 x_2}{T} - 140.110 \frac{x_1 x_2 (x_1 - x_2)}{T}$$
$$+ 86.948 \frac{x_1 x_2 (x_1 - x_2)^2}{T} \tag{14}$$

The model fits very well with the experimental data and the MRD was $0.71 \pm 0.62\%$. This is the first application of the Jouyban–Acree model for representing the molar volume data of solvent mixtures at various temperatures.

4. Conclusions

This article expands widely the experimental volumetric information about the glycerol formal + water cosolvent system because it includes the behaviour at eight temperatures commonly found in technological conditions. As was said earlier, this information could be employed in several engineering processes and for the theoretical understanding of the behaviour of cosolvent mixtures used in the chemical and pharmaceutical industries. It can be concluded that glycerol formal + water mixtures clearly show a non-ideal behaviour. Nevertheless, the observed deviations are lower than those observed earlier for aqueous mixtures containing ethanol, propylene glycol and 1,4-dioxane as cosolvents. These observations demonstrate clearly that it is necessary to characterise 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. It is important to keep in mind that the experimental information obtained for binary solvent mixtures could be used to estimate the physicochemical behaviour of ternary and quaternary mixtures from theoretical methods such as the one described by Mehlman *et al.* [28] based on artificial neural networks, among others. Besides, several methods have been described in literature to estimate activity coefficients from excess functions in binary mixtures [29].

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