

Volumetric Properties of Glycerol Formal + Propylene Glycol Mixtures at Several Temperatures and Correlation with the Jouyban–Acree Model

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Abstract Molar volumes, excess molar volumes, and partial molar volumes were investigated for glycerol formal + propylene glycol mixtures from density measurements at temperatures from (278.15 to 313.15) K. Mixture compositions were varied in 0.05 in mass fraction of both components. Excess molar volumes were fitted to the Redlich–Kister equation and compared with literature values for other systems. The system exhibits positive excess volumes probably due to increased non-specific interactions. The effect of temperature on the different volumetric properties studied was also analyzed. In addition, the volumetric thermal expansion coefficients were calculated. The Jouyban–Acree model was used for density and molar volume correlations of the mixtures at the different experimental temperatures. The mean relative deviations between experimental and calculated data are 0.04 ± 0.03 and 0.04 ± 0.05 , respectively, for the density and molar volumes, using the minimum number of data points, the Jouyban–Acree model can predict density and molar volume with acceptable accuracies (0.06 ± 0.04 and 0.08 ± 0.05 , respectively).

Keywords Glycerol formal · Propylene glycol · Binary liquid mixtures · Excess volumes · Partial volumes · Jouyban–Acree model

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1 Introduction

Cosolvent mixtures free of water have sometimes been used in human and veterinarian pharmacy in the design of injectable homogeneous dosage forms, in order to increase the solubility of drugs that are poorly soluble in water [1]. Ethanol and propylene glycol are the cosolvents most commonly used in design and sometimes they are employed as a blend [2]. Glycerol formal is a non-toxic and environmentally-friendly organic solvent [3], miscible with water, ethanol and propylene glycol in all proportions and it has been widely used as 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 also as the individual isomers [3, 7].

Mixtures obtained using these cosolvents are non-ideal due to increased interactions between unlike molecules and differences in molar volumes of the pure components, which leads to non-additive volumes of mixing [8, 9]. For this reason it is necessary to characterize the volumetric behavior of these binary mixtures as a function of temperature to extend the physicochemical information available for liquid mixtures used in pharmacy. This information is useful in understanding the intermolecular interactions present in liquid pharmaceutical systems and to facilitate the processes of medicine design at the industrial level [10].

In this report, the excess molar volumes and the partial molar volumes of the binary glycerol formal + propylene glycol system, as well as other volumetric properties, are reported at various temperatures. These physicochemical properties were calculated according to some procedures widely expressed in the literature [11–14]. This work is a continuation of work presented previously for volumetric properties of propylene glycol + water mixtures [15], ethanol + propylene glycol mixtures [16], and glycerol formal + water mixtures [17].

2 Experimental

2.1 Materials

In this investigation glycerol formal (the 5-hydroxy-1,3-dioxane isomer) from Lambiotte & Cie S.A. was employed and its purity is in agreement with the quality requirements indicated for veterinary medicinal products. The density and refractive index of this glycerol formal ($\rho = 1.2214 \text{ g}\cdot\text{cm}^{-3}$ and $n_D = 1.4535$ at 298.15 K, respectively) are in reasonably good agreement with the values reported for 5-hydroxy-1,3-dioxane ($\rho_4^{25} = 1.2200 \text{ g}\cdot\text{cm}^{-3}$ and $n_D^{25} = 1.4527$) [3, 18]. In the same way, dehydrated propylene glycol (Dow Chemical Company) was also used and its purity is in agreement with the quality requirements for medicinal products indicated in the American Pharmacopeia USP [19]. The dehydrated glycerol formal and propylene glycol employed were maintained over molecular sieves in order to obtain dry solvents prior to preparing the cosolvent mixtures.

2.2 Cosolvent Mixture Preparation

All glycerol formal + propylene glycol mixtures were prepared in quantities of 40.00 g, by mass, using a Ohaus Pioneer TM PA214 analytical balance with sensitivity $\pm 0.1 \text{ mg}$, at concentrations from 0.05 to 0.95 in 0.05 in mass fraction intervals, yielding 19 mixtures in addition to the two pure solvents. The estimated uncertainties were $\pm 2 \times 10^{-5}$ in the mole fractions. The mixtures were allowed to stand in Magni Whirl Blue M or Neslab RTE 10 Digital Plus (Thermo Electron Company) water baths at temperatures from 278.15 K to 313.15 K, spaced every 5.00 K; the respective temperature control was stable to $\pm 0.05 \text{ K}$ for at least 30 minutes prior to the density determinations.

2.3 Density Determination

Densities were 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 previously described procedure [20]. The equipment was calibrated according to Instruction Manual using air and water at the different temperatures studied [21]. From the density values, other thermodynamic properties were calculated as indicated in the next section.

3 Results and Discussion

In Table 1 the compositions of the glycerol formal + propylene glycol mixtures, both in mass (w_{GF}) and mole (x_{GF}) fraction, and the density values at several temperatures, are presented. No literature values are available for this binary system and therefore no direct comparison is possible. Nevertheless, it is important to note that Pineda et al. [22] and Arias et al. [23] reported density values at 298.15 K for binary mixtures obtained using the raw source material as solvents without drying them, just as these substances are employed in the pharmaceutical industries to develop and produce medicines. Accordingly, the cosolvents studied by these authors had some low quantities of water, i.e. 0.31 % mass/mass and 0.56 %

Table 1 Densities^{a,b} for glycerol formal + propylene glycol mixtures at various temperatures

Glycerol formal		Temperature / K							
w_{GF}	x_{GF}	278.15		283.15		288.15		293.15	
		Expt.	Calc.	Expt.	Calc.	Expt.	Calc.	Expt.	Calc.
0.0000	0.0000	1.0445	1.0445	1.0420	1.0420	1.0389	1.0389	1.0362	1.0362
0.0500	0.0352	1.0532	1.0523	1.0499	1.0497	1.0463	1.0466	1.0434	1.0438
0.1000	0.0714	1.0617	1.0603	1.0579	1.0576	1.0542	1.0544	1.0513	1.0515
0.1500	0.1089	1.0701	1.0685	1.0660	1.0657	1.0623	1.0624	1.0591	1.0595
0.2000	0.1476	1.0786	1.0768	1.0742	1.0740	1.0704	1.0706	1.0671	1.0676
0.2500	0.1875	1.0872	1.0854	1.0825	1.0825	1.0786	1.0791	1.0753	1.0759
0.3000	0.2289	1.0959	1.0942	1.0909	1.0911	1.0871	1.0877	1.0835	1.0845
0.3500	0.2716	1.1047	1.1032	1.0997	1.1000	1.0959	1.0965	1.0922	1.0932
0.4000	0.3159	1.1137	1.1124	1.1088	1.1091	1.1049	1.1056	1.1012	1.1021
0.4500	0.3617	1.1227	1.1218	1.1181	1.1184	1.1142	1.1148	1.1104	1.1113
0.5000	0.4092	1.1321	1.1314	1.1276	1.1280	1.1236	1.1243	1.1198	1.1207
0.5500	0.4584	1.1417	1.1412	1.1373	1.1377	1.1334	1.1340	1.1295	1.1303
0.6000	0.5095	1.1516	1.1513	1.1473	1.1477	1.1433	1.1439	1.1394	1.1401
0.6500	0.5626	1.1618	1.1616	1.1575	1.1578	1.1535	1.1540	1.1495	1.1501
0.7000	0.6177	1.1723	1.1721	1.1679	1.1682	1.1639	1.1644	1.1598	1.1604
0.7500	0.6751	1.1829	1.1828	1.1785	1.1789	1.1744	1.1750	1.1703	1.1708
0.8000	0.7348	1.1939	1.1937	1.1894	1.1897	1.1853	1.1857	1.1810	1.1815
0.8500	0.7969	1.2049	1.2048	1.2004	1.2007	1.1964	1.1967	1.1921	1.1924
0.9000	0.8617	1.2161	1.2161	1.2116	1.2119	1.2076	1.2079	1.2032	1.2035
0.9500	0.9294	1.2277	1.2276	1.2232	1.2233	1.2191	1.2193	1.2146	1.2148
1.0000	1.0000	1.2393	1.2393	1.2349	1.2349	1.2309	1.2309	1.2263	1.2263

Table 1 (Continued)

w_{GF}	x_{GF}	298.15		303.15		308.15		313.15	
		Expt.	Calc.	Expt.	Calc.	Expt.	Calc.	Expt.	Calc.
0.0000	0.0000	1.0328	1.0328	1.0289	1.0289	1.0251	1.0251	1.0214	1.0214
0.0500	0.0352	1.0402	1.0403	1.0360	1.0363	1.0323	1.0325	1.0285	1.0288
0.1000	0.0714	1.0478	1.0480	1.0438	1.0440	1.0399	1.0401	1.0360	1.0363
0.1500	0.1089	1.0556	1.0558	1.0516	1.0518	1.0476	1.0479	1.0438	1.0440
0.2000	0.1476	1.0636	1.0639	1.0595	1.0598	1.0556	1.0559	1.0519	1.0519
0.2500	0.1875	1.0718	1.0721	1.0678	1.0680	1.0639	1.0641	1.0602	1.0600
0.3000	0.2289	1.0802	1.0806	1.0762	1.0764	1.0724	1.0725	1.0687	1.0683
0.3500	0.2716	1.0888	1.0892	1.0849	1.0850	1.0811	1.0811	1.0773	1.0769
0.4000	0.3159	1.0976	1.0981	1.0937	1.0938	1.0900	1.0899	1.0862	1.0856
0.4500	0.3617	1.1068	1.1072	1.1029	1.1028	1.0992	1.0989	1.0952	1.0946
0.5000	0.4092	1.1161	1.1165	1.1122	1.1121	1.1086	1.1081	1.1045	1.1037
0.5500	0.4584	1.1257	1.1260	1.1217	1.1215	1.1181	1.1176	1.1140	1.1131
0.6000	0.5095	1.1354	1.1357	1.1315	1.1312	1.1280	1.1273	1.1238	1.1228
0.6500	0.5626	1.1455	1.1457	1.1414	1.1411	1.1379	1.1372	1.1337	1.1326
0.7000	0.6177	1.1556	1.1559	1.1514	1.1513	1.1480	1.1474	1.1437	1.1427
0.7500	0.6751	1.1661	1.1663	1.1618	1.1616	1.1584	1.1578	1.1539	1.1530
0.8000	0.7348	1.1767	1.1769	1.1723	1.1722	1.1689	1.1684	1.1644	1.1636
0.8500	0.7969	1.1876	1.1877	1.1832	1.1830	1.1797	1.1792	1.1750	1.1744
0.9000	0.8617	1.1986	1.1987	1.1941	1.1940	1.1906	1.1903	1.1858	1.1854
0.9500	0.9294	1.2098	1.2100	1.2052	1.2053	1.2017	1.2016	1.1968	1.1966
1.0000	1.0000	1.2214	1.2214	1.2167	1.2167	1.2131	1.2131	1.2081	1.2081

^a Units: $\text{g}\cdot\text{cm}^{-3}$

^b The mean standard deviation is $0.0001 \text{ g}\cdot\text{cm}^{-3}$

mass/mass for glycerol formal and propylene glycol, respectively. Table 1 shows that in all cases the density increases as the glycerol formal proportion increases in the mixtures and decreases linearly as the temperature increases, except for the mixtures with $0 \leq w_{GF} \leq 0.20$ where parabolic variations were obtained. On the other hand, density values decrease as the propylene glycol proportion increases in the mixtures, following convex parabolic trends.

3.1 Molar Volumes and Excess Molar Volumes

In Table 2 the molar volumes (V^0) for binary mixtures at all studied temperatures are presented; these were calculated from Eq. 1:

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

where M_1 and M_2 are the molar masses of the components, respectively ($104.10 \text{ g}\cdot\text{mol}^{-1}$ for glycerol formal and $72.09 \text{ g}\cdot\text{mol}^{-1}$ for propylene glycol [3]), x_1 and x_2 are the respective mole fractions of the components, and ρ is the mixture density.

Table 2 Experimental and calculated molar volumes, excess molar volumes, and partial molar volumes of components for glycerol formal + propylene glycol mixtures at various temperatures

T/K	Glycerol formal		$V^{0,a,b}$		$V^E a,b$	$\left(\frac{\partial V}{\partial w_{GF}}\right)^a$	$\bar{V}_{GF}^0 a,b$	$\bar{V}_{PG}^0 a,b$
	w_{GF}	x_{GF}	Expt.	Calc.				
278.15	0.0000	0.0000	69.02	69.02	0.000	-0.1445	84.63	69.02
	0.0500	0.0352	69.52	69.59	-0.028	-0.1450	84.51	68.98
	0.1000	0.0714	70.06	70.17	-0.034	-0.1455	84.42	68.95
	0.1500	0.1089	70.63	70.76	-0.025	-0.1460	84.36	68.95
	0.2000	0.1476	71.22	71.37	-0.013	-0.1465	84.31	68.95
	0.2500	0.1875	71.83	72.00	0.002	-0.1471	84.27	68.96
	0.3000	0.2289	72.47	72.64	0.019	-0.1476	84.24	68.98
	0.3500	0.2716	73.13	73.29	0.040	-0.1481	84.22	69.00
	0.4000	0.3159	73.81	73.97	0.058	-0.1486	84.19	69.02
	0.4500	0.3617	74.53	74.66	0.087	-0.1491	84.19	69.05
	0.5000	0.4092	75.25	75.37	0.099	-0.1496	84.17	69.08
	0.5500	0.4584	76.00	76.11	0.109	-0.1502	84.15	69.10
	0.6000	0.5095	76.77	76.87	0.111	-0.1507	84.13	69.12
	0.6500	0.5626	77.55	77.65	0.104	-0.1512	84.10	69.14
	0.7000	0.6177	78.37	78.45	0.089	-0.1517	84.07	69.15
	0.7500	0.6751	79.21	79.29	0.080	-0.1522	84.05	69.18
	0.8000	0.7348	80.09	80.16	0.056	-0.1527	84.02	69.19
	0.8500	0.7969	81.01	81.06	0.045	-0.1532	84.01	69.23
	0.9000	0.8617	81.97	81.99	0.034	-0.1538	84.00	69.26
	0.9500	0.9294	82.95	82.97	0.010	-0.1543	83.99	69.29
1.0000	1.0000	84.00	84.00	0.000	-0.1548	84.00	69.33	
283.15	0.0000	0.0000	69.19	69.19	0.000	-0.1412	85.21	69.19
	0.0500	0.0352	69.74	69.76	0.020	-0.1421	85.10	69.18
	0.1000	0.0714	70.31	70.34	0.042	-0.1430	85.01	69.18
	0.1500	0.1089	70.90	70.94	0.067	-0.1439	84.93	69.19
	0.2000	0.1476	71.51	71.55	0.093	-0.1448	84.86	69.20
	0.2500	0.1875	72.15	72.18	0.123	-0.1457	84.80	69.23
	0.3000	0.2289	72.80	72.82	0.155	-0.1465	84.75	69.26
	0.3500	0.2716	73.46	73.48	0.171	-0.1474	84.69	69.28
	0.4000	0.3159	74.14	74.16	0.177	-0.1483	84.63	69.30
	0.4500	0.3617	74.83	74.86	0.179	-0.1492	84.57	69.32
	0.5000	0.4092	75.55	75.58	0.179	-0.1501	84.51	69.35
	0.5500	0.4584	76.29	76.32	0.176	-0.1510	84.46	69.38
	0.6000	0.5095	77.05	77.09	0.165	-0.1518	84.42	69.41
	0.6500	0.5626	77.84	77.87	0.151	-0.1527	84.37	69.44
	0.7000	0.6177	78.66	78.69	0.136	-0.1536	84.34	69.48
	0.7500	0.6751	79.51	79.53	0.120	-0.1545	84.32	69.53
	0.8000	0.7348	80.39	80.41	0.095	-0.1554	84.29	69.58
	0.8500	0.7969	81.31	81.32	0.077	-0.1563	84.28	69.63
	0.9000	0.8617	82.27	82.27	0.058	-0.1572	84.29	69.70

Table 2 (Continued)

T/K	Glycerol formal		$V^{0a,b}$		$V^E_{a,b}$	$\left(\frac{\partial V}{\partial w_{GF}}\right)^a$	$\bar{V}^0_{GF a,b}$	$\bar{V}^0_{PG a,b}$
	w_{GF}	x_{GF}	Expt.	Calc.				
288.15	0.9500	0.9294	83.26	83.26	0.025	-0.1580	84.29	69.76
	1.0000	1.0000	84.30	84.30	0.000	-0.1589	84.30	69.84
	0.0000	0.0000	69.39	69.39	0.000	-0.1408	85.55	69.39
	0.0500	0.0352	69.98	69.97	0.051	-0.1418	85.47	69.42
	0.1000	0.0714	70.56	70.55	0.078	-0.1428	85.37	69.42
	0.1500	0.1089	71.15	71.15	0.100	-0.1438	85.28	69.42
	0.2000	0.1476	71.77	71.76	0.131	-0.1448	85.20	69.44
	0.2500	0.1875	72.41	72.39	0.165	-0.1457	85.14	69.47
	0.3000	0.2289	73.06	73.04	0.188	-0.1467	85.07	69.49
	0.3500	0.2716	73.72	73.70	0.201	-0.1477	85.00	69.51
	0.4000	0.3159	74.40	74.38	0.210	-0.1487	84.93	69.54
	0.4500	0.3617	75.10	75.08	0.210	-0.1497	84.86	69.56
	0.5000	0.4092	75.82	75.81	0.214	-0.1507	84.81	69.59
	0.5500	0.4584	76.56	76.55	0.202	-0.1516	84.75	69.62
	0.6000	0.5095	77.32	77.32	0.194	-0.1526	84.70	69.66
	0.6500	0.5626	78.11	78.11	0.177	-0.1536	84.65	69.70
	0.7000	0.6177	78.93	78.93	0.158	-0.1546	84.62	69.74
	0.7500	0.6751	79.79	79.78	0.145	-0.1556	84.60	69.80
	0.8000	0.7348	80.67	80.66	0.117	-0.1566	84.57	69.85
	0.8500	0.7969	81.58	81.57	0.088	-0.1575	84.55	69.91
0.9000	0.8617	82.54	82.53	0.066	-0.1585	84.56	69.99	
0.9500	0.9294	83.54	83.53	0.036	-0.1595	84.56	70.06	
1.0000	1.0000	84.58	84.58	0.000	-0.1605	84.58	70.14	
293.15	0.0000	0.0000	69.58	69.58	0.000	-0.1393	85.97	69.58
	0.0500	0.0352	70.17	70.15	0.060	-0.1404	85.89	69.60
	0.1000	0.0714	70.75	70.74	0.082	-0.1415	85.77	69.60
	0.1500	0.1089	71.36	71.34	0.119	-0.1426	85.68	69.61
	0.2000	0.1476	71.99	71.96	0.152	-0.1437	85.59	69.63
	0.2500	0.1875	72.63	72.59	0.180	-0.1448	85.51	69.65
	0.3000	0.2289	73.30	73.24	0.219	-0.1459	85.45	69.69
	0.3500	0.2716	73.97	73.91	0.233	-0.1470	85.37	69.72
	0.4000	0.3159	74.65	74.59	0.237	-0.1481	85.29	69.74
	0.4500	0.3617	75.35	75.30	0.237	-0.1492	85.21	69.77
	0.5000	0.4092	76.08	76.03	0.235	-0.1503	85.15	69.80
	0.5500	0.4584	76.82	76.78	0.223	-0.1514	85.08	69.83
	0.6000	0.5095	77.59	77.55	0.208	-0.1524	85.02	69.87
	0.6500	0.5626	78.38	78.35	0.191	-0.1535	84.97	69.91
	0.7000	0.6177	79.21	79.18	0.172	-0.1546	84.93	69.97
	0.7500	0.6751	80.07	80.04	0.152	-0.1557	84.90	70.02
0.8000	0.7348	80.96	80.93	0.130	-0.1568	84.88	70.09	
0.8500	0.7969	81.88	81.86	0.093	-0.1579	84.86	70.16	

Table 2 (Continued)

T/K	Glycerol formal		$V^{0a,b}$		$V^E_{a,b}$	$\left(\frac{\partial V}{\partial w_{GF}}\right)^a$	$\bar{V}^0_{GF\ a,b}$	$\bar{V}^0_{PG\ a,b}$
	w_{GF}	x_{GF}	Expt.	Calc.				
298.15	0.9000	0.8617	82.84	82.82	0.069	-0.1590	84.87	70.24
	0.9500	0.9294	83.85	83.83	0.038	-0.1601	84.88	70.32
	1.0000	1.0000	84.89	84.89	0.000	-0.1612	84.89	70.41
	0.0000	0.0000	69.80	69.80	0.000	-0.1402	86.21	69.80
	0.0500	0.0352	70.39	70.38	0.043	-0.1412	86.12	69.82
	0.1000	0.0714	70.99	70.97	0.081	-0.1422	86.04	69.83
	0.1500	0.1089	71.60	71.57	0.114	-0.1431	85.95	69.85
	0.2000	0.1476	72.22	72.19	0.143	-0.1441	85.88	69.86
	0.2500	0.1875	72.87	72.83	0.168	-0.1451	85.80	69.88
	0.3000	0.2289	73.52	73.49	0.188	-0.1461	85.73	69.90
	0.3500	0.2716	74.20	74.16	0.204	-0.1471	85.66	69.93
	0.4000	0.3159	74.90	74.85	0.217	-0.1481	85.60	69.95
	0.4500	0.3617	75.60	75.56	0.213	-0.1491	85.52	69.98
	0.5000	0.4092	76.33	76.29	0.212	-0.1501	85.46	70.01
	0.5500	0.4584	77.08	77.05	0.202	-0.1511	85.40	70.04
	0.6000	0.5095	77.86	77.83	0.195	-0.1521	85.36	70.08
	0.6500	0.5626	78.66	78.63	0.173	-0.1531	85.30	70.11
	0.7000	0.6177	79.50	79.47	0.162	-0.1541	85.28	70.16
	0.7500	0.6751	80.36	80.33	0.136	-0.1551	85.24	70.21
0.8000	0.7348	81.26	81.23	0.115	-0.1561	85.22	70.27	
0.8500	0.7969	82.19	82.17	0.085	-0.1571	85.21	70.33	
0.9000	0.8617	83.16	83.14	0.062	-0.1581	85.21	70.40	
0.9500	0.9294	84.18	84.16	0.038	-0.1590	85.22	70.48	
1.0000	1.0000	85.23	85.23	0.000	-0.1600	85.23	70.56	
303.15	0.0000	0.0000	70.07	70.07	0.000	-0.1421	86.39	70.07
	0.0500	0.0352	70.68	70.65	0.062	-0.1429	86.35	70.10
	0.1000	0.0714	71.26	71.24	0.084	-0.1438	86.26	70.11
	0.1500	0.1089	71.87	71.84	0.115	-0.1447	86.19	70.12
	0.2000	0.1476	72.50	72.46	0.148	-0.1455	86.14	70.14
	0.2500	0.1875	73.14	73.10	0.164	-0.1464	86.06	70.16
	0.3000	0.2289	73.80	73.76	0.182	-0.1473	86.00	70.18
	0.3500	0.2716	74.47	74.43	0.189	-0.1482	85.93	70.19
	0.4000	0.3159	75.16	75.13	0.199	-0.1490	85.88	70.22
	0.4500	0.3617	75.87	75.84	0.192	-0.1499	85.81	70.23
	0.5000	0.4092	76.60	76.57	0.189	-0.1508	85.75	70.26
	0.5500	0.4584	77.35	77.33	0.182	-0.1516	85.71	70.28
	0.6000	0.5095	78.13	78.12	0.166	-0.1525	85.66	70.31
	0.6500	0.5626	78.94	78.93	0.155	-0.1534	85.62	70.35
	0.7000	0.6177	79.79	79.76	0.148	-0.1542	85.60	70.40
	0.7500	0.6751	80.65	80.63	0.125	-0.1551	85.57	70.44
0.8000	0.7348	81.56	81.54	0.108	-0.1560	85.56	70.49	

Table 2 (Continued)

T/K	Glycerol formal		$V^{0a,b}$		$V^E_{a,b}$	$\left(\frac{\partial V}{\partial w_{GF}}\right)^a$	$\bar{V}^0_{GF\ a,b}$	$\bar{V}^0_{PG\ a,b}$
	w_{GF}	x_{GF}	Expt.	Calc.				
	0.8500	0.7969	82.49	82.48	0.075	-0.1568	85.54	70.54
	0.9000	0.8617	83.48	83.46	0.055	-0.1577	85.54	70.61
	0.9500	0.9294	84.50	84.49	0.035	-0.1586	85.55	70.68
	1.0000	1.0000	85.56	85.56	0.000	-0.1595	85.56	70.75
308.15	0.0000	0.0000	70.33	70.33	0.000	-0.1438	86.59	70.33
	0.0500	0.0352	70.93	70.90	0.055	-0.1446	86.54	70.36
	0.1000	0.0714	71.53	71.49	0.092	-0.1455	86.48	70.38
	0.1500	0.1089	72.15	72.10	0.130	-0.1463	86.43	70.40
	0.2000	0.1476	72.77	72.72	0.157	-0.1471	86.37	70.42
	0.2500	0.1875	73.41	73.36	0.173	-0.1480	86.30	70.43
	0.3000	0.2289	74.06	74.01	0.185	-0.1488	86.23	70.45
	0.3500	0.2716	74.73	74.69	0.192	-0.1497	86.17	70.46
	0.4000	0.3159	75.42	75.38	0.196	-0.1505	86.11	70.48
	0.4500	0.3617	76.12	76.09	0.190	-0.1513	86.04	70.50
	0.5000	0.4092	76.85	76.83	0.180	-0.1522	85.99	70.52
	0.5500	0.4584	77.60	77.58	0.174	-0.1530	85.94	70.55
	0.6000	0.5095	78.37	78.37	0.152	-0.1538	85.88	70.57
	0.6500	0.5626	79.18	79.18	0.141	-0.1547	85.85	70.61
	0.7000	0.6177	80.02	80.02	0.128	-0.1555	85.83	70.65
	0.7500	0.6751	80.89	80.88	0.106	-0.1564	85.80	70.69
	0.8000	0.7348	81.80	81.79	0.089	-0.1572	85.79	70.74
	0.8500	0.7969	82.74	82.73	0.065	-0.1580	85.78	70.80
	0.9000	0.8617	83.72	83.71	0.046	-0.1589	85.78	70.86
	0.9500	0.9294	84.75	84.74	0.027	-0.1597	85.80	70.93
	1.0000	1.0000	85.82	85.82	0.000	-0.1606	85.82	71.01
313.15	0.0000	0.0000	70.58	70.58	0.000	-0.1450	86.83	70.58
	0.0500	0.0352	71.19	71.16	0.059	-0.1457	86.81	70.62
	0.1000	0.0714	71.80	71.75	0.099	-0.1465	86.76	70.65
	0.1500	0.1089	72.41	72.36	0.127	-0.1472	86.71	70.66
	0.2000	0.1476	73.03	72.98	0.144	-0.1479	86.65	70.67
	0.2500	0.1875	73.66	73.62	0.156	-0.1487	86.59	70.68
	0.3000	0.2289	74.32	74.28	0.163	-0.1494	86.53	70.69
	0.3500	0.2716	74.99	74.96	0.174	-0.1501	86.48	70.71
	0.4000	0.3159	75.68	75.66	0.174	-0.1508	86.42	70.72
	0.4500	0.3617	76.40	76.37	0.177	-0.1516	86.38	70.75
	0.5000	0.4092	77.13	77.11	0.170	-0.1523	86.33	70.76
	0.5500	0.4584	77.89	77.88	0.159	-0.1530	86.28	70.79
	0.6000	0.5095	78.67	78.66	0.139	-0.1538	86.23	70.80
	0.6500	0.5626	79.48	79.48	0.123	-0.1545	86.20	70.83
	0.7000	0.6177	80.32	80.32	0.112	-0.1552	86.18	70.87
	0.7500	0.6751	81.21	81.20	0.099	-0.1560	86.16	70.91

Table 2 (Continued)

T/K	Glycerol formal		V^0 a,b		V^E a,b	$(\frac{\partial V}{\partial w_{GF}})^a$	\bar{V}_{GF}^0 a,b	\bar{V}_{PG}^0 a,b
	w_{GF}	x_{GF}	Expt.	Calc.				
0.8000	0.7348		82.11	82.11	0.077	-0.1567	86.14	70.95
0.8500	0.7969		83.07	83.06	0.061	-0.1574	86.14	71.00
0.9000	0.8617		84.06	84.05	0.043	-0.1582	86.15	71.06
0.9500	0.9294		85.10	85.08	0.025	-0.1589	86.16	71.12
1.0000	1.0000		86.17	86.17	0.000	-0.1596	86.17	71.18

a Units: $\text{cm}^3 \cdot \text{mol}^{-1}$

b The mean standard deviation for V^0 and V^E are $0.01 \text{ cm}^3 \cdot \text{mol}^{-1}$ while for \bar{V}_{GF}^0 and \bar{V}_{PG}^0 they are closer to $0.03 \text{ cm}^3 \cdot \text{mol}^{-1}$

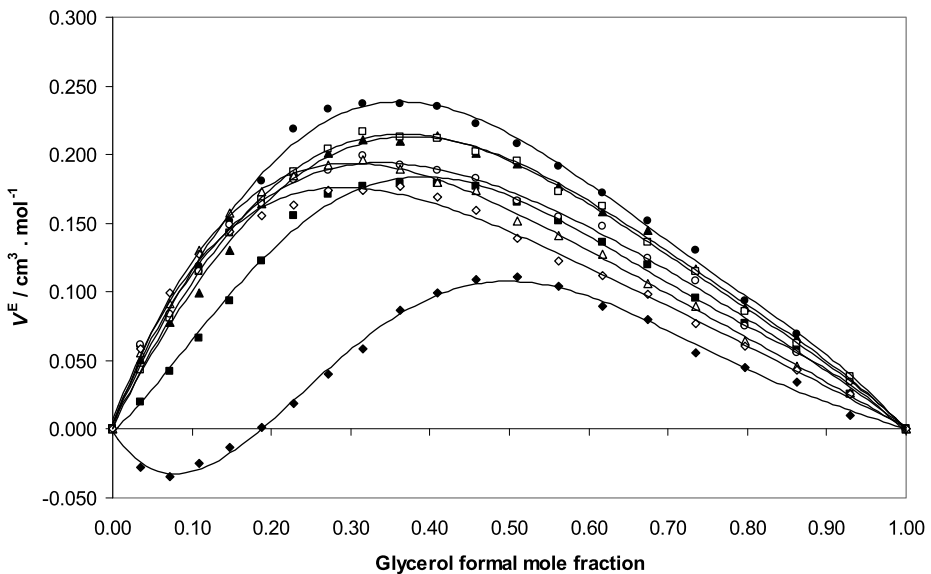


Fig. 1 Excess molar volumes of glycerol formal + propylene glycol mixtures at eight temperatures. Lines represent the best polynomial fit obtained at each temperature: (◆) 278.15 K; (■) 283.15 K; (▲) 288.15 K; (●) 293.15 K; (□) 298.15 K; (○) 303.15 K; (△) 308.15 K; (◇) 313.15 K

The excess molar volumes (V^E) calculated from Eq. 2 (where, ρ_1 and ρ_2 are the densities of pure components), are also presented in Table 2 at the studied temperatures. This behavior is shown graphically in Fig. 1 at all of these temperatures.

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

Opposite to the behavior obtained in other similar investigations [10–17], in almost all cases the excess volumes are positive (especially around 0.30–0.40 mole fraction of glycerol formal, where it is approximately $0.20 \text{ cm}^3 \cdot \text{mol}^{-1}$), indicating an expansion in volume. The exception is at 278.15 K in mixtures with compositions $0.00 < w_{GF} < 0.25$, where negative values of about $0.03 \text{ cm}^3 \cdot \text{mol}^{-1}$ are obtained. As was already said [15–17], according to Fort

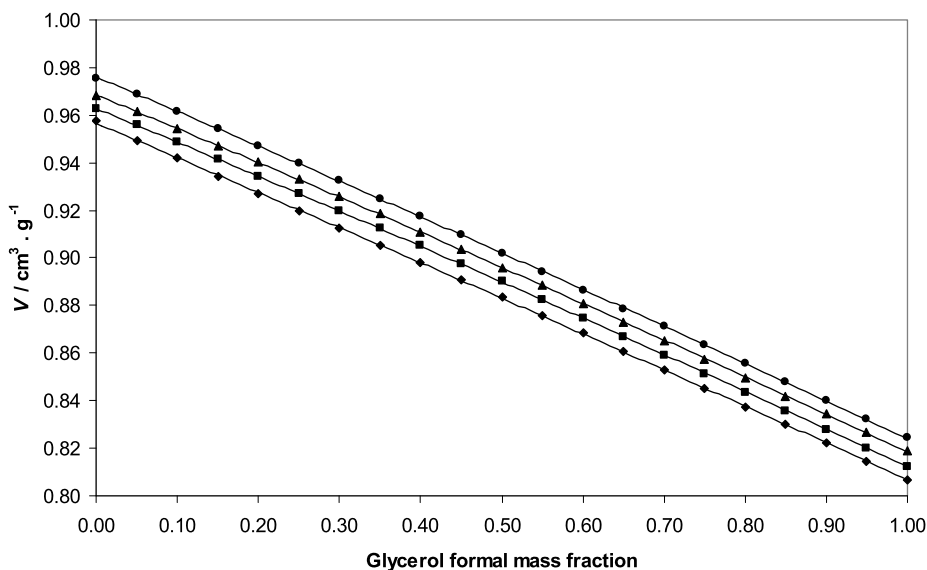


Fig. 2 Specific volumes of glycerol formal + propylene glycol mixtures as a function of the mixture composition at four temperatures: (◆) 278.15 K; (■) 288.15; (▲) 298.15 K; (●) 308.15 K

and Moore [24], positive excess volumes indicate weak interaction between the components and is attributed to dispersion forces (London interactions), which are likely to be operative in all cases.

In the present system, where hydrogen bonding is also important, the global expansion in volume can be interpreted in qualitative terms by considering the following events: first, expansion occurs due to depolymerization of propylene glycol by addition of glycerol formal; secondly, a contraction occurs due to the free volume difference of unlike molecules; and thirdly, a contraction occurs due to hydrogen bond formation between glycerol formal and propylene glycol through $-\text{OH} \cdots \text{O} <$ or $-\text{OH} \cdots \text{OH}$ bonding.

Thus, the positive values of excess volumes over the free volume contribution indicate that weak interactions (with predominance of London dispersive forces) and the formation of hydrogen bonds (between glycerol formal and propylene glycol) is less than the original propylene glycol–propylene glycol hydrogen bonding in neat propylene glycol.

The excess molar volumes become more positive as the temperature is raised from 278.15 to 293.15 K, while later they decrease with temperature, although the reason for this result is not clear at molecular level.

3.2 Partial Molar Volumes

The partial specific volumes of glycerol formal (\bar{V}_{GF}) and propylene glycol (\bar{V}_{PG}) were calculated using the classical Bakhuis–Roozeboom method, by means of Eqs. 3 and 4 applied to the variation of the respective specific volumes as a function of the glycerol formal mass fraction (Table 2, Fig. 2), and adjusting them to second-degree polynomials by least-squares regression analyses [25, 26]. The first derivatives of the polynomials obtained were taken and solved at each composition point to yield:

$$\bar{V}_{\text{GF}} = V + w_{\text{PG}} \frac{dV}{dw_{\text{GF}}} \quad (3)$$

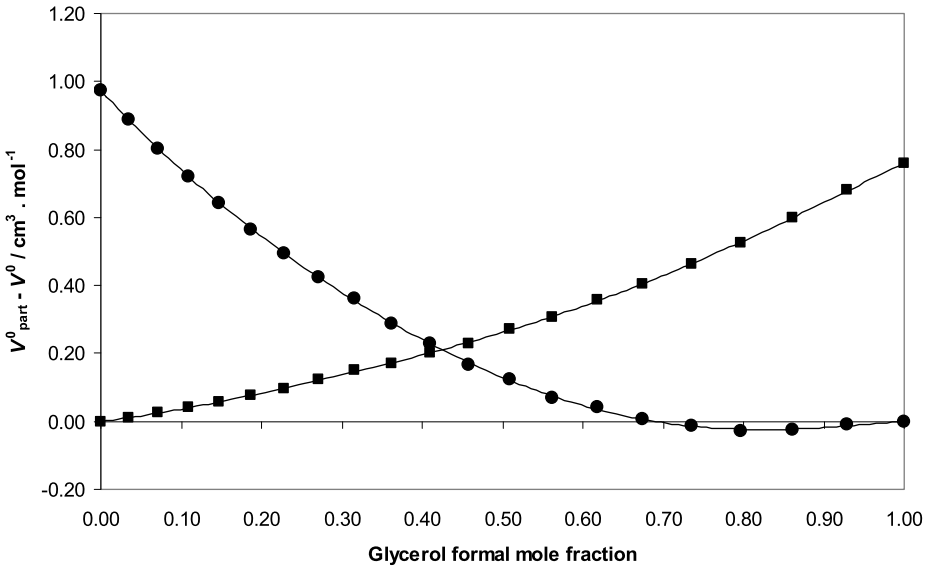


Fig. 3 Partial molar volumes of glycerol formal (●) and propylene glycol (■), calculated as differences relative to pure solvent volumes, in glycerol formal + propylene glycol mixtures at 298.15 K

$$\bar{V}_{\text{PG}} = V - w_{\text{GF}} \frac{dV}{dw_{\text{GF}}} \quad (4)$$

The partial molar volumes were calculated from the respective partial specific volumes multiplied by the molar masses. The resulting \bar{V}_{GF}^0 and \bar{V}_{PG}^0 values are also presented in Table 2 in addition to the slopes obtained (dV/dw_{GF}) at each composition and temperature. In the majority of cases the partial molar volumes for glycerol formal and propylene glycol in the mixtures are greater than those for the pure solvents, except in those mixtures where the respective cosolvent is in great excess, where slight contractions, smaller than $0.02 \text{ cm}^3 \cdot \text{mol}^{-1}$, are observed. In the cosolvent mixtures, the partial molar volumes of glycerol formal vary from $83.99 \text{ cm}^3 \cdot \text{mol}^{-1}$ (for $w_{\text{GF}} = 0.90$ at 278.15 K) to $86.14 \text{ cm}^3 \cdot \text{mol}^{-1}$ (for $w_{\text{GF}} = 0.85$ at 313.15 K), and for propylene glycol varied from $68.95 \text{ cm}^3 \cdot \text{mol}^{-1}$ (for $w_{\text{GF}} = 0.15$ at 278.15 K) to $71.12 \text{ cm}^3 \cdot \text{mol}^{-1}$ (for $w_{\text{GF}} = 0.95$ at 313.15 K). The results obtained for \bar{V}_{GF}^0 and \bar{V}_{PG}^0 are in agreement with the positive excess volumes obtained. The variation of these two properties are presented in Fig. 3 as a function of the glycerol formal mole fraction at 298.15 K. 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 increases as their respective proportion in the mixtures diminishes in those mixtures where they are in minor proportion.

3.3 Redlich–Kister Equation

The Redlich–Kister equation has been used in recent decades for representing several kinds of physicochemical properties of mixtures such as excess volumes, excess viscosities, solubilities in cosolvent mixtures, among others [27]. For excess molar volumes,

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

Table 3 Redlich–Kister regression results in mole fractions for the excess volumes of glycerol formal + propylene glycol mixtures at various temperatures

T/K	a_0	a_1	a_2	a_3	R^2	$\sigma/\text{cm}^3\cdot\text{mol}^{-1}$
278.15	0.4405	-0.0468	-0.8182	0.6488	0.9873	0.0049
283.15	0.6949	-0.4561	-0.1992	0.4517	0.9499	0.0057
288.15	0.7720	-0.3670	0.1506	-0.0825	0.9201	0.0077
293.15	0.8481	-0.4697	0.1890	-0.0606	0.9092	0.0091
298.15	0.7757	-0.5200	0.1508	0.1781	0.9954	0.0031
303.15	0.6724	-0.3460	0.3750	-0.3065	0.9392	0.0079
308.15	0.6335	-0.5388	0.3872	-0.1183	0.9952	0.0030
313.15	0.5539	-0.3989	0.4925	-0.3735	0.9879	0.0078

In the analysis of our excess volume data, Eq. 5 was used in the form of third degree polynomial equations. Using least-squares analyses, the four a_i coefficients of Eq. 6 are obtained:

$$\frac{V^E}{x_1x_2} = a_0 + a_1(x_1 - x_2) + a_2(x_1 - x_2)^2 + a_3(x_1 - x_2)^3 \quad (6)$$

The Redlich–Kister parameters for glycerol formal + propylene glycol mixtures at all temperatures studied are presented in Table 3, along with the related correlation 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, 19 and 4 respectively). Figure 4 shows the Redlich–Kister equation applied to the glycerol formal + propylene glycol data at several temperatures.

$$\sigma(V^E) = \sqrt{\frac{\sum(V_{\text{expt}}^E - V_{\text{calc}}^E)^2}{D - N}} \quad (7)$$

The correlation coefficient values greater than 0.94 (except at 288.15 and 293.15 K) indicate that the regular polynomial regressions adequately describe the excess volumes. In a similar way, the standard deviations are comparable to those presented in the literature for other mixtures [10–15]. On the other hand, the σ values obtained for glycerol formal + propylene glycol mixtures are generally similar to those obtained for propylene glycol + water (near $0.030 \text{ cm}^3\cdot\text{mol}^{-1}$) [15], ethanol + propylene glycol (varying from 0.003 to $0.021 \text{ cm}^3\cdot\text{mol}^{-1}$) [16], and glycerol formal + water (near $0.008 \text{ cm}^3\cdot\text{mol}^{-1}$) [17].

3.4 Volumetric Thermal Expansion

In pharmaceutical pre-formulation studies, it is very important to know the variation of physicochemical properties related to pharmaceutical dosage forms with respect to temperature changes, especially for properties that affect the concentration of active ingredients. Thus, the volume thermal expansion coefficients (α) were calculated by means of Eq. 8 [28] by using the variation of molar volumes with temperature (Table 2):

$$\alpha = \frac{1}{V^0} \left(\frac{\partial V^0}{\partial T} \right)_{p,x} \quad (8)$$

Table 4 summarizes the $(\partial V^0/\partial T)$ and α values for all mixtures and the corresponding pure solvents. For mixtures of $0.00 \leq w_{\text{GF}} \leq 0.15$, quadratic polynomial models of V^0 versus T were used, whereas for mixtures of $0.20 \leq w_{\text{GF}} \leq 1.00$, linear models were obtained.

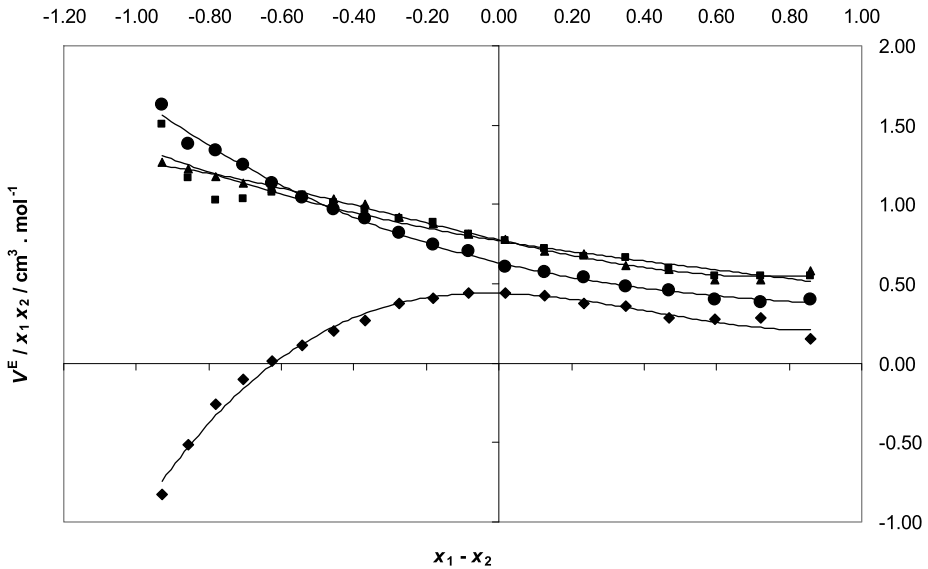


Fig. 4 Regression with the Redlich–Kister equation in mole fractions, using four terms for glycerol formal + propylene glycol mixtures, at four temperatures: (◆) 278.15 K; (■) 288.15; (▲) 298.15 K; (●) 308.15 K

It is remarkable that, in all cases, the obtained correlation coefficients are greater than 0.999. The α values varied from $6.69 \times 10^{-4} \text{ K}^{-1}$ in propylene glycol to $7.28 \times 10^{-4} \text{ K}^{-1}$ in pure glycerol formal at 298.15 K and this variation is not linear with the mixture composition.

3.5 Data Correlation Using the Jouyban–Acree Model

The Jouyban–Acree model has been used to correlate physicochemical properties of solutions in mixed solvents, including the dielectric constants [29], viscosities [30], solvatochromic parameters [31], densities [32], velocities of sound [33, 34] and, more recently, molar volumes [35]. This model uses the physicochemical properties of the individual solvents as input data and a number of curve-fitting parameters represent the effects of solvent–solvent interactions in the solution. It was basically derived by Acree [36] for representing the solvent effects on the solubility of non-polar solutes in nearly ideal solvent mixtures under isothermal conditions, and then its applications were extended to the solubility of polar solutes in water + cosolvent mixtures under isothermal conditions [37]. Further extensions were made to represent the solvent composition and temperature effects on the solubility of drugs [38], along with some other parameters such as acid dissociation constants [39], electrophoretic mobility in capillary electrophoresis [40], and retention factors in high performance liquid chromatography [41].

The model for representing the solvent composition and temperature effects on the densities of solvent mixtures is:

$$\ln \rho_{m,T} = x_1 \ln \rho_{1,T} + x_2 \ln \rho_{2,T} + \frac{x_1 x_2}{T} \cdot \sum_{i=0}^2 J_i (x_1 - x_2)^i \tag{9}$$

where $\rho_{m,T}$, $\rho_{1,T}$, $\rho_{2,T}$ are densities of the mixed solvent, solvents 1 (glycerol formal) and 2 (propylene glycol), at different temperatures (T). The x_1 and x_2 are mole fractions of glyce-

Table 4 Volumetric thermal expansion coefficients of glycerol formal + propylene glycol mixtures at 298.15 K

Glycerol formal		$100 (\partial V^0/\partial T)/\text{cm}^3 \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$	$10^4 \alpha/\text{K}^{-1}$
w_{GF}	x_{GF}		
0.0000	0.0000	4.671	6.69
0.0500	0.0352	4.850	6.89
0.1000	0.0714	4.984	7.02
0.1500	0.1089	5.075	7.09
0.2000	0.1476	5.097	7.06
0.2500	0.1875	5.130	7.04
0.3000	0.2289	5.151	7.01
0.3500	0.2716	5.194	7.00
0.4000	0.3159	5.239	7.00
0.4500	0.3617	5.259	6.96
0.5000	0.4092	5.291	6.93
0.5500	0.4584	5.259	6.82
0.6000	0.5095	5.376	6.90
0.6500	0.5626	5.457	6.94
0.7000	0.6177	5.570	7.01
0.7500	0.6751	5.647	7.03
0.8000	0.7348	5.769	7.10
0.8500	0.7969	5.858	7.13
0.9000	0.8617	5.960	7.17
0.9500	0.9294	6.110	7.26
1.0000	1.0000	6.205	7.28

erol formal and propylene glycol, respectively. The J_i terms are coefficients of the model computed by using a zero intercept regression analysis:

$$\begin{aligned} \ln \rho_{m,T} - (x_1 \ln \rho_{1,T} + x_2 \ln \rho_{2,T}) \\ = J_0 \left(\frac{x_1 x_2}{T} \right) + J_1 \frac{x_1 x_2 (x_1 - x_2)}{T} + J_2 \frac{x_1 x_2 (x_1 - x_2)^2}{T} \end{aligned} \quad (10)$$

The following equation was obtained for correlating the densities of mixtures of glycerol formal and propylene glycol at different temperatures:

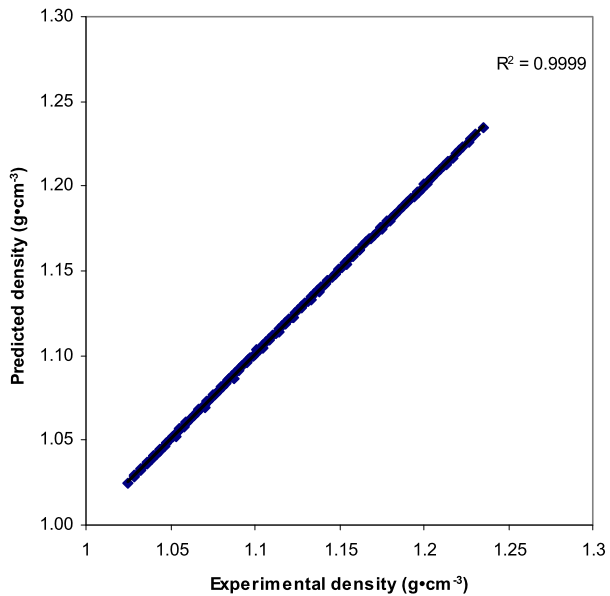
$$\ln \rho_{m,T} = x_1 \ln \rho_{1,T} + x_2 \ln \rho_{2,T} + 11.393 \left(\frac{x_1 x_2}{T} \right) - 0.322 \frac{x_1 x_2 (x_1 - x_2)}{T} \quad (11)$$

The calculated density values using Eq. 11 are presented in Table 1. The mean relative deviation (MRD) between experimental and calculated data was calculated as an accuracy criterion using:

$$\text{MRD} = \frac{100}{N} \left(\frac{|\text{Calculated} - \text{Experimental}|}{\text{Experimental}} \right) \quad (12)$$

and is 0.04 ± 0.03 for Eq. 11. The N value in Eq. 12 is the number of data points in the data set.

Fig. 5 The predicted density values in $\text{g}\cdot\text{cm}^{-3}$, calculated using Eq. 14, against the corresponding experimental values



An adapted version of Eq. 11 was used to represent the effects of solvent composition and temperature on the molar volume of mixed solvents in a recent work [35]. A similar model can be trained to represent the molar volumes of glycerol formal + propylene glycol at various temperatures, giving:

$$\ln V_{m,T} = x_1 \ln V_{1,T} + x_2 \ln V_{2,T} + 8.439 \left(\frac{x_1 x_2}{T} \right) - 2.122 \frac{x_1 x_2 (x_1 - x_2)}{T} \quad (13)$$

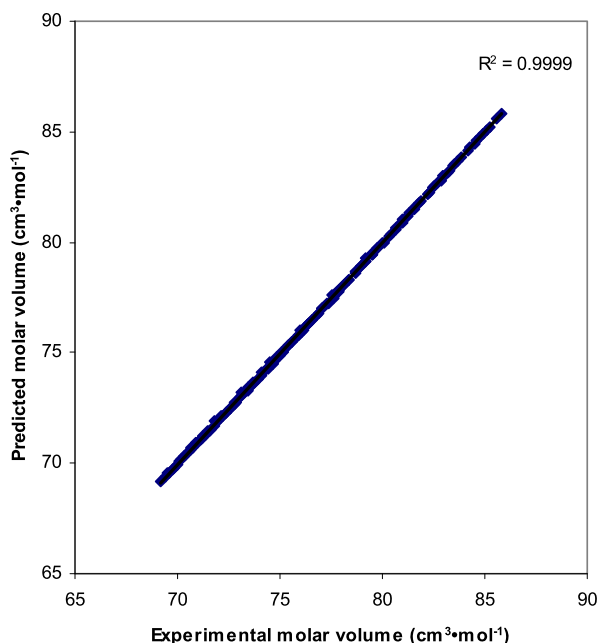
The calculated molar volume values are presented in Table 2. The model represents the experimental data very well and the MRD is 0.04 ± 0.05 . This model was previously applied to represent molar volume data using aqueous mixture data, and this is the first application of the model for representing the molar volume data of non-aqueous solvent mixtures at various temperatures. In addition to the fitting capability of the model, it can be used to predict molar volumes using the trained version of the model employing the minimum number of experimental data points. For this purpose, a minimum numbers of experimental data (the 11 odd data points of the set at 273.15 K and the 11 odd data points of the set at 313.15 K) were used for the density and molar volume data sets and the following equations were obtained:

$$\ln \rho_{m,T} = x_1 \ln \rho_{1,T} + x_2 \ln \rho_{2,T} + 12.257 \left(\frac{x_1 x_2}{T} \right) - 1.379 \frac{x_1 x_2 (x_1 - x_2)}{T} \quad (14)$$

$$\ln V_{m,T} = x_1 \ln V_{1,T} + x_2 \ln V_{2,T} + 7.495 \left(\frac{x_1 x_2}{T} \right) - 1.056 \frac{x_1 x_2 (x_1 - x_2)}{T} \quad (15)$$

The MRD values of Eqs. 14 and 15 for predicted densities and molar volumes, respectively, are 0.06 ± 0.05 and 0.08 ± 0.05 ($N = 146$). Figures 5 and 6 show the predicted values of density and molar volume versus the experimental values, respectively. High regression coefficient values ($R^2 = 0.9999$ for density and $R^2 = 0.9999$ for molar volume) indicate the predictability and applicability of the Jouyban–Acree model in this newly presented approach.

Fig. 6 The predicted molar volume values in $\text{cm}^{-3}\cdot\text{mol}^{-1}$, calculated using Eq. 15, against the corresponding experimental values



In the case of excess molar volumes, the general form of the Jouyban–Acree model produces acceptable results, except for data at 278.15 K. This might be due to their negative values, which are not present in other composition and temperature regions. However, the model produces acceptable results at each temperature (the results of these calculations are not provided here).

4 Conclusions

This work reports experimental information about the volumetric behavior of glycerol formal + propylene glycol mixtures at eight temperatures commonly encountered under technological conditions. It can be concluded that this binary system shows non-ideal behavior exhibiting positive deviations. These observations demonstrate that it is necessary to systematically characterize representative binary systems in order to have complete experimental information about the physical and chemical properties needed for understanding liquid pharmaceutical systems. Also, the Jouyban–Acree model can predict the density and molar volume of a solution in solvent mixtures at different temperatures using a minimum number of experimental data points, with acceptable accuracy. Furthermore, the reported experimental values could be used to challenge other theoretical methods developed for estimation of thermophysical properties of liquid mixtures [42].

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