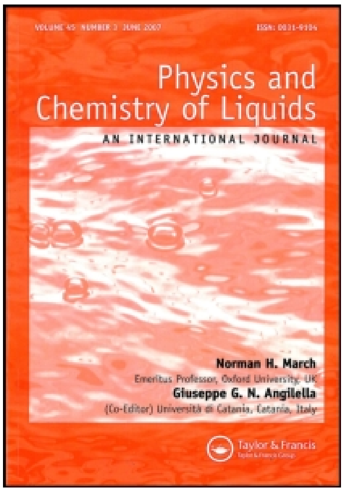

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Excess Molar Volumes and Partial Molar Volumes for Binary Mixtures of Water With 1,2-Ethanediol, 1,2-Propanediol, and 1,2-Butanediol at 293.15, 303.15 and 313.15 K

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EXCESS MOLAR VOLUMES AND PARTIAL MOLAR VOLUMES FOR BINARY MIXTURES OF WATER WITH 1,2-ETHANEDIOL, 1,2-PROPANEDIOL, AND 1,2-BUTANEDIOL AT 293.15, 303.15 AND 313.15 K

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From dilatometric method at 293.15, 303.15, and 313.15 K for binary mixtures of water and 1,2-alkane diols, the excess molar volumes, V^E and the partial molar volumes, $\bar{V}_i$ of both components at 293.15 K have been obtained as a function of mixtures composition. Excess molar volumes were calculated and correlated by a Redlich-Kister type function in terms of mole fraction. The partial molar volumes have been extrapolated to zero concentration to obtain the limiting values at infinite dilution, $\bar{V}_i^\circ$. All mixtures showed negative values and decreases with the chain length of diols. The values become less negative with increasing temperature. The results are explained in terms of dissociation of the self-associated diol molecules and the formation of aggregates between unlike molecules.

Keywords: Excess molar volumes; 1,2-alkanediol; hydrogen bond

1. INTRODUCTION

Following our study on the measurement of thermodynamic properties of nonelectrolyte solutions in which specific interactions between unlike molecules can occur [1-3] we present here excess molar

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volumes, V^E at 293.15, 303.15, and 313.15 K and also partial molar volumes, $\bar{V}_i$ of water with the series of three 1,2-alkanediols at 293.15 K. For these completely miscible (water + organic) mixtures, there is interest in using volumetric data for calculations of the effects of pressure on thermodynamic properties and also to extend our understanding of molecular interactions in (water + organic) mixtures. Temperature dependence on excess molar volumes and study of influence of associated species of diols by dilution with water is considered. By extrapolation of partial molar volumes to infinite dilution, limiting partial molar volumes, $\bar{V}_i^\circ$ are also obtained. These values are interesting from a theoretical point of view since at infinite dilution the only interactions present are solute–solvent interactions.

2. EXPERIMENTAL SECTION

Characterization data for the chemicals used in this study are listed in Table I. Diols used were purified by distillation using a 1 m fractionation column. The purified components were stored in brown glass bottles and fractionally distilled immediately before use. Water was double distilled and degassed before use. Purity of each component was ascertained by the constancy of the boiling point, and also from the density and refractive index. Densities were measured at 293.15 K using a bicapillary pycnometer with an accuracy of 5 parts in 10^5. Refractive indexes were measured at 293.15 K with an Abb'e refractometer. Water was circulated to the refractometer from a constant-temperature bath at 293.15 K. The accuracy of the refractive index measured is on the order of 0.0002.

TABLE I Source, purity grades, densities, ρ and refractive indexes, n_D of pure components at 293.15 K

Component	*Source*	*Purity*	ρ $(g{\cdot}cm^{-3})$		n_D	
			expt.	*lit.*	*expt.*	*lit.*
1,2-ethanediol	Merck	99%	1.10891	1.1088[a]	1.4314	1.4317[a]
1,2-propanediol	Aldrich	99.5%	1.0362	1.0361[b]	1.4323	1.4324[b]
1,2-butanediol	Fluka	99%	1.00345	1.0034[c]	1.4382	1.4380

[a] Ref. [4].
[b] Ref. [5].
[c] Ref. [6].

Table I also gives the density and refractive index measurements which agree with values obtained from the literature [4–6]. Excess molar volumes were measured with an accuracy of $0.003\,\mathrm{cm}^3 \cdot \mathrm{mol}^{-1}$, using a two-limb pyrex glass dilatometer described earlier [7]. Known amounts of the two components were confined over mercury in the absence of air in the two-limbs of the dilatometer. The dilatometer (mounted on a stand) was immersed in a thermostat bath which was controlled to ± 0.01 K. Mixing was achieved by rocking the cell back and forth through a defined angle. Eight dilatometers with different capacities were used to cover the entire composition range. The composition of the mixture was determined by direct weighing on an electronic balance (Mettler AE100, Switzerland) accurate to 0.001 g.

The test system benzene + cyclohexane at 298.15 K was studied in an effort to evaluate the accuracy of the experimental technique and the equipment used in this investigation. The measured excess molar volumes for this system are in good agreement with the earlier values reported in literature [8].

3. RESULTS AND DISCUSSION

The measured excess molar volumes of binary mixtures of $\{x\,\text{water} + (1-x)\text{diol}\}$ at 293.15, 303.15, and 313.15 K are listed in Table II. The experimental data at 293.15 K are graphically presented in Figure 1. The graphs of the other two temperatures are similar to Figure 1. Each set of results were fitted using a Redlich-Kister equation of the type

$$V^E/(\mathrm{cm}^3 \cdot \mathrm{mol}^{-1}) = x(1-x)\sum_{k=1} A_k(1-2x)^{k-1} \qquad (1)$$

where A_k are the coefficient obtained by a linear least squares fitting procedure and x is the mole fraction of water. In each case, the optimum number of coefficients was ascertained from an examination of the variation of the standard deviation $\sigma(V^E)$ with

$$\sigma(V^E) = \left[\sum (V^E_{\exp t.} - V^E_{\mathrm{calcd.}})^2/(n-p)\right]^{(1/2)} \qquad (2)$$

TABLE II Experimental excess molar volumes[a], V^E for the binary mixtures of $\{x\text{water} + (1 - x)\text{diols}\}$

1,2-*ethanediol*		1,2-*propanediol*		1,2-*butanediol*	
x	V^E	x	V^E	x	V^E
		$T = 293.15$ K			
.0702	−.125	.1111	−.198	.0812	−.098
.1466	−.215	.1536	−.250	.1352	−.151
.2016	−.290	.1966	−.318	.1914	−.228
.2888	−.402	.2610	−.396	.2532	−.290
.3610	−.505	.3211	−.487	.3109	−.368
.4201	−.572	.3978	−.592	.3821	−.452
.4992	−.671	.4566	−.661	.4478	−.519
.5437	−.731	.5219	−.722	.5056	−.555
.6081	−.779	.5830	−.742	.5637	−.603
.6828	−.803	.6446	−.729	.6202	−.641
.7514	−.783	.7007	−.684	.6920	−.659
.8229	−.702	.7699	−.603	.7511	−.660
.8810	−.555	.8121	−.507	.8094	−.633
.9203	−.431	.8597	−.401	.8822	−.511
		.9136	−.272	.9316	−.346
		303.15 K			
.0777	−.119	.0956	−.131	.0777	−.121
.1414	−.211	.1554	−.198	.1326	−.195
.1905	−.282	.2002	−.255	.1966	−.257
.2691	−.385	.2639	−.331	.2848	−.365
.3488	−.469	.3337	−.403	.3663	−.448
.4012	−.529	.3920	−.455	.4105	−.478
.4883	−.613	.4646	−.541	.4879	−.530
.5338	−.656	.5221	−.591	.5608	−.580
.5905	−.701	.5996	−.641	.6226	−.610
.6455	−.733	.6666	−.662	.6821	−.618
.7192	−.754	.7311	−.659	.7555	−.611
.7617	−.739	.7821	−.633	.8219	−.575
.8277	−.675	.8440	−.552	.8855	−.482
.8941	−.526	.8921	−.456	.9411	−.301
.9305	−.394	.9506	−.244		
		313.15 K			
.0810	−.135	.0521	−.075	.0613	−.091
.1331	−.206	.1162	−.161	.1215	−.159
.1852	−.269	.1877	−.255	.1902	−.233
.2449	−.349	.2419	−.316	.2411	−.306
.3008	−.422	.3202	−.396	.3129	−.363
.3663	−.512	.4144	−.481	.3892	−.444
.4159	−.583	.4911	−.544	.4516	−.485
.4811	−.653	.5833	−.603	.5080	−.521
.5409	−.706	.6419	−.618	.5711	−.547
.6011	−.733	.7191	−.594	.6135	−.566
.6891	−.711	.7988	−.487	.6855	−.581
.7313	−.667	.8408	−.401	.7377	−.569
.7918	−.553	.8941	−.266	.7981	−.542
.8489	−.399	.9229	−.188	.8514	−.488
.9166	−.201	.9611	−.085	.9243	−.310
.9505	−.115			.9302	−.298

[a] $\text{cm}^3 \cdot \text{mol}^{-1}$.

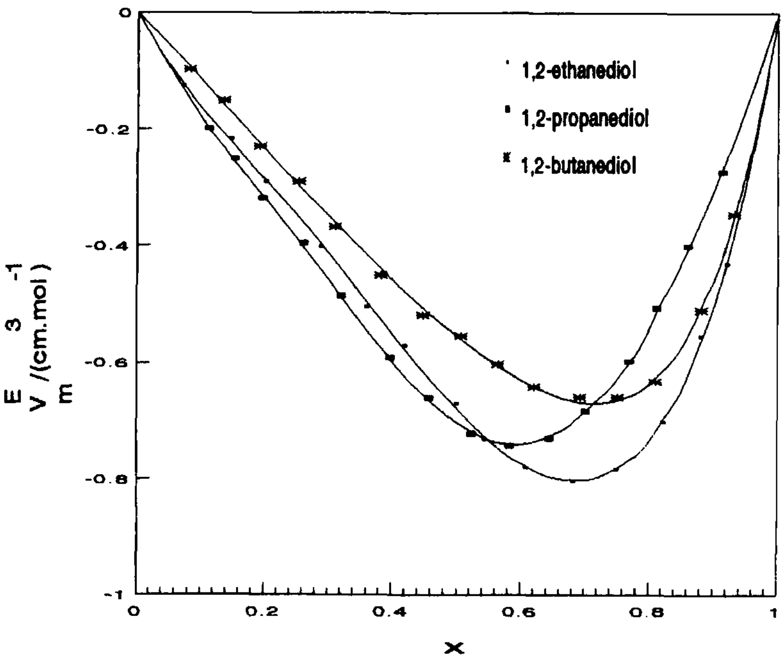

FIGURE 1 Excess molar volumes of {$x$water + $(1-x)$1,2-diol} at 293.15 K, Continuous curves were calculated from coefficients of Eq. (1) given in Table III.

in which n is the number of results and p is the number of parameters retained in Eq. (1). The values adopted for the coefficients, A_k and the standard deviation, $\sigma(V^E)$ estimated associated with the use of Eqs. (1, 2), respectively are summarized in Table III.

While mixing diol with water one observes, as in the case of diol with N, N-dimethyleformamide [3], a contraction of the molar volume $(V^E \langle \circ)$, over the whole range of composition. Negative values of V^E increase for three temperatures in the order 1,2-ethanediol$\rangle$ 1,2-propanediol$\rangle$ 1,2-butanediol.

Our V^E values become less negative with increasing temperature, as is common and Figure 2 shows dependence of V^E on temperature. We propose that breaking the intermolecular hydrogen bonds in diols and formation of a strong attractive interaction between water and the two hydroxy groups on the diols causes the decrease in volume.

TABLE III Redlich-Kister equation fitting coefficients, A_k in Eq. (1) and standard deviation, $\sigma(V^E)$ in Eq. (2) for {$x$water + $(1-x)$diols}

A/K	A_1	A_2	A_3	A_4	A_5	$\sigma(V^E)^a$
			water + 1,2-ethanediol			
293.15	−2.7234	2.2995	−.9076	.0849	−.9814	.006
303.15	−2.5029	1.8078	−1.7066	1.0347	−.1769	.003
315.15	−.2.7070	1.9907	.1684	−2.0895	.6858	.005
			water + 1,2-propanediol			
293.15	−2.8164	1.4989	.7307	−1.0122	−.9041	.005
303.15	−2.2662	1.7325	−1.2216	.4382	−.1515	.005
313.15	−.2.2089	1.6097	−1.0097	−1.3597	1.6490	.003
			water + 1,2-butanediol			
293.15	−2.2218	1.7515	−1.2297	.9377	−.4223	.008
303.15	−2.1707	1.2982	−1.2082	1.0841	−.7887	.006
313.15	−2.0617	1.2496	−.9528	.6861	−.5220	.007

[a] $cm^3 \cdot mol^{-1}$.

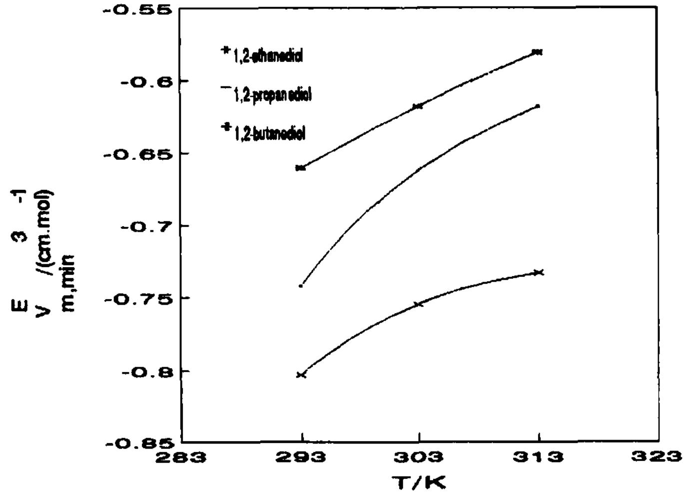

FIGURE 2 Minimum excess molar volumes *vs* temperature for the mixtures of {$x$water + $(1-x)$diol} at 293.15, 303.15, and 313.15 K.

The partial molar volumes of components, $\bar{V}_i$ in a binary mixture can be determined from excess molar volume data as follows:

$$\bar{V}_1 = V^E + V_1^* + (1-x)\left(\frac{\partial V^E}{\partial x}\right) \tag{3}$$

$$\bar{V}_2 = V^E + V_2^* - x\left(\frac{\partial V^E}{\partial x}\right) \tag{4}$$

in which V_1^* and V_2^* are molar volumes of the pure components, x and $(1 - x)$ are the mole fraction of water and diol, respectively.

To obtain values of the partial molar volumes, we start by differentiation of Eq. (1) with respect to x and substitution of the result in Eq. (3,4) leads to the following equations for the partial molar volumes of water, $\bar{V}_1$ and diol, $\bar{V}_2$

$$\bar{V}_1 = V_1^* + (1-x)^2 \sum_{k=1} A_k (1-2x)^{k-1} - 2x(1-x)^2 \sum_{k=1} A_k (k-1)(1-2x)^{k-2} \tag{5}$$

$$\bar{V}_2 = V_2^* + x^2 \sum_{k=1} A_k (1-2x)^{k-1} + 2x^2(1-x) \sum_{k=1} A_k (k-1)(1-2x)^{k-2} \tag{6}$$

Partial molar volumes of water, $\bar{V}_1$ and of diols, $\bar{V}_2$ for all compositions can be calculated by using the Redlich-Kister coefficients (Tab. III) in Eqs. (5, 6). Results at 293.15 K are listed in Table IV and $\bar{V}_2$ *vs* composition for diols in mixtures shown in Figure 3.

Much of our present interest in the volumetric properties of (water + organic) systems is focussed on the partial molar volumes of the water at in infinite dilution ($x = 0$) in diols and of diols in water at infinite dilution ($x = 1$). Setting $x = 0$ in Eq. (5) leads to

$$\bar{V}_1^\circ = V_1^* + \sum_{k=1} A_k \tag{7}$$

Similarly, setting $x = 1$ in Eq. (6) leads to

$$\bar{V}_2^\circ = V_2^* + \sum_{k=1} A_k (-1)^{k-1} \tag{8}$$

In Eqs. (7, 8), $\bar{V}_1^\circ$ and $\bar{V}_2^\circ$ represent the partial molar volume of water at infinite dilution in diols and the partial molar volume of diols at infinite dilution in water, respectively. All partial molar volumes at infinite dilution, $\bar{V}_i^\circ$ were calculated at different temperatures by using the Redlich-Kister coefficients (Tab. III) in Eqs. (7, 8) and are listed in Table V. We note that all of the $\bar{V}_1^\circ$ and $\bar{V}_2^\circ$ values are smaller than the

TABLE IV Partial molar volumes[a] of water, $\bar{V}_1$ and diols, $\bar{V}_2$ in Eqs. (5,6), for {xwater + (1 − x)diol} at 293.15 K

x	$\bar{V}_1$	$\bar{V}_2$	x	$\bar{V}_1$	$\bar{V}_2$
		water + 1,2-ethanediol			
.0702	16.59	55.90	.5437	16.39	56.30
.1466	16.76	55.94	.6081	16.54	56.30
.2016	16.69	55.96	.6828	16.78	56.24
.2888	16.50	56.04	.7514	16.98	56.07
.3610	16.38	56.13	.8229	17.26	55.68
.4201	16.36	56.22	.8810	17.79	55.09
.4992	16.33	56.29	.9203	17.72	54.45
		water + 1,2-propanediol			
.1111	16.62	73.40	.5830	17.28	72.76
.1536	16.68	73.39	.6446	17.50	72.39
.1966	16.65	73.39	.7007	17.68	72.03
.2610	16.60	73.42	.7699	17.83	71.56
.3211	16.59	73.42	.8121	17.92	71.30
.3978	16.68	73.36	.8597	17.99	70.99
.4566	16.83	73.75	.9136	18.02	70.63
.5219	17.05	73.03			
		water + 1,2-ebutanediol			
.0812	16.88	89.81	.5637	17.13	89.62
.1352	16.89	89.82	.6202	17.21	89.50
.1914	16.87	89.80	.6920	17.34	89.26
.2532	16.89	89.81	.7511	17.47	88.91
.3109	16.92	89.79	.8094	17.62	88.33
.3821	16.95	89.76	.8822	17.83	87.13
.4478	16.99	89.72	.9136	17.97	85.89
.5056	17.07	89.69			

[a] $cm^3 \cdot mol^{-1}$.

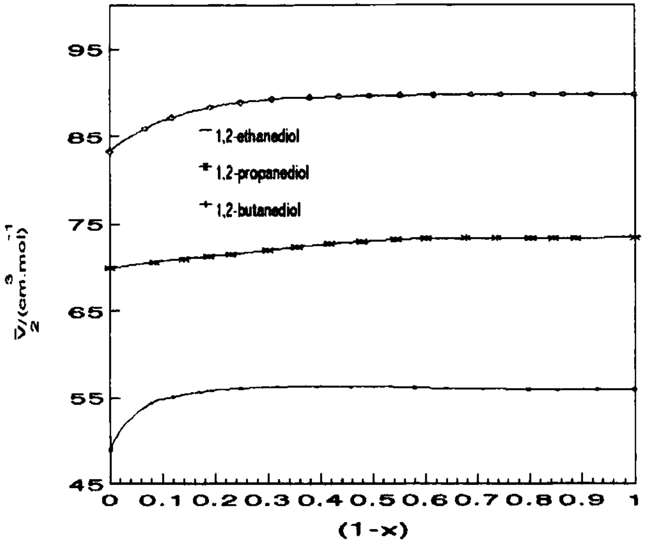

FIGURE 3 Partial molar volume of 1,2-diol in mixtures of {xwater + (1 − x)diol} at 293.15 K.

TABLE V Partial molar volumes of water at infinite dilution in diols[a], $\bar{V}_1^\circ$ and diols at infinite dilution in water[a], $\bar{V}_2^\circ$ in Eqs. (7, 8) for {$x$water + $(1-x)$diols}

T/K	$\bar{V}_1^\circ$	$\bar{V}_2^\circ$
	water + 1,2-ethanediol	
293.15	15.83	48.97
303.15	16.55	54.22
313.15	16.21	54.61
	water + 1,2-propanediol	
293.15	15.54	69.96
303.15	16.63	67.98
313.15	16.84	72.33
	water + 1,2-butanediol	
293.15	16.86	83.25
303.15	16.49	85.06
313.15	16.55	85.75

[a] $\text{cm}^3 \cdot \text{mol}^{-1}$.

corresponding molar volumes of the pure water, V_1^* and diols, V_2^*. This observation is consistent with the ideal that the molar volume of pure water is a result of the sum of the "actual" molecular volumes plus the "empty" volume that arises from the hydrogen-bonded open structure of liquid water.

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