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P. Venkateswarlu<sup>a</sup>; A. B. Manjubhashni<sup>a</sup>; S. Renuka Kumari<sup>a</sup>; G. K. Raman<sup>a</sup>

<sup>a</sup> Department of Chemistry, College of Engineering, Sri Venkateswara University, Tirupathi, India

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# Volumetric Behaviour of an Alcohol with 1,2-Dibromoethane

P. VENKATESWARLU, A. B. MANJUBHASHNI,  
S. RENUKA KUMARI and G. K. RAMAN

*Department of Chemistry, College of Engineering,  
Sri Venkateswara University, Tirupathi 517 502, India.*

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Excess volumes ( $V^E$ ) for the binary liquid mixtures of 1,2-dibromoethane with *n*-propanol, *n*-butanol, *n*-pentanol, *n*-hexanol, *n*-heptanol, *n*-octanol and *n*-decanol have been measured as a function of composition at 303.15 K by a dilatometric method.  $V^E$  is positive over the entire range of composition in all the seven systems. The positive excess volumes increase with increase in chain length from ( $C_3$  to  $C_{10}$ ). The results are explained in terms of the break up of hydrogen bonds, interstitial accommodation of 1,2-dibromoethane molecules in self associated alcohol and the possible hydrogen bond interaction of the type  $\text{Br}\cdots\text{H}-\text{O}$  between unlike molecules.

## 1 INTRODUCTION

Alcohols are strongly self associated<sup>1,2</sup> and for binary solutions rich in alcohol a three dimensional network of hydrogen bonded alcohol molecules is believed to be present.<sup>3,4</sup> Excess volumes for the binary mixtures of 1,2-dichloroethane with alkanes,<sup>5</sup> alcohols,<sup>6</sup> ketones<sup>7</sup> and 1,2-dibromoethane with acids<sup>8</sup> and ketones<sup>9</sup> have been reported earlier. But no attempt has been made to study the excess volumes for the binary mixtures of 1,2-dibromoethane with homologous series of *n*-alcohols. The purpose of this paper is to report the measurement of excess volumes of non-electrolyte solutions of 1,2-dibromoethane with *n*-propanol, *n*-butanol, *n*-pentanol, *n*-hexanol, *n*-heptanol, *n*-octanol and *n*-decanol at 303.15 K.

TABLE I  
Densities of pure liquids at 303.15 K

Component	Density ( $\rho$ )/g cm <sup>-3</sup>	
	Present	Literature
1,2-dibromoethane	2.15967	2.15970
<i>n</i> -Propanol	0.79604	0.79600
<i>n</i> -Butanol	0.80201	0.80206
<i>n</i> -Pentanol	0.80760	0.80764
<i>n</i> -Hexanol	0.81204	0.81201
<i>n</i> -Heptanol	0.81573	0.81570
<i>n</i> -Octanol	0.94160	0.94155

## 2 EXPERIMENTAL

All materials were purified by the methods, described by Riddick and Benger. 1,2-dibromoethane and alcohols were purified by the method described earlier.<sup>9,6</sup> The purity of the samples were checked by comparing the measured densities of the components with those reported in literature.<sup>11</sup> Densities were determined using a bicapillary type pycnometer which offered an accuracy of 2 points in 10.<sup>5</sup> The measured density data are reported in Table I along with those reported in the literature.

The excess volumes were measured using the dilatometer described by Rao and Naidu.<sup>12</sup>

## 3 RESULTS AND DISCUSSION

The experimental excess volumes of the seven binary mixtures are presented in Table II and also represented graphically in Figure 1. The dependence of  $V^E$  on composition may be expressed by an empirical equation of the form.

$$V^E/\text{cm}^3 \text{ mol}^{-1} = x_A x_B (a_0 + a_1(x_A - x_B) + a_2(x_A - x_B)^2) \quad (1)$$

where  $a_0$ ,  $a_1$  and  $a_2$  are adjustable parameters and  $x_A$  the mole fraction of component A. The values of parameters obtained by the least square method are included in Table III, along with standard deviation  $\sigma(V^E)$ . Values of  $V^E$  are positive over the entire range of compositions in all the seven binary mixtures. The excess volumes fall in order *n*-decanol > *n*-octanol > *n*-heptanol > *n*-hexanol > *n*-pentanol > *n*-butanol >

TABLE II

Excess volumes ( $V^E$ ) for the binary liquid mixtures of 1,2-dibromoethane with *n*-alcohols at 303.15 K.

1,2-dibromoethane + <i>n</i> -propanol		1,2-dibromoethane + <i>n</i> -butanol	
$X_A$	$V^E$	$X_A$	$V^E$
0.1121	0.048	0.1014	0.107
0.1905	0.088	0.2125	0.180
0.3787	0.148	0.3510	0.236
0.4727	0.175	0.3734	0.251
0.5514	0.180	0.5358	0.284
0.6018	0.195	0.5727	0.290
0.7468	0.185	0.7923	0.248
0.8708	0.127	0.8864	0.173
1,2-dibromoethane + <i>n</i> -pentanol		1,2-dibromoethane + <i>n</i> -hexanol	
$X_A$	$V^E$	$X_A$	$V^E$
0.1221	0.154	0.1636	0.228
0.2633	0.273	0.2754	0.348
0.3217	0.316	0.3385	0.400
0.4323	0.364	0.4766	0.480
0.4526	0.374	0.6343	0.492
0.6011	0.395	0.6764	0.480
0.8105	0.305	0.8127	0.376
0.9085	0.185	0.9199	0.200
1,2-dibromoethane + <i>n</i> -heptanol		1,2-dibromoethane + <i>n</i> -octanol	
$X_A$	$V^E$	$X_A$	$V^E$
0.1862	0.342	0.1311	0.270
0.2812	0.448	0.2630	0.470
0.3884	0.535	0.3374	0.550
0.4411	0.560	0.5230	0.660
0.6270	0.575	0.6238	0.654
0.6752	0.556	0.6715	0.635
0.8639	0.348	0.7875	0.522
0.9197	0.230	0.9378	0.209
1,2-dibromoethane + <i>n</i> -decanol			
$X_A$	$V^E$	$X_A$	$V^E$
	0.2226		0.523
	0.3536		0.692
	0.4465		0.769
	0.5589		0.816
	0.6487		0.806
	0.8172		0.620
	0.8468		0.550
	0.9335		0.297

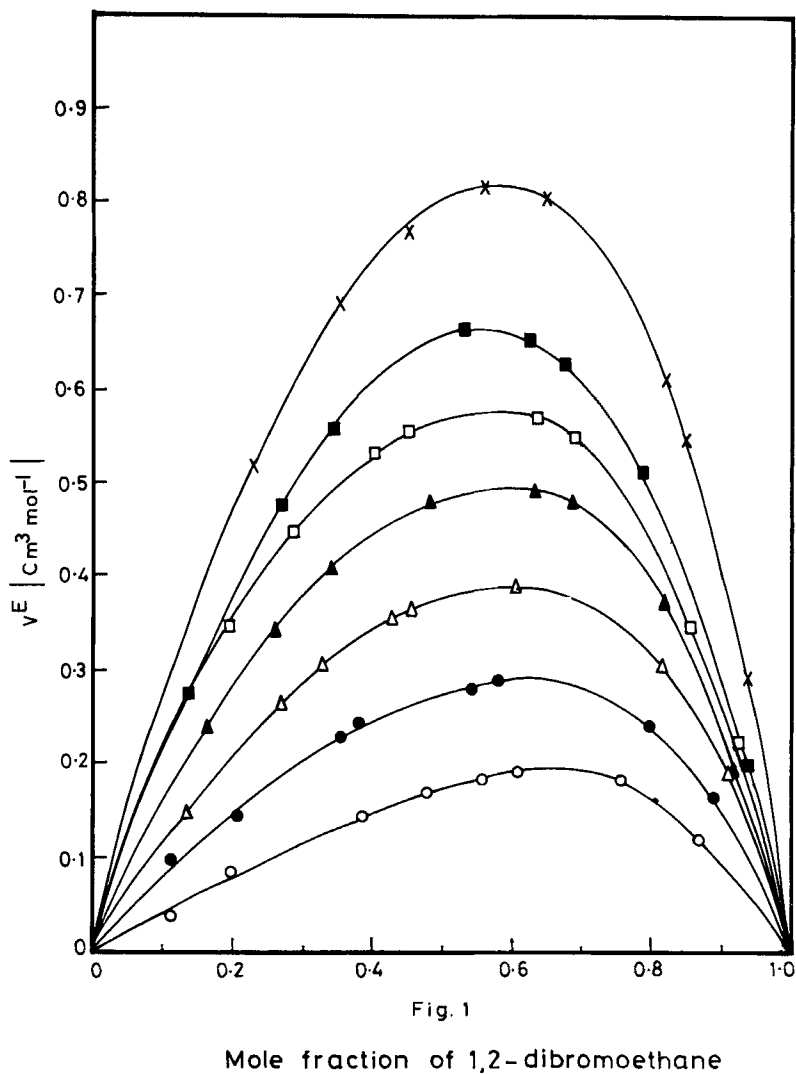


FIGURE 1 The values of  $V^E$  against mole fraction ( $x_2$ ) for the binary mixtures of 1,2-dibromoethane with ○: *n*-Propanol; ●: *n*-Butanol; △: *n*-Pentanol; ▲: *n*-Hexanol; □: *n*-Heptanol; ■: *n*-Octanol; ×: *n*-Decanol.

TABLE III

Values of parameters  $a_0$ ,  $a_1$  and  $a_2$  of the Eq. (1) and the standard deviation  $\sigma(V^E)$ .

System	$a_0$	$a_1$	$a_2$	$\sigma(V^E)$
1) 1,2-dibromoethane + <i>n</i> -propanol	0.730	0.354	0.148	0.004
2) 1,2-dibromoethane + <i>n</i> -butanol	1.112	0.377	0.544	0.003
3) 1,2-dibromoethane + <i>n</i> -pentanol	1.537	0.419	0.450	0.004
4) 1,2-dibromoethane + <i>n</i> -hexanol	1.941	0.621	0.350	0.004
5) 1,2-dibromoethane + <i>n</i> -heptanol	2.312	0.457	0.587	0.002
6) 1,2-dibromoethane + <i>n</i> -octanol	2.604	0.659	0.498	0.004
7) 1,2-dibromoethane + <i>n</i> -decanol	3.184	0.858	1.080	0.004

*n*-propanol. This order is similar to that of observed for mixtures of 1,2-dichloroethane with alcohols. The values of  $V^E$  may be explained in terms of the following: (i) deassociation of self-associated alcohols, (ii) difference in size and shape of the two components, (iii) interstitial accommodation of 1,2-dibromoethane in hydrogen bonded aggregates of alcohols and (iv) possible hydrogen bond interaction of the type  $\text{Br}\cdots\text{H}-\text{O}$ , between unlike molecules. While the first two factors contribute to expansion in volume, the remaining two factors may lead to contraction in volume. The actual values of  $V^E$  would depend upon the balance between the two opposing contributions. The experimental values indicate that the factors responsible for expansion in volume are dominant in all the mixtures.

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