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Excess Volumes of Ethanoic, Propanoic, and Butanoic Acids with 1,2-Dichloroethane and 1,2-Dibromoethane

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Excess volumes (V^E) have been determined at 303.15 K for the binary systems of 1,2-dichloroethane and 1,2-dibromoethane with ethanoic, propanoic, and butanoic acids. V^E is positive over the whole range of composition, indicating the dissociation of dimers and higher polymers of aliphatic carboxylic acids on dilution.

Introduction

A survey of the literature has shown that many attempts have been made to measure excess volumes for mixtures of haloalkanes with 1—alkanols (*1*, *2*), 1-alkanes (*3*, *4*), aromatic hydrocarbons (*5*, *6*), and ketones (*7*,–*10*) and of cyclohexane with an acid (*11*). But no attempt has been made to measure the excess volumes of aliphatic carboxylic acids with haloalkanes. Aliphatic carboxylic acids are all associated in the pure state through intermolecular hydrogen bonding. Dilution of such liquids with polar solvents like haloalkanes is expected to bring about dissociation of dimers and polymers of acids and formation of intermolecular hydrogen bonds between unlike molecules. With a view to study the effect of these hydrogen-bond interactions between unlike molecules on V^E we have measured excess volumes for the systems 1,2-dichloroethane and 1,2-dibromoethane with ethanoic, propanoic, and butanoic acids at 303.15 K.

Experimental Section

Excess volumes were measured with the dilatometer described by Rao and Naidu (*12*). The mixing cell contained two bulbs of different capacities which were connected through a U-tube having mercury to separate the two components. One end of the bulb was fitted with a capillary (1-mm i.d.) and the other end of the second bulb was fixed with a ground-glass stopper. The V^E values were accurate to ±0.003 $\text{cm}^3\ \text{mol}^{-1}$.

Purification of Materials. 1,2-Dichloroethane, 1,2-dibromoethane, and the acids were purified by the standard methods described in the literature (*13*). 1,2-Dichloroethane (BDH) was washed with potassium hydroxide solution and water, dried over anhydrous calcium chloride, and fractionally distilled. 1,2-Dibromoethane (BDH) was washed with concentrated sulfuric acid, sodium carbonate solution, and water, dried over calcium chloride, and fractionally distilled. Ethanoic acid (BDH) was washed with a calculated amount of acetic anhydride for about 10 h. It was then distilled with a fractionating column. Propanoic and butanoic acids (E. Merck) were dried over anhydrous sodium sulfate for 2 days and the samples were distilled over potassium permanganate. The purity of the samples was checked by comparing the measured densities with those reported in the literature (*14*). Densities were determined with a bicapillary type pycnometer with an accuracy of 2 parts in 10^5. The densities of the pure liquids are given in Table I.

Table I. Densities of the Pure Components at 303.15 K

component	$\rho/(\text{g cm}^{-3})$ present work	$\rho/(\text{g cm}^{-3})$ lit. (*14*)
1,2-dichloroethane	1.238 32	1.238 31
1,2-dibromoethane	2.159 67	2.159 70
ethanoic acid	1.037 90	1.038 02
propanoic acid	0.983 10	0.982 60
butanoic acid	0.947 80	0.947 97

Table II. Values of V^E for the Binary Mixtures of 1,2-Dichloroethane and 1,2-Dibromoethane with Acids at 303.15 K

X_A	$V^E/(\text{cm}^3\ \text{mol}^{-1})$	X_A	$V^E/(\text{cm}^3\ \text{mol}^{-1})$
1,2-Dichloroethane + Ethanoic Acid		1,2-Dibromoethane + Ethanoic Acid	
0.1541	0.332	0.1716	0.517
0.1880	0.394	0.2370	0.623
0.3689	0.575	0.3061	0.687
0.4291	0.595	0.4058	0.725
0.5753	0.565	0.5359	0.695
0.6414	0.515	0.6467	0.608
0.7140	0.448	0.7916	0.418
0.8041	0.340	0.8447	0.338
1,2-Dichloroethane + Propanoic Acid		1,2-Dibromoethane + Propanoic Acid	
0.1399	0.155	0.1134	0.205
0.2716	0.258	0.2487	0.353
0.3426	0.285	0.2950	0.391
0.4844	0.321	0.4615	0.430
0.5910	0.310	0.5650	0.406
0.6911	0.278	0.6817	0.351
0.7212	0.260	0.7570	0.291
0.8395	0.171	0.8465	0.210
1,2-Dichloroethane + Butanoic Acid		1,2-Dibromoethane + Butanoic Acid	
0.1571	0.160	0.1248	0.183
0.2809	0.247	0.2015	0.267
0.3208	0.270	0.2880	0.324
0.3722	0.289	0.3706	0.368
0.5309	0.312	0.5235	0.380
0.6400	0.300	0.6396	0.331
0.7808	0.219	0.7780	0.245
0.8853	0.127	0.8823	0.142

Results

The experimental V^E data for the mixtures of 1,2-dichloroethane and 1,2-dibromoethane with three acids are given in Table II and graphically represented in Figures 1 and 2. The dependence of V^E on composition may be expressed by an empirical equation of the form

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

where a_0, a_1, and a_2 are adjustable parameters and X_A is the mole fraction of 1,2-dichloroethane and 1,2-dibromoethane. The values of parameters obtained by the least-squares method are included in Table III along with the standard deviation $\sigma(V^E)$. The values of $\sigma(V^E)$ were obtained by using the equation

$$\sigma(V^E) = \left[\frac{\sum(V^E_{\text{calcd}} - V^E_{\text{exptl}})^2}{n - P}\right]^{1/2} \quad (2)$$

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Table III. Values of Parameters a_0, a_1, and a_2 in Eq 1 and the Standard Deviation $\sigma(V^E)$

system	a_0	a_1	a_2	$\sigma(V^E)$
1,2-dichloroethane + ethanoic acid	2.368	−0.338	−0.059	0.005
1,2-dichloroethane + propanoic acid	1.290	−0.005	−0.011	0.003
1,2-dichloroethane + butanoic acid	1.276	0.076	−0.092	0.004
1,2-dibromoethane + ethanoic acid	2.839	−0.820	0.600	0.004
1,2-dibromoethane + propanoic acid	1.699	−0.292	0.208	0.004
1,2-dibromoethane + butanoic acid	1.507	−0.205	0.038	0.004

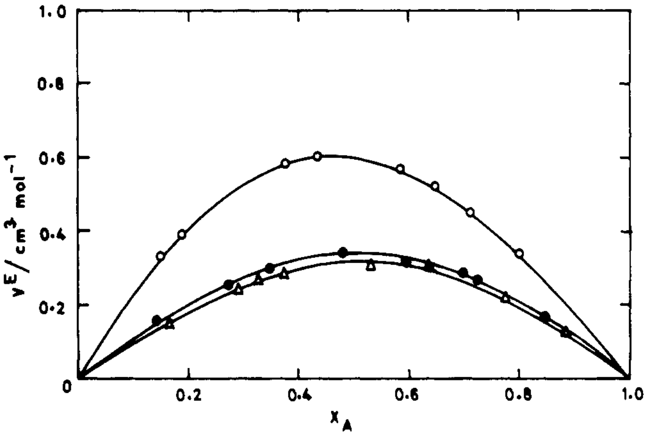

Figure 1. V^E vs. mole fraction (X_A) for the system of 1,2-dichloroethane with (○) ethanoic acid, (●) propanoic acid, and (△) butanoic acid.

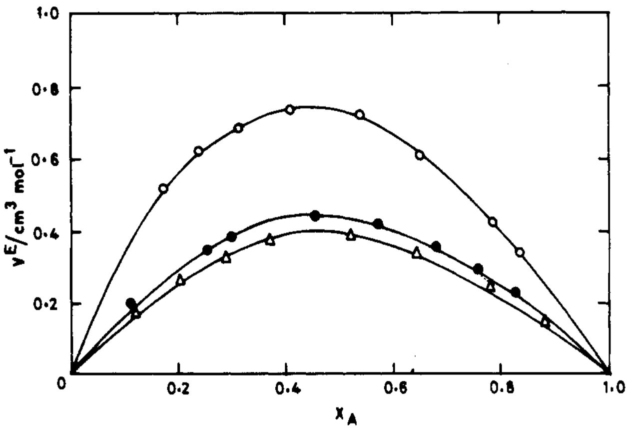

Figure 2. V^E vs. mole fraction (X_A) for the system of 1,2-dibromoethane with (○) ethanoic acid, (●) propanoic acid, and (△) butanoic acid.

where n is the number of experimental data and P is the number of parameters.

Discussion

The data included in Table II and curves represented in Figures 1 and 2 show that V^E for all the systems under investigation are positive over the whole mole fraction range. The following factors influence the excess volume: (a) Dissociation of self-associated carboxylic acids, (b) the decrease in dipolar association of the components, (c) interstitial accommodation of haloalkanes in hydrogen-bonded acid aggregates, and (d) weak hydrogen-bonding interaction between unlike molecules. While the first two factors contribute to increase in excess volumes, the last two factors contribute to decrease in excess volumes. The reported positive excess volumes pointed out that the factors influencing the expansion in volume are dominant over the factors influencing the contraction in volume. The positive excess volumes of 1,2-dichloroethane and 1,2-dibromoethane with three acids fall in the order ethanoic acid > propanoic acid > butanoic acid. This order shows that the increase in chain length contributes to the decrease in excess volume.

Registry No. Ethanoic acid, 64-19-7; propanoic acid, 79-09-4; butanoic acid, 107-92-6; 1,2-dichloroethane, 107-06-2; 1,2-dibromoethane, 106-93-4.

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