Excess Volumes of Binary Mixtures of 1,3-Dichloropropane with Isomeric Butanols at 298.15 and 313.15 K

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Excess molar volumes, V_m^E, for binary mixtures of 1,3-dichloropropane with 1-butanol, 2-butanol, 2-methyl-1-propanol, and 2-methyl-2-propanol have been determined from density measurements at 298.15 and 313.15 K by means of an Anton Paar DMA-58 vibrating tube densimeter. V_m^E is positive over the whole composition range except for mixtures containing 1-butanol and 2-methyl-1-propanol at 298.15 K in which V_m^E shows negative values at low mole fractions of dichloroalkane.

Introduction

Butanols and halogenated derivates have an important application in the chemical industry. Furthermore, from a theoretical point of view these mixtures are useful for studying the interaction between the OH group and the Cl group. Continuing our research into the thermodynamic properties of binary mixtures containing an isomeric butanol (*1–3*) or an α,ω-dichloroalkane (*4*, *5*), we report here the results obtained from density measurements for the excess molar volumes, V_m^E, of 1,3-dichloropropane with the four isomeric butanols at 298.15 and 313.15 K.

Experimental Section

Materials. The liquids used, 1-butanol (better than 99.8 mol %), 2-methyl-1-propanol and 2-methyl-2-propanol (better than 99.5 mol %), and 2-butanol and 1,3-dichloropropane (better than 99 mol %), were obtained from Aldrich. No further purification was attempted because the purity of chemicals had been previously checked by gas chromatography using a semicapillary methyl silicone column (o.d. 530 μm) and a flame-ionization detector. The analysis showed that the major peak area exceeds 99.8%. All isomeric butanols were dried over activated molecular sieves type 0.3 nm from Merck.

Density Measurements. Densities, ρ, of pure components and mixtures were measured from an Anton Paar DMA-58 vibrating tube densimeter. Table I shows the experimental values for the pure components at 298.15 K, compared with the published values (*6*, *7*). Calibration was carried out with deionized doubly-distilled water and dry air. The composition of each mixture was determined directly by weighing.

The uncertainty of the density measurements was $\pm 1 \times 10^{-2}$ kg m^{-3}.

Results and Discussion

The excess molar volumes calculated from density measurements are given in Table II and graphically presented in Figures 1 and 2. The data were fitted to the polynomial expression

$$V_m^E/(10^{-6}\ \mathrm{m^3\ mol^{-1}}) = x_1(1 - x_1)[a_1 + a_2(2x_1 - 1) + ...] \quad (1)$$

where a_1, a_2, etc. are adjustable parameters and x_1 is the mole fraction of 1,3-dichloropropane. The values of the parameters, computed by the least-squares method, are also given in Table II together with the standard deviation, $\sigma(V_m^E)$:

$$\sigma(V_m^E) = [\sum (V_{m,\mathrm{calc}}^E - V_{m,\mathrm{exp}}^E)^2/(n - p)]^{1/2} \quad (2)$$

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

The results show that V_m^E is positive over the whole composition range except for mixtures containing 1-butanol and 2-methyl-1-propanol at 298.15 K in which V_m^E shows

Table I. Densities, ρ, of Pure Components at 298.15 K and Comparison with Literature Data

component	ρ/(kg m^{-3}) this paper	ρ/(kg m^{-3}) lit.
1,3-dichloropropane	1180.25	1180.0 (*6*)
1-butanol	805.85	806.0 (*7*)
2-butanol	802.40	802.6 (*7*)
2-methyl-1-propanol	797.98	797.8 (*7*)
2-methyl-2-propanol	764.75[a]	764.9[a] (*7*)

[a] Note: Density at 313.15 K.

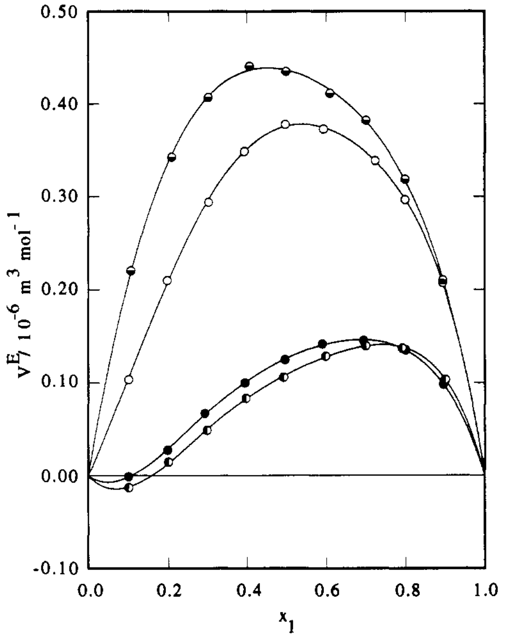

Figure 1. Excess molar volumes, V_m^E, of 1,3-dichloropropane (1) + isomeric butanols (2) at 298.15 K as a function of mole fraction x_1: (●) 1-butanol; (○) 2-butanol; (◐) 2-methyl-1-propanol; (⊖) 2-methyl-2-propanol.

Table II. Excess Molar Volumes, V_m^E, Coefficients, a_i, of Equation 1, and Standard Deviations, $\sigma(V_m^E)$, for 1,3-Dichloropropane (1) + Isomeric Butanols (2) as a Function of Mole Fraction x_1 at Temperature T

x_1	V_m^E/ $(10^{-6}\ m^3\ mol^{-1})$	x_1	V_m^E/ $(10^{-6}\ m^3\ mol^{-1})$	x_1	V_m^E/ $(10^{-6}\ m^3\ mol^{-1})$
1,3-Dichloropropane (1) + 1-Butanol (2) at 298.15 K					
0.1002	−0.0011	0.3943	0.1001	0.6937	0.1455
0.1974	0.0276	0.4960	0.1250	0.7997	0.1355
0.2931	0.0667	0.5898	0.1419	0.8949	0.0980
$a_1 = 0.5071, a_2 = 0.3956, a_3 = 0.0201, a_4 = 0.4287$					
$\sigma(V_m^E)/(10^{-6}\ m^3\ mol^{-1}) = 0.0011$					
1,3-Dichloropropane (1) + 2-Butanol (2) at 298.15 K					
0.0994	0.1036	0.3934	0.3490	0.7238	0.3389
0.1964	0.2102	0.4968	0.3779	0.7987	0.2968
0.3019	0.2941	0.5927	0.3728	0.8930	0.2074
$a_1 = 1.4980, a_2 = 0.2007, a_3 = 0.2584, a_4 = 0.6814$					
$\sigma(V_m^E)/(10^{-6}\ m^3\ mol^{-1}) = 0.0031$					
1,3-Dichloropropane (1) + 2-Methyl-1-propanol (2) at 298.15 K					
0.1010	−0.0130	0.3966	0.0832	0.6995	0.1398
0.1995	0.0148	0.4917	0.1063	0.7915	0.1374
0.2989	0.0485	0.5981	0.1289	0.9003	0.1036
$a_1 = 0.4363, a_2 = 0.4427, a_3 = 0.1013, a_4 = 0.5618$					
$\sigma(V_m^E)/(10^{-6}\ m^3\ mol^{-1}) = 0.0013$					
1,3-Dichloropropane (1) + 2-Methyl-2-propanol (2) at 298.15 K					
0.1054	0.2206	0.4072	0.4410	0.7007	0.3823
0.2082	0.3428	0.4994	0.4353	0.7995	0.3190
0.3018	0.4075	0.6094	0.4117	0.8934	0.2103
$a_1 = 1.7441, a_2 = -0.1933, a_3 = 0.8426, a_4 = 0.2239$					
$\sigma(V_m^E)/(10^{-6}\ m^3\ mol^{-1}) = 0.0035$					
1,3-Dichloropropane (1) + 1-Butanol (2) at 313.15 K					
0.0936	0.0746	0.4016	0.2343	0.7035	0.2578
0.2060	0.1399	0.4900	0.2593	0.8154	0.2085
0.3127	0.1929	0.6095	0.2740	0.8998	0.1320
$a_1 = 1.0442, a_2 = 0.4465, a_3 = 0.1811, a_4 = -0.1002$					
$\sigma(V_m^E)/(10^{-6}\ m^3\ mol^{-1}) = 0.0024$					
1,3-Dichloropropane (1) + 2-Butanol (2) at 313.15 K					
0.0954	0.1697	0.3943	0.4800	0.6973	0.4660
0.1974	0.3181	0.4993	0.5120	0.7997	0.3823
0.2947	0.4146	0.5990	0.5076	0.9013	0.2418
$a_1 = 2.0421, a_2 = 0.2078, a_3 = 0.4404, a_4 = 0.3688$					
$\sigma(V_m^E)/(10^{-6}\ m^3\ mol^{-1}) = 0.0028$					
1,3-Dichloropropane (1) + 2-Methyl-1-propanol (2) at 313.15 K					
0.0857	0.0357	0.4004	0.2023	0.7062	0.2309
0.2161	0.1121	0.4978	0.2283	0.8097	0.2042
0.3079	0.1589	0.6158	0.2405	0.8997	0.1390
$a_1 = 0.9105, a_2 = 0.3883, a_3 = 0.1524, a_4 = 0.4371$					
$\sigma(V_m^E)/(10^{-6}\ m^3\ mol^{-1}) = 0.0023$					
1,3-Dichloropropane (1) + 2-Methyl-2-propanol (2) at 313.15 K					
0.1128	0.2664	0.4144	0.4962	0.7439	0.4223
0.2327	0.4114	0.5069	0.5099	0.8208	0.3388
0.3140	0.4685	0.6325	0.4802	0.9098	0.2018
$a_1 = 2.0281, a_2 = -0.0099, a_3 = 0.8545, a_4 = -0.2368$					
$\sigma(V_m^E)/(10^{-6}\ m^3\ mol^{-1}) = 0.0032$					

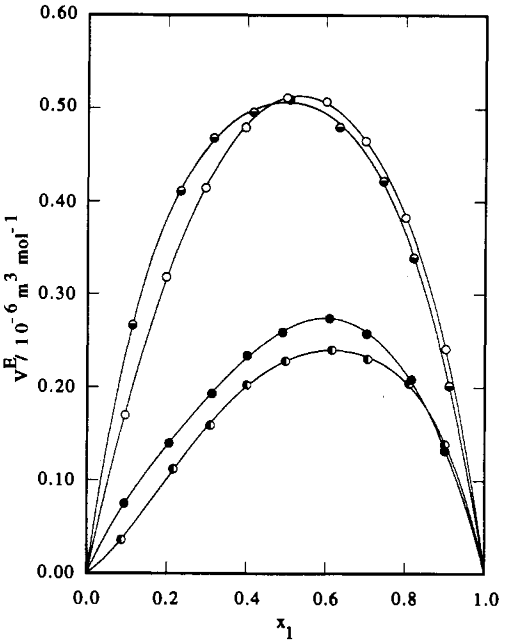

Figure 2. Excess molar volumes, V_m^E, of 1,3-dichloropropane (1) + isomeric butanols (2) at 313.15 K as a function of mole fraction x_1: (●) 1-butanol; (○) 2-butanol; (◐) 2-methyl-1-propanol; (⊖) 2-methyl-2-propanol.

negative values at low mole fractions of dichloroalkane; the results also indicate that V_m^E is related to the structure of the butanols. It can be seen that isomeric butanols of similar structure, 1-butanol and 2-methyl-1-propanol on the one hand and 2-butanol and 2-methyl-2-propanol on the other, lead to similar excess molar volumes. The temperature coefficient of V_m^E is positive, but the increase in V_m^E for the mixture containing 2-methyl-2-propanol is lower for the others. At 298.15 K V_m^E increases in the order 2-methyl-1-propanol < 1-butanol < 2-butanol < 2-methyl-2-propanol while at 313.15 K this arrangement changes little because it can be observed that the mixtures containing 2-butanol and 2-methyl-2-propanol present similar maximum values of V_m^E. The presence of atoms of chlorine in the aliphatic chain leads to a decreases in V_m^E values compared with the V_m^E values observed for mixtures of an isomeric butanol with an aliphatic chain (*1*). The excess molar volumes observed for the mixtures studied are due to three factors, a large positive contribution due to the breaking of hydrogen bonds in butanols by the addition of 1,3-dichloropropane, another positive contribution coming from the breaking of the dipole–dipole interaction between the dichloroalkane molecules, and a negative contribution due to the specific interaction between the hydroxyl hydrogen of butanol and the chlorine in the dichloroalkane molecules.

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