# Excess Volumes, Speeds of Sound, and Isentropic Compressibilities of 2-Propyn-1-ol + 1,2-Dichloroethane, +1,1,1-Trichloroethane, +1,1,2,2-Tetrachloroethane, and +Trichloroethylene at 303.15 K

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Excess volumes and speeds of sound for the binary systems 2-propyn-1-ol + 1,2-dichloroethane, +1,1,1-trichloroethane, +1,1,2,2-tetrachloroethane, and +trichloroethylene have been measured at 303.15 K. The data were used to calculate isentropic compressibilities. The excess volumes for all the mixtures were found to be positive. The positive excess volumes and positive deviation in isentropic compressibilities have been attributed to the dissociation of self-associated alcohols with chloroalkanes or chloroalkene.

## Introduction

Excess volumes, speeds of sound, and isentropic compressibilities of methanol with chloroalkanes at 303.15 K have been reported by Vijayakumar et al. (1994). The excess volumes were measured in order to determine the effect of successive chlorine atom substitution in alkanes and alkenes, and also $\pi$-bond interaction. Speeds of sound are of increasing interest in physical chemistry because they have often been used to understand liquid structure and interaction between molecules (Nath and Dubey, 1980; Reddy et al., 1962; Vitali et al., 1980, 1981). While indicating specific interaction between molecules, they also enable calculation of the degree of intermolecular interaction, molecular free-path, and isentropic compressibility. We report here data on volume and speed of sound for 2-propyn-1-ol + 1,2-dichloroethane, +1,1,1-trichloroethane, 1,1,2,2-tetrachloroethane, and +trichloroethylene at 303.15

## Experimental Section

Molar excess volumes, $V_m^E$, were measured using a batch dilatometer, similar to the one described by Rao and Naidu (1974). The excess volumes were accurate to ±0.003 $mol^{-1}$. The mixing cell contained two bulbs of different volumes, contacted through a U-tube, having mercury to separate the two components. One end of the first bulb was fitted with a capillary outlet, and the opposite end of the second bulb was closed with a ground glass stopper. Four dilatometers of this type were used to cover the entire composition range. The composition of each mixture was determined directly by mass with corrections for buoyancy. The speed of sound was measured with a single crystal interferometer at a frequency of 2 MHz and accurate to ±0.15%. Isentropic compressibility was calculated from density ($\rho$) and speed of sound ($u$) using the relation

$$K_s = u^{-2}\rho^{-1} \quad (1)$$

The density was calculated from the molar excess volume $V_m^E$ using the relation

$$\rho = (x_1M_1 + x_2M_2)/(V_m + V_m^E) \quad (2)$$

where $x_i$ is the mole fraction, $M_i$ is the molecular weight of component $i$, and $V_m$ is the additive molar volume, given by

$$V_m = x_1V_1 + x_2V_2$$

All the measurements were carried out at 303.15 K by employing a thermostat that could be maintained to ±0.05 K.

All the materials were purified by the methods described by Riddick et al. (1986). 2-Propyn-1-ol (Fluka, >99 mol % pure) was fractionally distilled twice, and the middle fraction was collected. 1,2-Dichloroethane, 1,1,1-trichloroethane, 1,1,2,2-tetrachloroethane, and trichloroethylene were purified as described earlier (Vijayakumar et al., 1995).

The purities of the samples were checked by comparing the measured densities, using a bicapillary pycnometer accurate to 2 parts in $10^5$, and refractive indices, using an Abbe-type refractometer accurate to 2 parts in $10^5$, of the purified samples with those reported in the literature. The measured values were in good agreement with the literature data (Riddick et al., 1986), as seen in Table 1.

**Table 1. Experimental Densities $\rho$ and Refractive Indices $n_D$ at 298.15 K Compared with Literature Values**

| | $\rho$/kg·m$^{-3}$ | | $n_D$ | |
|---|---|---|---|---|
| component | present work | lit.[a] | present work | lit.[a] |
| 2-propyn-1-ol | 945.20 | 945.00 | 1.430 10 | 1.430 00 |
| 1,2-dichloroethane | 1246.82 | 1246.37 | 1.442 16 | 1.442 10 |
| 1,1,1-trichloroethane | 1329.50 | 1329.90 | 1.435 88 | 1.435 90 |
| 1,1,2,2-tetrachloroethane | 1586.66 | 1586.66 | 1.491 87 | 1.491 40 |
| trichloroethylene | 1455.37 | 1455.41[b] | 1.474 48 | 1.474 57[b] |

[a] Riddick et al. (1986). [b] Driesbach (1955).

## Results and Discussion

The molar excess volumes for the 2-propyn-1-ol + 1,2-dichloroethane, +1,1,1-trichloroethane, +1,1,2,2-tetrachloroethane, and +trichloroethylene at 303.15 K are given in Table 2 and shown in Figure 1 and have been fitted by the method of least squares to the following empirical equation

$$V_m^E/cm^3\cdot mol^{-1} = x_1x_2[A_0 + A_1(x_1 - x_2) + A_2(x_1 - x_2)^2] \quad (3)$$

where $x_1$ refers to the mole fraction of 2-propyn-1-ol and $x_2$ refers to the mole fraction of chloroalkane or chloroalk-

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**Table 2. Excess Volume $V_m^E$, Speed of Sound $u$, Isentropic Compressibility $K_s$, and Excess Isentropic Compressibility $K_s^E$, of the Binary Systems at 303.15 K**

| $x$ 2-propyn-1-ol + $(1-x)$ 1,2-dichloroethane | | $\phi$ 2-propyn-1-ol + $(1-\phi)$ 1,2-dichloroethane | | | |
|---|---|---|---|---|---|
| | | | | TPa$^{-1}$ | |
| $x$ | $V_m^E$/cm$^3$·mol$^{-1}$ | $\phi$ | $u$/m·s$^{-1}$ | $K_s$ | $K_s^E$ |
| 0.0361 | 0.072 | 0.0271 | 1175.6 | 589 | 3 |
| 0.1198 | 0.206 | 0.0920 | 1177.5 | 597 | 14 |
| 0.2130 | 0.305 | 0.1677 | 1184.0 | 602 | 22 |
| 0.3489 | 0.372 | 0.2852 | 1198.0 | 607 | 30 |
| 0.4671 | 0.371 | 0.3949 | 1215.3 | 607 | 34 |
| 0.5777 | 0.334 | 0.5046 | 1238.2 | 602 | 33 |
| 0.6109 | 0.311 | 0.5474 | 1250.0 | 597 | 30 |
| 0.7215 | 0.246 | 0.6586 | 1280.0 | 587 | 24 |
| 0.8359 | 0.151 | 0.7913 | 1321.0 | 572 | 14 |
| | | 0.9635 | 1376.8 | 554 | 2 |

| $x$ 2-propyn-1-ol + $(1-x)$ 1,1,1-trichloroethane | | $\phi$ 2-propyn-1-ol + $(1-\phi)$ 1,1,1-trichloroethane | | | |
|---|---|---|---|---|---|
| | | | | TPa$^{-1}$ | |
| $x$ | $V_m^E$/cm$^3$·mol$^{-1}$ | $\phi$ | $u$/m·s$^{-1}$ | $K_s$ | $K_s^E$ |
| 0.0572 | 0.069 | 0.0345 | 952.0 | 844 | 1 |
| 0.1262 | 0.147 | 0.0784 | 964.6 | 833 | 3 |
| 0.2702 | 0.273 | 0.1791 | 993.4 | 811 | 12 |
| 0.3528 | 0.319 | 0.2431 | 1015.2 | 792 | 7 |
| 0.4277 | 0.342 | 0.3057 | 1036.2 | 776 | 15 |
| 0.5892 | 0.329 | 0.4579 | 1096.6 | 728 | 13 |
| 0.6482 | 0.306 | 0.5205 | 1123.1 | 708 | 12 |
| 0.7243 | 0.261 | 0.6075 | 1166.6 | 676 | 6 |
| 0.8418 | 0.165 | 0.7582 | 1250.5 | 621 | −3 |
| 0.9336 | 0.073 | 0.8923 | 1330.5 | 575 | −8 |

| $x$ 2-propyn-1-ol + $x$) 1,1,2,2-tetrachloroethane | | $\phi$ 2-propyn-1-ol + $(1-\phi)$ 1,1,2,2-tetrachloroethane | | | |
|---|---|---|---|---|---|
| | | | | TPa$^{-1}$ | |
| $x$ | $V_m^E$/cm$^3$·mol$^{-1}$ | $\phi$ | $u$/m·s$^{-1}$ | $K_s$ | $K_s^E$ |
| 0.0582 | 0.068 | 0.0334 | 1134.5 | 499 | 3 |
| 0.1497 | 0.149 | 0.0897 | 1137.2 | 509 | 10 |
| 0.2739 | 0.209 | 0.1743 | 1149.6 | 517 | 13 |
| 0.3287 | 0.219 | 0.2151 | 1154.0 | 522 | 16 |
| 0.4196 | 0.217 | 0.2880 | 1165.9 | 528 | 18 |
| 0.5332 | 0.188 | 0.3899 | 1186.6 | 538 | 19 |
| 0.6736 | 0.125 | 0.5359 | 1222.4 | 542 | 17 |
| 0.7325 | 0.095 | 0.6051 | 1243.6 | 542 | 14 |
| 0.8124 | 0.057 | 0.7079 | 1277.3 | 544 | 10 |
| 0.9052 | 0.021 | 0.8423 | 1324.4 | 547 | 6 |

| $x$ 2-propyn-1-ol + − $x$) trichloroethylene | | $\phi$ 2-propyn-1-ol + $(1-\phi)$ trichloroethylene | | | |
|---|---|---|---|---|---|
| | | | | TPa$^{-1}$ | |
| $x$ | $V_m^E$/cm$^3$·mol$^{-1}$ | $\phi$ | $u$/m·s$^{-1}$ | $K_s$ | $K_s^E$ |
| 0.0645 | 0.085 | 0.0433 | 1018.8 | 675 | 8 |
| 0.1144 | 0.145 | 0.0783 | 1025.2 | 675 | 13 |
| 0.2820 | 0.293 | 0.2052 | 1045.6 | 681 | 34 |
| 0.3324 | 0.318 | 0.2466 | 1054.8 | 680 | 39 |
| 0.4050 | 0.341 | 0.3091 | 1070.0 | 678 | 44 |
| 0.5728 | 0.318 | 0.4684 | 1120.4 | 659 | 45 |
| 0.6693 | 0.266 | 0.5708 | 1160.8 | 642 | 39 |
| 0.7774 | 0.182 | 0.6965 | 1216.4 | 618 | 31 |
| 0.8199 | 0.148 | 0.7495 | 1245.0 | 604 | 24 |
| 0.9343 | 0.049 | 0.9033 | 1330.0 | 571 | 9 |

ene. $A_0$, $A_1$, and $A_2$, the parameters of the fitting equation, are given along with the standard deviation, $\sigma(V_m^E)$, in Table 3.

The excess compressibilities based on volume fractions were calculated using the relation

$$K_s^E = K_s - \phi_1 K_{s,1} - \phi_2 K_{s,2} \quad (4)$$

where $K_{s,1}$ and $K_{s,2}$ refer to the isentropic compressibilities of component 1 and component 2, respectively, and $\phi_i$ refers to the volume fraction of component $i$, calculated using the volume of the pure components.

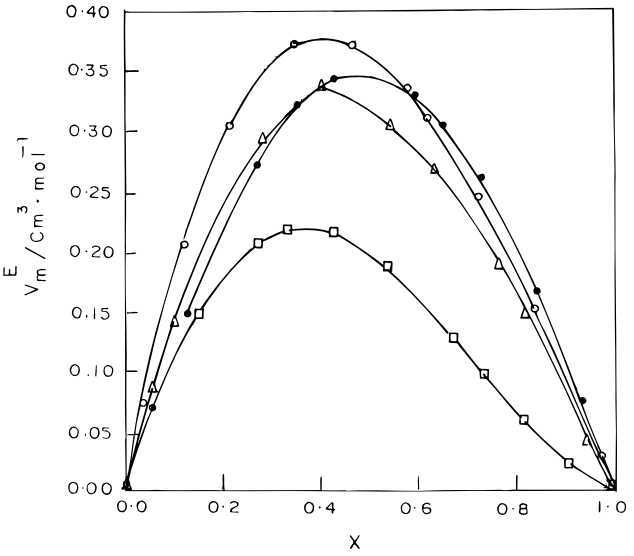


**Figure 1.** $V_m^E$ versus mole fraction of 2-propyn-1-ol ($x$) at 303.15 K: (○) 2-propyn-1-ol ($x$) + 1,2-dichloroethane ($1-x$); (●) 2-propyn-1-ol ($x$) + 1,1,1-trichloroethane ($1-x$); (□) 2-propyn-1-ol ($x$) + 1,1,2,2-tetrachloroethane ($1-x$); (△) 2-propyn-1-ol ($x$) + trichloroethylene ($1-x$).

**Table 3. Values of Parameters $A_0$, $A_1$, and $A_2$ from Eq 3 and the Standard Deviation $\sigma(V_m^E)$ from Eq 6**

| system | $A_0$ | $A_1$ | $A_2$ | $\sigma(V_m^E)$/ cm$^3$·mol$^{-1}$ |
|---|---|---|---|---|
| $x$ 2-propyn-1-ol + $(1-x)$ 1,2-dichloroethane | 1.4561 | −0.5968 | 0.0674 | 0.002 |
| $x$ 2-propyn-1-ol + $(1-x)$ 1,1,1-trichloroethane | 1.3867 | −0.0732 | −0.2048 | 0.001 |
| $x$ 2-propyn-1-ol + $(1-x)$ 1,1,2,2-tetrachloroethane | 0.7952 | −0.6039 | −0.1048 | 0.001 |
| $x$ 2-propyn-1-ol + $(1-x)$ trichloroethylene | 1.3574 | −0.3515 | −0.3349 | 0.001 |

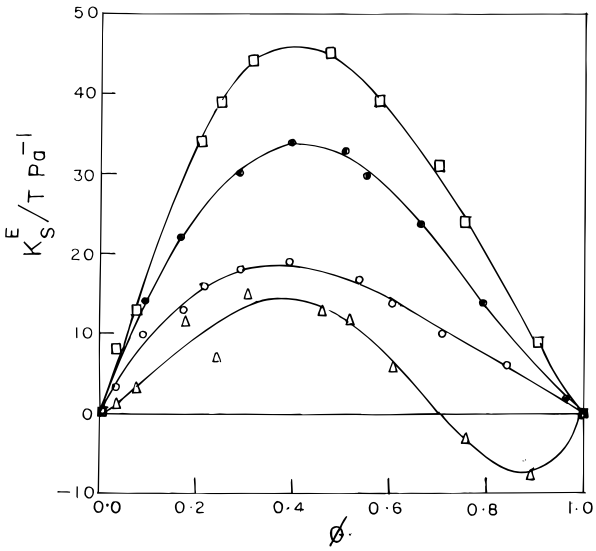


**Figure 2.** $K_s^E$ versus volume fraction of 2-propyn-1-ol ($\phi$) at 303.15 K: (●) 2-propyn-1-ol ($\phi$) + 1,2-dichloroethane ($1-\phi$); (△) 2-propyn-1-ol ($\phi$) + 1,1,1-trichloroethane ($1-\phi$); (○) 2-propyn-1-ol ($\phi$) + 1,1,2,2-tetrachloroethane ($1-\phi$); (□) 2-propyn-1-ol ($\phi$) + trichloroethylene ($1-\phi$).

The excess isentropic compressibilities, $K_s^E$, are also given in Table 2 and shown in Figure 2 and have been fitted by the method of least squares to the following equation

$$K_s^E/\text{TPa}^{-1} = \phi_1\phi_2[B_0 + B_1(\phi_1 - \phi_2) + B_2(\phi_1 - \phi_2)^2] \quad (5)$$

$\phi_1$ refers to the volume fraction of 2-propyn-1-ol, and $\phi_2$

**Table 4. Values of Parameters $B_0$, $B_1$, and $B_2$ from Eq 5 and the Standard Deviation $\sigma(K_s^E)$ from Eq 6**

| system | $B_0$ | $B_1$ | $B_2$ | $\sigma(K_s^E)$/TPa$^{-1}$ |
|---|---|---|---|---|
| $x$ 2-propyn-1-ol + $(1 - x)$ 1,2-dichloroethane | 132.50 | −47.24 | −45.40 | 1.3 |
| $x$ 2-propyn-1-ol + $(1 - x)$ 1,1,1-trichloroethane | 53.32 | −83.61 | −116.17 | 1.2 |
| $x$ 2-propyn-1-ol + $(1 - x)$ 1,1,2,2-tetrachloroethane | 70.24 | −45.20 | −12.31 | 0.7 |
| $x$ 2-propyn-1-ol + $(1 - x)$ trichloroethylene | 181.28 | −69.85 | −62.13 | 1.7 |

refers to the volume fraction of chloroalkane or chloroalkene. $B_0$, $B_1$, and $B_2$, the parameters of the fitting equation, are given along with the standard deviation, $\sigma(K_s^E)$, in Table 4. The standard deviations in the excess volume and excess isentropic compressibility have been calculated using the relation

$$\sigma(X^E) = [\sum (X^E_{obs} - X^E_{cal})^2/(n - p)]^{1/2} \quad (6)$$

where $X^E$ refers to the excess quantity and $n$ and $p$ refer to the number of data points and number of parameters, respectively.

The excess volumes for 2-propyn-1-ol + 1,2-dichloroethane, +1,1,1-trichloroethane, +1,1,2,2-tetrachloroethane, +trichloroethylene are positive over the whole composition at 303.15 K and are in the following order: 1,2-dichloroethane > 1,1,1-trichloroethane > trichloroethylene 1,1,2,2-tetrachloroethane.

The expansion in volume can be explained as due to the dissociation of self-associated alcohols, i.e., depolymerization of alcohol aggregates.

The excess isentropic compressibilities for 2-propyn-1-ol + 1,2-dichloroethane, +1,1,1-trichloroethane, +1,1,2,2-tetrachloroethane, + trichloroethylene are in the following order at 303.15 K: trichloroethylene > 1,2-dichloroethane > 1,1,2,2-tetrachloroethane > 1,1,1-trichloroethane.

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