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**Note**

# COHESION ENERGIES AND SOLUBILITY PARAMETERS FOR TRIETHYLBORON AND DIETHYLZINC

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Because of the great utility of cohesion energies and solubility parameters in predicting miscibility, solubility, and molecular association, such data are widely cited [1–5]. However, there is a general lack of data of this type for inorganic and organometallic compounds other than for a few volatile halides [3–5]. Accordingly, we have begun a study of solubility parameters for inorganic and organometallic compounds where suitable data (vapor pressures and densities) are available [6,7]. This report presents cohesion energies, solubility parameters, and related molecular parameters for triethylboron and diethylzinc.

## METHODS

In order to calculate the cohesion energy in the usual way [7], it is necessary to have an analytical means of representing the vapor pressure of a liquid as a function of temperature [8]. This is most conveniently handled using the Antoine equation

$$\log P = A - \frac{B}{C + t} \tag{1}$$

where $A$, $B$ and $C$ are constants. However, values for $A$, $B$ and $C$ are not readily available for $(C_2H_5)_3B$ and $(C_2H_5)_2Zn$. Vapor pressures [9] for these compounds were used with a weighted nonlinear least-squares procedure to determine constants for the Antoine equations for the compounds [10]. Solubility parameters, $\delta$, were calculated from

$$\delta = \left( E_c / \overline{V} \right)^{1/2} \tag{2}$$

where $E_c$ is given by

$$E_c = \frac{\mathrm{d} \log P}{\mathrm{d}(1/T)} - RT \tag{3}$$

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When the vapor pressure is given by the Antoine equation, eqn. (3) becomes

$$E_c = RT\left(\frac{2.303\,BT}{(C+t)^2} - 1\right) \tag{4}$$

Related molecular parameters were calculated from the cohesion energies as previously described [7]

## RESULTS AND DISCUSSION

Table 1 shows the Antoine constants obtained for vapor pressures of $(C_2H_5)_3B$ and $(C_2H_5)_2Zn$. Using the Antoine equations, the calculated heats of vaporization are 36.6 and 37.9 kJ mole$^{-1}$, respectively, for these compounds at calculated boiling points of 95.0 and 124.0°C. Cohesion energies appear to be in the range expected for organometallic compounds of this type. The solubility parameters of $(C_2H_5)_3B$ and $(C_2H_5)_2Zn$ are found to be 7.52 (at 20°C) and 8.89 cal$^{1/2}$ cm$^{-3/2}$ (at 25°C) respectively, and these values are typical of "nonassociated", nonpolar liquids [5]. Since the value of $\delta$ changes only slowly with temperature, the values would be approximately corrected at other temperatures close to these. The effective radii of 3.83 Å for $(C_2H_5)_3B$ and 3.46 Å for the linear $(C_2H_5)_2Zn$ are reasonable [7]. The van der Waals **a** parameters are characteristic of nonassociated, monomeric liquids.

It is interesting to compare the heats of vaporization of the compounds, which are calculated from d(log $P$)/d(1/$T$), and the entropies of vaporization obtained from $\Delta S_v = \Delta H_v/T$ where $T$ is the boiling point (K). It has

TABLE 1

Antoine constants, cohesion energies, and derived data for triethylboron and diethylzinc

| Parameter | $(C_2H_5)_3B$ | $(C_2H_5)_2Zn$ |
|---|---|---|
| Antoine $A$ | 7 413 | 7 468 |
| Antoine $B$ | 1544 2 | 1755 6 |
| Antoine $C$ | 245 74 | 258 74 |
| $T$(°C) | 20 | 25 |
| Density (g ml$^{-1}$) | 0 691 | 1 18 |
| $\bar{V}$(cm$^3$ mole$^{-1}$) | 141 8 | 104 7 |
| $E_c$(cal mole$^{-1}$) | 8016 | 8277 |
| $E_c$(l atm mole$^{-1}$) | 311 0 | 341 7 |
| $\delta$(cal$^{1/2}$ cm$^{-3/2}$) | 7 52 | 8 89 |
| van der Waals **a** (l$^2$ atm mole$^{-2}$) | 46 94 | 35 77 |
| effective $r$ (Å) | 3.83 | 3 46 |
| $\Delta H_v$(calc) (cal mole$^{-1}$) | 8748 | 9066 |
| b p (calc) (°C) | 95 | 124 |
| $\Delta S_v$(cal mole$^{-1}$ deg$^{-1}$) | 23 76 | 22 83 |

previously been discussed that $(CH_3)_3B$ does not dimerize to form $(CH_3)_6B_2$ [11–13]. The results of this work support a similar conclusion for $(C_2H_5)_3B$. For $(C_2H_5)_3B$, the entropy of vaporization is calculated to be 23.76 cal $mole^{-1}$ $deg^{-1}$ which is characteristic of nonassociated liquids. In the case of $(CH_3)_2AlCl$ and $CH_3AlCl_2$, the liquid and vapor states both contain dimers and the $\Delta S_v$ values are 22.94 and 23.26 cal $mole^{-1}$ $deg^{-1}$, respectively [14] These values are sufficiently close to the value of 21 cal $mole^{-1}$ $deg^{-1}$ predicted by Trouton's rule that no significant change in molecular aggregation occurs on vaporization [15]. A larger value of Trouton's constant than 21 cal $mole^{-1}$ $deg^{-1}$ indicates that molecular aggregates in the vapor are smaller that in the liquid. However, the value of 14.9 cal $mole^{-1}$ $deg^{-1}$ for acetic acid is indicative of the formation of dimers in the vapor. Consequently, the $\Delta S_v$ of 23.76 cal $mole^{-1}$ $deg^{-1}$ for $(C_2H_5)_3B$ is indicative of the same molecular units in both the liquid and vapor phase. Thus, $(C_2H_5)_3B$ appears to be similar to $(CH_3)_3B$ in behavior. However, $(C_2H_5)_3Al$ has an entropy of vaporization of 42.2 cal $mole^{-1}$ $deg^{-1}$ indicating dimers in the liquid phase that rupture to produce monomers in the vapor phase [16]. It may be that dimerization occurs in $(C_2H_5)_3Al$ but not in $(C_2H_5)_3B$ because of the larger size of aluminum compared to boron [11,13]. The dimers of $(C_2H_5)_3Al$ are not sufficiently stable, however, to exist in the vapor phase, at least at temperatures as high as the boiling point of 187°C. From this work, diethylzinc appears, as expected, to be also monomeric in the vapor phase.

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