*Thermochimica Acta*, 69 (1983) 361–366
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

# COHESION ENERGIES AND SOLUBILITY PARAMETERS FOR TETRA-*n*-ALKYLGERMANES

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(Received 18 April 1983)

## ABSTRACT

Previously published vapor pressure and density data for tetra-*n*-alkylgermanes ($C_1$ to $C_5$) have been used to calculate cohesion energies and solubility parameters in the range 273–400 K. Antoine constants are also reported for these compounds. The van der Waals constants ($a$) and the effective molecular radii have been determined for these molecules. These parameters show normal ranges and relationships for liquids interacting only by London dispersion forces.

## INTRODUCTION

The cohesion energy of a liquid, $E_c$, is its heat of vaporization at constant volume and is related to the usual heat of vaporization, $\Delta H_v$, by

$$E_c = \Delta H_v - RT \tag{1}$$

The term $RT$ represents the work done during the vaporization. A closely related property is the specific cohesion or cohesion density, $E_c/\overline{V}$, where $\overline{V}$ is the molar volume. From basic thermodynamics, we obtain

$$\left(\frac{\partial E_c}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P \tag{2}$$

where $P$ is the external pressure [1,2]. It is also apparent that the internal pressure, $P_i$, is given by

$$P_i = T\left(\frac{\partial P}{\partial T}\right)_V \tag{3}$$

and that

$$\left(\frac{\partial P}{\partial T}\right)_V = -\frac{(\partial V/\partial T)_P}{(\partial V/\partial P)_T} \tag{4}$$

so that

$$P_i = T\left(\frac{\alpha}{\beta}\right) \tag{5}$$

where $\alpha$ is the coefficient of thermal expansion and $\beta$ is the compressibility. Thus

$$\left(\frac{\partial E}{\partial V}\right)_T = P_i - P \simeq P_i \qquad (6)$$

since usually $P_i \gg P$ [1]. For non-associated liquids, the internal pressure is equal to the cohesion density. One of the most useful ways to use the cohesion energy of a liquid is by means of the solubility parameter, $\delta$, which is

$$\delta = \left(\frac{E}{\bar{V}}\right)^{1/2} \qquad (7)$$

The solubility parameters are of great use in predicting liquid state and solution properties [3–7]. While numerous attempts have been made to correlate cohesion energies and solubility parameters with other properties, such studies have not included organometallic compounds. Furthermore, the usual tabulations of $\delta$ values do not include values for such compounds [7]. Consequently, we have begun a study of cohesion energies and related properties for organometallic compounds and we report here the results of studies on the tetra-*n*-alkylgermanes.

## METHOD

The cohesion energy is most conveniently calculated by means of the equation [5]

$$E_c = \frac{\mathrm{d} \log P}{\mathrm{d}(1/T)} - RT \qquad (8)$$

The vapor pressure is represented accurately as a function of temperature by the Antoine equation

$$\log P = A - \frac{B}{C + t} \qquad (9)$$

where $A$, $B$ and $C$ are constants [8,9]. Therefore, the cohesion energy is given by

$$E_c = RT\left(\frac{2.303BT}{(C+t)^2} - 1\right) \qquad (10)$$

where $B$ and $C$ are constants from the Antoine equation. For the tetra-*n*-alkylgermanes, the Antoine constants have not been reported. Therefore, the vapor pressure data reported by Mogul et al. [10] were used to compute the values of $A$, $B$ and $C$ using a non-linear least-squares method [11]. In order to determine the molar volumes, the density is needed as a function of temperature. Mogul et al. have reported densities of the tetra-*n*-alkylgermanes [10], and these values were fitted to the equation

$$\rho = a + bT + cT^2 \qquad (11)$$

where $a$, $b$ and $c$ are constants using a least-squares technique. After obtaining the constants for use in eqns. (10) and (11), the cohesion energies, molar volumes and solubility parameters were computed for temperatures in the range 273.15–400 K.

## RESULTS AND DISCUSSION

Fitting the vapor pressure data of Mogul et al. to the Antoine equation gave the values for the constants $A$, $B$ and $C$ shown in Table 1. By selectively removing some data points, the least-squares analysis showed that in some cases individual values contain sizeable errors.

In fitting the density data to eqn. (11), it was found that the constants obtained for $Ge(C_3H_7)_4$ were virtually identical to those reported [10]. The values of the constants for $Ge(C_2H_5)_4$, $Ge(C_4H_9)_4$ and $Ge(C_5H_{11})_4$ were in reasonable agreement with the reported values, but the constants obtained for $Ge(CH_3)_4$ are quite different. The previously reported values are: $a = 1.5633$, $b = -2.6019 \times 10^{-3}$ and $c = 2.0560 \times 10^{-6}$ [10]. Table 1 shows the values for the constants obtained in this work. For $Ge(CH_3)_4$ the values are: $a = 1.63582$, $b = -3.15691 \times 10^{-3}$ and $c = 3.0201 \times 10^{-6}$. Densities calculated using either the constants obtained in this work or those previously reported were acceptably close to the experimental values except for the case of $Ge(CH_3)_4$. For that compound, the constants obtained in this work give calculated densities that agree exactly with experimental values at each temperature reported [10]. The difference between the values of the constants may reflect either a different mathematical algorithm for computation or the fact that reported values were based on additional density data not published [10].

Having obtained the Antoine constants and the density functions to calculate molar volumes, the cohesion energies and solubility parameters

TABLE 1

Constants obtained for the temperature dependence of vapor pressure and density

| Compound | Vapor pressure | | | Density | | |
|---|---|---|---|---|---|---|
| | $A$ | $B$ | $C$ | $a$ | $-b \times 10^3$ | $c \times 10^7$ |
| $Ge(CH_3)_4$ | 4.8234 | 315.13 | 113.750 | 1.63582 | 3.15691 | 30.201 |
| $Ge(C_2H_5)_4$ | 5.7259 | 843.16 | 127.773 | 1.36338 | 1.53028 | 9.311 |
| $Ge(C_3H_7)_4$ | 6.2421 | 1219.02 | 130.352 | 1.26611 | 1.27273 | 7.102 |
| $Ge(C_4H_9)_4$ | 6.4481 | 1386.86 | 107.031 | 1.23295 | 1.23272 | 7.033 |
| $Ge(C_5H_{11})_4$ | 6.6413 | 1581.94 | 97.070 | 1.21739 | 1.17407 | 6.497 |

TABLE 2

Cohesion energies and solubility parameters for tetra-*n*-alkylgermanes

| $T$ (K) | $Ge(CH_3)_4$ | | $Ge(C_2H_5)_4$ | | $Ge(C_3H_7)_4$ | | $Ge(C_4H_9)_4$ | | $Ge(C_5H_{11})_4$ | |
|---|---|---|---|---|---|---|---|---|---|---|
| | $E_c$ [a] | $\delta$ [b] | $E_c$ [a] | $\delta$ [b] | $E_c$ [a] | $\delta$ [b] | $E_c$ [a] | $\delta$ [b] | $E_c$ [a] | $\delta$ [b] |
| 273.15 | 7772 | 7.65 | 17089 | 9.58 | 23950 | 9.75 | 40788 | 11.34 | 56773 | 12.26 |
| 280 | 7216 | 7.33 | 16133 | 9.28 | 22675 | 9.45 | 37806 | 10.88 | 51992 | 11.70 |
| 290 | 6534 | 6.93 | 14936 | 8.88 | 21073 | 9.07 | 34199 | 10.30 | 46331 | 10.99 |
| 298.15 | 6065 | 6.63 | 14102 | 8.60 | 19953 | 8.80 | 31767 | 9.90 | 42589 | 10.50 |
| 300 | 5969 | 6.57 | 13927 | 8.54 | 19718 | 8.74 | 31267 | 9.81 | 41827 | 10.40 |
| 310 | 5494 | 6.26 | 13065 | 8.23 | 18558 | 8.44 | 28842 | 9.38 | 38170 | 9.89 |
| 320 | 5089 | 5.99 | 12320 | 7.95 | 17554 | 8.17 | 26806 | 9.00 | 35149 | 9.45 |
| 330 | 4740 | 5.74 | 11670 | 7.70 | 16677 | 7.93 | 25075 | 8.67 | 32617 | 9.07 |
| 340 | 4435 | 5.52 | 11099 | 7.48 | 15905 | 7.71 | 23587 | 8.37 | 30466 | 8.73 |
| 350 | 4167 | 5.32 | 10592 | 7.27 | 15220 | 7.51 | 22295 | 8.11 | 28619 | 8.43 |
| 360 | | | 10139 | 7.08 | 14608 | 7.33 | 21163 | 7.87 | 27017 | 8.15 |
| 370 | | | 9733 | 6.90 | 14057 | 7.16 | 20164 | 7.65 | 25616 | 7.91 |
| 380 | | | 9365 | 6.74 | 13560 | 7.00 | 19276 | 7.45 | 24381 | 7.68 |
| 390 | | | 9031 | 6.59 | 13108 | 6.85 | 18482 | 7.26 | 23284 | 7.48 |
| 400 | | | 8726 | 6.45 | 12696 | 6.72 | 17767 | 7.09 | 22303 | 7.29 |

[a] cal $mole^{-1}$.

[b] $cal^{1/2}$ $cm^{-3/2}$.

were calculated. Table 2 shows these values in the range 273.15–400 K for the tetra-*n*-alkylgermanes. This temperature range was selected as being most appropriate for correlating $E_c$ and $\delta$ with other measured properties.

The solubility parameters show several interesting trends. First, the $\delta$ values are in the range expected for non-polar compounds for which there is no possibility of hydrogen bonding, i.e. non-associated liquids. Second, the values for each compound show the usual decrease with increasing temperature and the decrease is approximately linear in a small temperature range. A third trend is revealed by the increase in $\delta$ values as the molecular weight increases. This is expected when London dispersion forces are the only intermolecular forces. This is not the case for $XeF_2$ and $XeF_4$ where considerable bond polarity leads to molecular association [12,13]. It is interesting, however, that the $\delta$ values for $Ge(C_2H_5)_4$ and $Ge(C_3H_7)_4$ are so nearly equal. From a comparison of the $\delta$ values, it appears that the value for $Ge(C_3H_7)_4$ is lower than expected.

For a fluid with molecular interaction by van der Waals forces, the cohesion energy can be expressed as

$$E_c = -\frac{a}{\bar{V}} \tag{12}$$

where $a$ is one of the constants in the van der Waals equation and $\bar{V}$ is the molar volume. However, it has also been suggested that the equation might

TABLE 3

Molecular attraction parameters ($a$) and effective molecular radii

| Compound | $a$ (atm $l^2$ mole$^{-2}$) | $r$ (Å) |
|---|---|---|
| $Ge(CH_3)_4$ | 34.51 | 3.79 |
| $Ge(C_2H_5)_4$ | 111.07 | 4.23 |
| $Ge(C_3H_7)_4$ | 212.47 | 4.68 |
| $Ge(C_4H_9)_4$ | 425.54 | 5.05 |
| $Ge(C_5H_{11})_4$ | 678.91 | 5.35 |

better be written as

$$E_c = -\frac{a}{\bar{V}^n} \tag{13}$$

where $n$ is a constant in the range 1.0 to 2.0 [5]. In the present case, eqn. (12) has been used to compute the van der Waals constant, $a$, for each of the $GeR_4$ compounds. Furthermore, it is possible to obtain an estimate of the effective molecular radius in the liquid from

$$\bar{V} = \tfrac{4}{3}\pi r^3 N_0 \tag{14}$$

where $N_0$ is Avogadro's number. Table 3 shows the molecular parameters computed for the $GeR_4$ compounds. The effective radii increase by a nearly constant amount in progressing from $Ge(CH_3)_4$ to $Ge(C_5H_{11})_4$ although the difference between $Ge(C_4H_9)_4$ and $Ge(C_5H_{11})_4$ is somewhat smaller, being about 0.30 Å. The values of the van der Waals constants are similar to those for other molecules of similar mass and complexity.

In view of the fact that $\delta$ values can be useful in making predictions regarding solubility, miscibility, heats of mixing and related properties [1–6], it is essential that solution studies be based on these parameters. This work has shown that organometallic compounds can be studied as pure compounds in the liquid state using physical models that have proved useful in other areas of chemistry.

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