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MOLECULAR ASSOCIATION IN TRIALKYLALUMINUM AND ALKYLALUMINUM CHLORIDE COMPOUNDS DETERMINED FROM SOLUBILITY PARAMETERS AND RELATED THERMODYNAMIC QUANTITIES

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Summary

Available vapor pressure data for trialkylaluminum and alkylaluminum chloride compounds have been used to determine the constants for the Antoine equation relating vapor pressure and temperature for each compound. These constants and other available data have been used to calculate cohesion energies, solubility parameters, Van der Waals constants, and effective molecular radii for these compounds. From these and related thermodynamic parameters, information is presented on the extent of molecular association in the liquid and vapor phases.

Introduction

The use of solubility parameters for predicting miscibility, solubility, and other properties is well established [1–4]. A number of ways to obtain numerical values for the solubility parameters (δ) have been described [1] but the simplest way is to use

$$\delta = (E_c/\bar{V})^{1/2} \tag{1}$$

where E_c is the cohesion energy and $\bar{V}$ is the molar volume. The cohesion energy is conveniently taken as the heat of vaporization at constant volume,

$$E_c = \left(\frac{d(\log p)}{d(1/T)} - RT\right) \tag{2}$$

The most convenient and accurate representation of log p is the Antoine equation [5],

$$\log p = A - \frac{B}{C + t} \tag{3}$$

so that eq. 2 becomes

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

Compilations of solubility parameters include few inorganic or organometallic

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compounds [4]. Consequently, we have begun a series of studies to obtain solubility parameters and related properties for inorganic [6] and organometallic compounds [7]. This report presents the results of work on trialkylaluminum and alkylaluminum chloride compounds. While the association of alkylaluminum compounds is well known [8–13], none of the previous studies have made use of solubility parameters or cohesion energies of the pure liquids. Most studies on the association of these compounds have been conducted on solutions or vapors and have utilized a limited series of compounds. The approach taken here is, therefore, supportive to the previous studies.

Methods

The use of eq. 4 to calculate the cohesion energy necessitates knowing values for the constants *B* and *C* of the Antoine equation. Such values appear not to have been reported for the compounds studied and, accordingly, they have been determined using existing vapor pressure data [14]. In order to determine accurate values for the constants *A*, *B*, and *C* of eq. 3, it is necessary to use a least squares procedure to fit the *p*, *t* data [5]. We have used a weighted nonlinear least squares routine for this analysis [15]. Densities used in computing molar volumes were those previously

TABLE 1

CONSTANTS FOR THE ANTOINE EQUATION AND THERMODYNAMIC QUANTITIES FOR VAPORIZATION

Compound	*A*	*B*	*C*	Calc. b.p. (°C)	ΔH_v (cal mol^{-1})	ΔS_v (cal mol^{-1} deg^{-1})
$(CH_3)_3Al$	7.269	1506.2	217.22	126.0	10735	26.90
$(C_2H_5)_3Al$	8.999	2361.2	199.34	186.2	19404	42.20
$(n\text{-}C_3H_7)_3Al$	11.963	4899.7	345.71	192.8	14067	30.11
$(i\text{-}C_4H_9)_3Al$	7.121	1710.3	189.24	214.1	15746	32.32
$(C_2H_5)_2AlCl$	8.244	2518.3	261.59	208.0	12836	26.68
$C_2H_5AlCl_2$	8.328	2501.3	265.35	193.8	12404	26.55
$(CH_3)_3Al_2Cl_3$	6.659	1230.9	182.08	143.7	11912	28.56
$(C_2H_5)_3Al_2Cl_3$	7.868	2192.7	235.94	203.7	13454	28.20

TABLE 2

COHESION ENERGIES, SOLUBILITY PARAMETERS, AND RELATED MOLECULAR PARAMETERS

Compound	*T* (°C)	Density (g ml^{-1})	E_c (cal mol^{-1})	*a* (l^2 atm mol^{-1})	*r* (Å)	δ (cal$^{1/2}$ cm$^{-3/2}$)
$(CH_3)_3Al$	20	0.752	9942	39.35	3.36	10.18
$(C_2H_5)_3Al$	25	0.8324	18490	104.7	3 79	11.61
$(n\text{-}C_3H_7)_3Al$	20	0.8241	13139	102.9	4.22	8.32
$(i\text{-}C_4H_9)_3Al$	20	0.7876	14778	153.6	4.64	7.66
$(C_2H_5)_2AlCl$	25	0.958	11879	61.73	3 68	9.72
$C_2H_5AlCl_2$	25	1.232	11476	48.83	3.44	10.55
$(CH_3)_3Al_2Cl_3$	25	1.1629	11083	80.84	4.12	7.92
$(C_2H_5)_3Al_2Cl_3$	25	1.092	12506	117.0	4.88	7.43

available [14]. Procedures used to calculate other properties were similar to those described elsewhere [7].

Results

Table 1 presents the values for the Antoine constants for the aluminum compounds studied in this work. Equations using these constants accurately reproduce the vapor pressures of the compounds. Also shown in Table 1 are the calculated boiling points and the enthalpies and entropies of vaporization for these compounds. The cohesion energies, solubility parameters, Van der Waals *a* parameters, and effective molecular radii are shown in Table 2.

Discussion

The primary interest in this work was to investigate association of organoaluminum compounds by means of solubility parameters and thermodynamics of vaporization. In order to determine the solubility parameters, it was first necessary to analyze vapor pressure data to determine Antoine constants since they were not previously available. This has been done and accurate equations are now available for representing vapor pressures of these compounds as functions of temperature. These numerical relationships permit the calculation of a number of molecular and thermodynamic parameters that are shown in Tables 1 and 2. Several of these parameters show manifestations of molecular association, but perhaps the most direct interpretation of molecular association is provided by the ΔS_v values.

Previously reported work on CH_3AlCl_2 and $(CH_3)_2AlCl$ by Ufnalski and Sporzynski provides $\Delta S_v/R$ values of 11.70 and 11.54 (ΔS_v values of 23.25 and 22.93 cal mol^{-1} deg^{-1}), respectively [16]. These values were cited as proof of complete dimerization in the liquid that is retained in the vapor. Thus, these compounds satisfactorily obey Trouton's rule ($\Delta S_v = \Delta H_v/T \simeq 21$ cal mol^{-1} deg^{-1}) since the molecular aggregates are the same in both states. If multimers in an ordered liquid state are ruptured during vaporization, ΔS_v will be larger than 21 cal mol^{-1} deg^{-1} and if a disordered liquid forms discrete, tightly bound aggregates in the vapor, ΔS_v will be smaller than 21 cal mol^{-1} deg^{-1}. We have found that for $(C_2H_5)_3B$ and $(C_2H_5)_2Zn$ the entropies of vaporization are 23.76 and 22.83 cal mol^{-1} deg^{-1}, respectively [17]. For these cases dimerization does not occur so that the values are indicative of monomer liquids that become monomer vapors [11–13].

A quite different situation is seen for the organoaluminum compounds studied here. The $(C_2H_5)_3Al$ for which $\Delta S_v = 42.20$ cal mol^{-1} deg^{-1} is most obvious. This value is twice that predicted from Trouton's rule and, therefore, indicates that dimerization is complete in the liquid but that the vapor consists of monomers. This compound has previously been shown to be dimeric in both the pure liquid state and in dilute solutions [18]. The abnormally high value for ΔH_v thus represents both separation of dimers and the vaporization process. All the other cases indicate intermediate behavior but there are some important differences.

In the case of $(CH_3)_3Al$, there is no doubt that the liquid consists of dimers [11–13,16]. However, if the vapor consisted of monomers only, the ΔS_v would be near that for $(C_2H_5)_3Al$. Since it is not, it can be concluded that the vapor consists primarily of dimers, but there is a significant degree of dissociation (estimated to be

28% based on the deviation from Trouton's rule). The difference between $(CH_3)_3Al$ and $(C_2H_5)_3Al$ probably lies in the fact that there is a 61°C difference in the boiling points. It would be of interest to determine the extent to which $(CH_3)_3Al$ remains dimerized at 187°C, the boiling point of $(C_2H_5)_3Al$, in order to compare the stability of dimers of the two compounds. The strong association of $(CH_3)_3Al$ and $(C_2H_5)_3Al$ in the liquid state is also indicated by the high δ values for these compounds (10.18 and 11.61 $cal^{1/2}$ $cm^{-3/2}$, respectively). For the nonassociated $Ge(CH_3)_4$ and $Ge(C_2H_5)_4$, which have higher molecular weights, the δ values are 6.63 and 8.88 $cal^{1/2}$ $cm^{-3/2}$, respectively [6].

The other compounds give values for ΔS_v that are significantly higher than the 21 cal mol^{-1} deg^{-1} predicted by Trouton's rule. It is tempting, therefore, to ascribe this to the partial dissociation of dimers in the vapor phase as in the case of $(CH_3)_3Al$. However, this seems not to be the situation. For example, it would make little sense to assume complete dissociation of $(C_2H_5)_3Al$ dimers in the vapor but not those of $(n\text{-}C_3H_7)_3Al$ and $(i\text{-}C_4H_9)_3Al$ which have higher boiling points. For these latter two compounds, the solubility parameters are particularly revealing. These δ values are 8.32 and 7.66 $cal^{1/2}$ $cm^{-3/2}$, respectively, both of which are significantly lower than the values of 10.18 and 11.61 $cal^{1/2}$ $cm^{-3/2}$ for $(CH_3)_3Al$ and $(C_2H_5)_3Al$, respectively, even though the latter compounds have lower molecular weights. Since the solubility parameters are related to types and strengths of intermolecular interactions [4], it appears that the low values reflect liquids that are less strongly associated in the case of the n-propyl and i-butyl compounds. This has been shown to be the case for the i-butyl compound, both in the pure liquid and in tetradecane solutions [9]. Accordingly, the entropies of vaporization for these compounds probably reflect incomplete dimerization in the liquid state with complete dissociation in the vapor rather than a dimerized liquid that only partially dissociates into monomers during vaporization. This is in agreement with the observation that the i-butyl compound is not completely associated in the liquid state [9]. Similarly, the lower cohesion energies (compared to that for $(C_2H_5)_3Al$) indicates less molecular association in liquid $(n\text{-}C_3H_7)_3Al$ and $(i\text{-}C_4H_9)_3Al$ than in the triethyl compound, in accord with previous results [9].

A similar indication of these conclusions is also seen from the *a* parameters where the mixture of monomers and dimers results in a smaller *a* value for $(n\text{-}C_3H_7)_3Al$ than for $(C_2H_5)_3Al$ where dimerization is complete. Although the difference is slight, the ΔS_v value and the much higher *a* value for $(i\text{-}C_4H_9)_3Al$ indicate a somewhat greater degree of dimerization of $(i\text{-}C_4H_9)_3Al$ than for $(n\text{-}C_3H_7)_3Al$ in the liquid state. The difference between the ΔS_v values may reflect a greater degree of alkyl group rotation which is possible for the terminal groups in the dimer of $(n\text{-}C_3H_7)_3Al$ which is also possible in the monomer in the vapor state. However, alkyl groups in the dimer of the $(i\text{-}C_4H_9)_3Al$ may have hindered rotation, but may have free rotation possible in the monomeric vapor.

In the case of the $(C_2H_5)_2AlCl$ and $C_2H_5AlCl_2$, it is probable that there is complete dimerization in the liquid as there is for the corresponding methyl compounds [16]. This is also indicated by the rather high solubility parameters of the ethyl compounds. Therefore, the ΔS_v values of 26.68 and 26.55 cal mol^{-1} deg^{-1} for $(C_2H_5)_2AlCl$ and $C_2H_5AlCl_2$, respectively, probably reflect some dissociation of a completely dimerized liquid during vaporization. The methyl and ethyl sesquichlorides appear to behave similarly. Since no great change in molecular volume occurs on dimerization (compared to that of two monomers), the variations in r do not show any unusual trends whether dimerization in the liquid is complete or not.

The results of the present study provide Antoine constants, cohesion energies, solubility parameters, and other data for organoaluminum compounds. These data, while useful for reference and predictive work [4], also provide rather direct evidence on the nature of intermolecular association of the compounds in the liquid and vapor phases. The associations predicted are in accord with those previously described [8–13].

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