Vapor Pressure and Vapor Composition of Diethylgallium Chloride and Diethylaluminum Chloride

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The vapor pressures of the metal organic halogen compounds diethylgallium chloride (DEGaCl) and diethylaluminum chloride (DEAlCl) have been measured by a capacitance manometer in the temperature range 5 < θ < 60 °C. The measurements for DEAlCl correlate and extrapolate well to existing data in the literature. The measurements for DEGaCl replace the previous data point measured at 60 °C. The dependences of the vapor pressures of DEAlCl and DEGaCl on temperature are log (P_{DEAlCl}/Torr) = 8.780 - 2815(K/T) and log (P_{DEGaCl}/Torr) = 8.943 - 3080(K/T), respectively. The results of mass transport measurements, combined with the measured compound vapor pressures, indicate that the vapor phase of these compounds is likely to be dominated by dimers.

Introduction

The metal organic sources diethylgallium chloride (DEGaCl) and diethylaluminum chloride (DEAlCl) have been used as Ziegler–Natta catalysts for the polymerization of polyenes (*1*, *2*). In addition, these compounds have recently been used for the epitaxial growth of GaAs and $Al_xGa_{1-x}As$ during chemical vapor deposition with AsH_3 (*3*). The selective deposition of these compounds on GaAs or $Al_xGa_{1-x}As$ surfaces as opposed to SiO_2 or Si_xN_y is a useful property for the growth of semiconductor devices on masked substrates. However, the lack of a good summary of the vapor pressure data for DEAlCl (*4–6*) and the paucity of vapor pressure data for DEGaCl (*2*) make process analysis difficult. We have used a capacitance manometer to determine the vapor pressures of DEGaCl and DEAlCl. In addition, we have performed a mass transport experiment to determine that both compounds form significant concentrations of associated complexes in the gas phase, most likely dimers.

Results and Discussion

Both compounds were provided in electronic grade purity (99.9995% metals basis) by Alfa Products in stainless steel bubblers. Repeated freeze–pump–thaw–pump cycles were used to purge the bubblers of the argon gas used for back-filling the bubbler until steady measurements were achieved. The freeze cycle was performed at 77 K and the pumping performed with a turbo pump. The materials were then used without further purification. The bubblers were heated in an isothermal water bath, and pressure measurements were made at each temperature after allowing sufficient time for the compound to thermally equilibrate. The vapor pressures were measured with a capacitance manomer (MKS Instruments, Model 127AA) with 1-Torr maximum capacity and 0.0001-Torr resolution to an accuracy of ±0.001 Torr. This pressure gauge was checked against another capacitance manometer with a calibrated 10-Torr maximum capacity and 0.002-Torr accuracy (MKS, Model 122A) and found to agree within ±1% in the range of 0–1 Torr. Temperatures of the isothermal water bath were measured with two thermocouple gauges (Omega Instruments, Model 871) to an accuracy of ±0.1 °C. The readings of the two thermocouple gauges were averaged in the results. The lower range of the gauges were checked against an acetone slush bath, and both agreed within ±2 °C of the melting point, Θ_M = -95 °C, of acetone (*7*).

Table I. Vapor Pressures of Compounds

DEGaCl θ/°C	DEGaCl P/Torr	DEAlCl θ/°C	DEAlCl P/Torr
9.6	0.011	5.0	0.049
19.6	0.028	10.0	0.068
29.8	0.058	15.0	0.097
40.8	0.133	20.0	0.140
50.2	0.258	25.0	0.210
59.9	0.509	30.0	0.280
		35.0	0.403
		40.0	0.605
		45.0	0.800

The resulting vapor pressure data for DEAlCl and DEGaCl are shown in Table I, plotted along with existing data from the literature, and then fitted by the expressions in Figure 1 after excluding two datum. The 1-Torr vapor pressure measurement for DEAlCl (*5*) was excluded because the authors feel it extends beyond the accuracy of the measuring apparatus used. The single datum obtained prior to these measurements for DEGaCl (*2*) is excluded from the fit because it is listed to a precision of only 1 Torr. The resultant expressions for the vapor pressures of DEAlCl and DEGaCl are

$$\log (P_{DEAlCl}/\mathrm{Torr}) = 8.780 - 2815(\mathrm{K}/T) \quad \text{for} \quad 0 < \Theta < 200\ ^\circ\mathrm{C} \quad (1a)$$

$$\log (P_{DEGaCl}/\mathrm{Torr}) = 8.943 - 3080(\mathrm{K}/T) \quad \text{for} \quad 0 < \Theta < 60\ ^\circ\mathrm{C} \quad (1b)$$

The Θ_M values for DEGaCl and DEAlCl were determined to be -7 and <-90 °C, respectively. The Θ_M value for DEAlCl lies below those previously published in the literature: -74, -85 °C (*4*). Caution should be used with the compound DEAlCl since long exposures of the bubbler to elevated temperatures ($\Theta \simeq$ 60 °C) may result in the formation of other group III compounds in the source due to intermolecular reactions in the bubbler (e.g. ethylaluminum dichloride and triethylaluminum (*2*)).

Many group III alkyls, halides, and alkylhalides in the gas, liquid, and solid phases are found to exist as associated complexes (e.g. dimers, trimers, etc. (*2*)). These associated complexes are formed from monomer units connected by electron-deficient bonds in the bridging ligands. Hence, the vapor species above the DEGaCl and DEAlCl liquids are likely to consist of a mixture of both monomers and associated complexes. The concentrations of these associated complexes are dependent on the temperature and partial pressure of the gas but should be relatively constant over the narrow band of temperatures studied in this experiment. The aluminum compounds have a strong tendency to associate as dimers in all the gas-phase alkyl, halogen, and alkyl-halogen compounds. The DEAlCl is known to form a significant concentration of dimers in the gas phase (*2*, *8*). However, gallium compounds are dominantly monomeric alkyls, though they are known to form

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Table II. Mass Transport Measurements

compound	θ/°C	P/Torr	P_{bubbler}/Torr	F_{He}/Torr	m/g	t/min	$(\mathrm{d}m/\mathrm{d}t)$/(g/min)	dimer concn/(mol %)
DEAlCl	24.5	0.210	755	250	0.465	720	6.46×10^{-4}	72 ± 16
	45.0	0.856	750	125	0.505	360	1.40×10^{-3}	83 ± 16
DEGaCl	45.0	0.183	746	250	0.570	720	7.92×10^{-4}	77 ± 15
	45.0	0.183	750	250	0.550	720	7.64×10^{-4}	72 ± 14

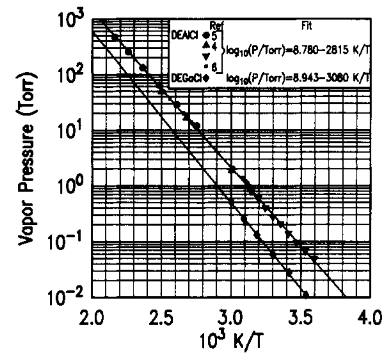

Figure 1. Vapor pressure measurements for DEAlCl and DEGaCl from Table I. Published data not considered trustworthy were excluded from the plot.

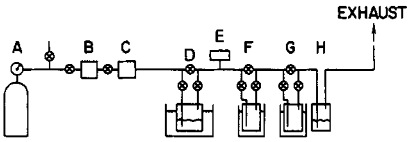

Figure 2. Experimental apparatus for mass transport: (A) helium tank, (B) purifier, (C) mass flow controller, (D) DEGaCl or DEAlCl bubbler, (E) capacitance manometer, (F and G) primary and back-up liquid nitrogen trapped Pyrex U tubes, (H) vapor block. Back-up U tube allows trapping before and after transport experiment.

associated complexes in the halogen compounds. The degree to which DEGaCl forms these complexes in the gas phase was not determined prior to this study. However, it would also be expected to form a significant concentration of associated complexes by analogy to dimethylgallium chloride (DMGaCl), which is known to form dominantly dimer species in the gas phase (*9*).

To more clearly determine the gas-phase composition of DEAlCl and DEGaCl we ran a mass transport experiment. A calibrated flow of helium (F_{He}) was saturated with the metal–organic sources having partial pressures determined from eq 1a,b. The metal organics were then condensed downstream in a preweighed liquid nitrogen cooled trap. The apparatus is shown in Figure 2. The helium (99.999%) (A) was purified (Semi Gas Systems, Nanochem purifier) (B) to remove H_2O and O_2 (which typically decompose metal–organic molecules) to levels below 10 ppb. The helium flow was controlled with a mass flow controller from Sierra Instruments (Model 840) (C), calibrated to within 5% of its set point throughout its range. The bubblers were maintained in an isothermal bath (D), and a capacitance manometer (MKS, Model 127AA) with 1000-Torr maximum capacity was used to determine the pressure above the bubbler (E). Liquid nitrogen trapped Pyrex U tubes (F and G) were used to condense the transport material. An oil-filled vapor block (H) was used prior to exhausting the He effluent. Lines of $^1/_4$-in. stainless steel were used to connect the components in the system. All components from the mass flow controller to the exhaust were heated above the temperature of the bubbler. The mass transport rate (dm/dt) was determined from the transported mass and the length of time of the transport. The precision and accuracy of the mass measurement was ±0.01 g. From the experimental mass transport measurements and the theoretical mass transport rate of a multicomponent gas, we calculate the gas composition, assuming a mixture of monomer and dimer species. The theoretical mass transport rate of a multicomponent gas saturating the He flow in the bubbler is derived in Appendix A. The experimental results for both DEGaCl and DEAlCl are summarized in Table II under two different operating conditions.

The experimental mass transport rates of both the DEAlCl and DEGaCl exceeded the theoretical mass transport rates calculated for a purely monomer gas via eq 3. On the basis of the assumption that the gas-phase composition consists of only monomers and dimers and by use of eq 3 coupled with the fact that the sum of the monomer and dimer partial pressures is the equilibrium pressure shown in Figure 1, one can calculate the dimer concentration in the gas phase. Consequently, averaging the results for each compound, the gas phases of DEAlCl and DEGaCl are calculated to consist of dimer concentrations of 78 and 75 mol %, respectively. The accuracy of the experimental apparatus introduced a maximum error of ±16% into the calculation of the gas-phase dimer concentrations. The use a self-consistent set of data to determine the dimer concentration for DEAlCl (vapor pressure determined solely from our data) indicates that the gas phase is even more strongly dominated by dimers: 91 ± 16%. The observation of a significant concentration of associated complexes for DEAlCl, assumed in the above calculation to be dimers, agrees qualitatively with a mass spectroscopic investigation in which 83% of the observed ion current was attributed to a dimer species (*8*). We conclude that the gas phases of DEAlCl and DEGaCl, in the temperature range of investigation, consist of 75 ± 15 and 91 ± 16% dimers, respectively.

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Glossary

θ	temperature, °C
θ_M	melting point, °C
T	temperature, K
P_i	equilibrium partial pressure of gas component i, Torr
P_{bubbler}	total pressure over bubbler, Torr
F_{He}	helium volume flow rate at standard temperature and pressure (θ = 0 °C, P = 760 Torr)
sccm	cubic centimeters per minute at standard temperature and pressure
m	transported mass
dm/dt	mass transport rate
M_i	molecular weight of gas component i
(V/n)	molar volume at standard temperature and pressure

Appendix A

The total mole flow rate out of the bubbler is described by

$$\text{total mole flow rate} = \frac{F_{\mathrm{He}}}{V/n}\,\frac{P_{\mathrm{bubbler}}}{P_{\mathrm{bubbler}} - \sum_i P_i} \qquad (2)$$

where F_{He} is the volume flow rate at standard temperature and pressure, P_{bubbler} the pressure over the bubbler, $\sum P_i$ the sum of the compound partial pressures above the compound in the bubbler, and V/n the molar volume at standard temperature

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and pressure. The factor $P_{\text{bubbler}}/[P_{\text{bubbler}} - \sum P_i]$ accommodates the increase in the mole flow rate due to the saturation of the He flow with the partial pressures above the compound. The mass flow rate of a single gas-phase species i is calculated by multiplying the total mole flow rate by the mole fraction and the molecular weight of component i. The total mass flow rate of the multicomponent gas mixture is then shown by

$$\text{total mass flow rate} = \frac{dm}{dt} = \frac{F_{\text{He}}}{V/n}\,\frac{\sum_i (P_i M_i)}{P_{\text{bubbler}} - \sum_i P_i} \tag{3}$$

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Total Pressure Measurements for *n*-Pentane–Methanol–2-Butanol at 303.15 K

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The total pressure is reported as a function of liquid-phase composition for *n*-pentane–methanol–2-butanol and each of its constituent binary systems at 303.15 K. The data were reduced by using Baker's method. The modified Margules equation was found to fit the binary measurements adequately. The ternary measurements were modeled with an expression for the excess Gibbs free energy which includes contributions from the binary systems plus additional terms containing ternary parameters.

Introduction

Recently, renewed interest is being shown in solution models which invoke chemical equilibria to model hydrogen bonding between associating species. In these models, a component that is known to exhibit hydrogen bonding is assumed to exist as a distribution of *n*-mers in solution. If several associating species are present in a mixture, each forms *n*-mers with the other associating species in addition to itself. To test solution models which account for cross association, it is important that experimental data be available for systems which contain more than one associating component.

The present work reports total pressure measurements for *n*-pentane–methanol–2-butanol and its constituent binary at 303.15 K and is part of a larger study involving mixtures of two associating species and one nonpolar diluent. In an earlier study (*1*), total pressure data were reported for the ethanol–*n*-heptane–2-methyl-1-propanol system.

Experimental Section

Apparatus and Procedure. The apparatus and procedure have been described previously (*1*). Briefly, the apparatus is of the Van Ness type (*2*), in which, for binary measurements, each pure chemical is stored in a piston injector. A portion of one of the components is metered into the equilibrium cell, and its vapor pressure is determined. Measured amounts of the second component are then added, and the total pressure is recorded after each addition. After approximately half of the composition range is covered, the equilibrium cell is emptied and charged with a measured amount of the second component, and successive amounts of the first component are added until the entire composition range is covered. The two sides of the isotherms are made to overlap at one or more compositions to check the internal consistency of the results.

For ternary measurements, one of the piston injectors is filled with pure *n*-pentane and the other is filled with a gravimetrically prepared mixture of methanol and 2-butanol. The procedure is the same as that for a binary system with the result that the overall composition in the equilibrium cell for a given run follows a straight line on a triangular diagram between the *n*-pentane (1) vertex and the composition of the methanol–2-butanol mixture. The methanol (2)–2-butanol (3) mixtures are characterized by the parameter C'

$$C' = \frac{z_2}{z_2 + z_3} \tag{1}$$

where z_2 and z_3 are the overall mole fractions of methanol and 2-butanol in the equilibrium cell. Three different values of C' (0.2459, 0.5087, and 0.7562) were examined in this work.

The temperature of the water bath in which the equilibrium cell is suspended is controlled to within 0.02 K. Accuracy of the pressure measurements (not including the effect of variations in bath temperature) is within 0.1%. Volumes of each component displaced into the equilibrium cell were converted to moles by using saturated liquid density data at room temperature. Saturated liquid density information for *n*-pentane was taken from ref 3, while that for methanol and 2-butanol was obtained from ref 4. For the ternary system measurements, excess volumes given by Polak et al. (*5*) were used to calculate the densities of the methanol–2-butanol mixtures in the piston injector. The maximum uncertainty in the reported

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