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INTERMOLECULAR ASSOCIATION OF ALIPHATIC ORGANOALUMINUM COMPOUNDS

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SUMMARY

Ebullioscopic data is presented for a variety of trialkylalanes, dialkylalkoxyalanes, and dialkoxyalkylalanes in a noncomplexing solvent under standardized conditions. Intermolecular association of these materials occurs to an extent consistent with the steric limitations of the alkyl and alkoxy groups bound to aluminum. Generalities concerning steric limitations and their relationship to intermolecular association of organoaluminum compounds are presented.

INTRODUCTION

Organoaluminum compounds are known to exist in solution as intermolecularly associated compounds. That the degree of association (*i*) of organoaluminum compounds in noncomplexing media is to a large extent determined by the structure, size, and/or inductive effects of the alkyl and alkoxy groups bonded to aluminum is apparent by examination of the chemical literature. Several approaches to the problem of intermolecular association have provided data which must be clarified before a thorough understanding of such phenomena is possible.

This work has been limited to study of the structural factors responsible for intermolecular association for the following types of compounds: R_3Al (trialkylalanes); $R_2Al(OR')$ (alkoxydialkylalanes); and $RAl(OR')_2$ (dialkoxyalkylalanes)*. No attempt was made to study compounds of the type $Al(OR)_3$ since ample and reliable information is available in the chemical literature to characterize these systems adequately[1-3]. The method chosen for obtaining molecular weight data has been previously described by Ashby[4].

The information obtained in this study was derived by analysis of molecular weight data. Molecular weight data was obtained ebullioscopically in n-pentane.

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* In the subsequent discussion, the designation of organometallic derivatives of aluminum will be as follows: $(R)_3Al$ will be referred to as trialkylalanes; similarly, systems such as $(R)_2Al(OR')$ and $(R)Al(OR')_2$ will be referred to as alkoxydialkylalanes and dialkoxyalkylalanes, respectively. The suffix alane rather than aluminum is preferred for the sake of brevity and because of a growing trend to use of this terminology.

RESULTS AND DISCUSSION

A. Tri-n-alkylalanes

Experimental data obtained during the study of the trialkylalanes is presented in Table 1 and represented graphically in Fig. 1. Although molecular weight data for the trialkylalanes examined in this study is already present in the chemical literature[5-11], some of these systems were re-examined under standardized conditions over a wide concentration range such that comparative evaluation of the experimental molecular weight data would be possible.

From Fig. 1 it is apparent that in dilute solutions these systems fall into two general categories, $i \cong 2$ and $i \cong 1$ (*i.e.*, dimers and monomers). The tri-n-alkylalanes which are the least sterically hindered represent the most highly associated class of trialkylalanes ($i \cong 2$). Figure 1 demonstrates that, for a given concentration, as the

TABLE 1

EBULLIOSCOPIC DATA FOR TRIALKYLALANES IN n-PENTANE

System studied	*Stoichiometric molality range examined*	*i value range obtained*	*i at infinite dilution*	*Number of determinations*
$(C_2H_5)_3Al$	0.200–1.86	2.00–2.01	2.00	6
$(n\text{-}C_4H_9)_3Al$	0.045–1.83	1.92–1.72	1.97	10
$(n\text{-}C_6H_{13})_3Al$	0.231–1.99	1.78–1.54	1.89	11
$(n\text{-}C_8H_{17})_3Al$	0.027–1.77	1.77–1.45	1.77	9
$(neo\text{-}C_5H_{11})_3Al$	0.070–0.471	1.01–0.97	1.02	8
$[CH_3(CH_2)_3CH(C_2H_5)CH_2]_3Al$	0.162–1.00	0.93–0.91	0.93	6

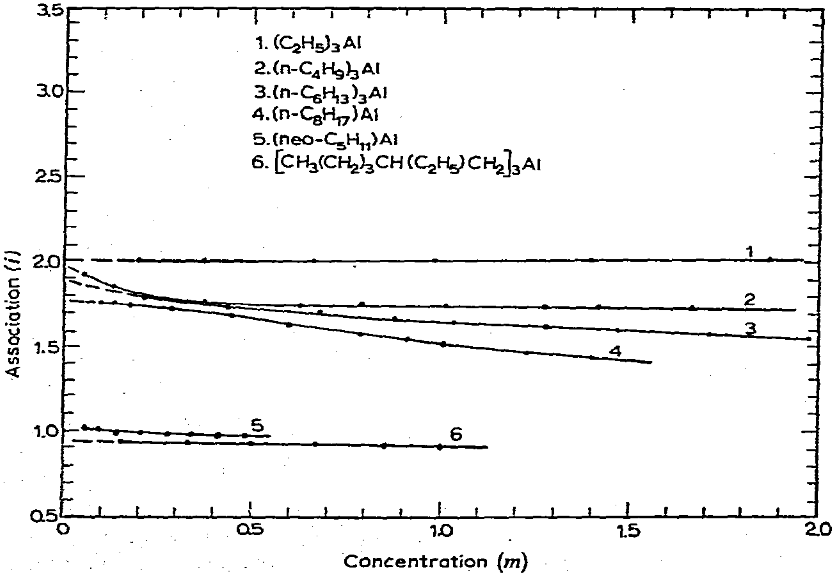

Fig. 1. Association of trialkylalanes in n-pentane.

length of the alkyl group is increased the observed *i* values at $m=0$ decrease progressively from the value of 2.

Model equilibria (1)–(4) have been proposed to explain concentration dependent changes of intermolecular association[9,12,13]. Assumption of such equilibria

$$2\,R_3Al \rightleftharpoons R_3Al\cdots R_2AlH + \text{olefin} \tag{1}$$

$$2\,R_3Al \rightleftharpoons (R_3Al)_2 \tag{2}$$

$$nA_1 \rightleftharpoons A_n \tag{3}$$

$$2\,A_1 \rightleftharpoons A_2;\, 3\,A_1 \rightleftharpoons A_3;\, \cdots;\, qA_1 \rightleftharpoons A_q \tag{4}$$

either individually or collectively cannot generate concentration dependent molecular weight data in agreement with experiment. Such equilibria do not adequately describe the shape of the plotted *i* value data. Hence, the best interpretation of the experimental data indicates that the tri-n-alkylalanes are essentially dimeric and do not participate in equilibria such as Equations (1)–(4) under these experimental conditions and within the concentration ranges studied*. The progressive trend to diminished *i* values ($i < 2$) as a function of concentration and solute formula weight is adequately explained in terms of deviations from ideal behavior as described by Ashby[12].

Examination of the limited data presented for branched trialkylalanes indicates rather dramatically that the steric requirements of the alkyl groups bound to aluminum is the predominate factor determining the experimentally observed *i* values for these systems. The data indicates clearly that trineopentylalane and tris(2-ethylhexyl)-alane are monomeric within experimental error. Such findings are consistent with cryoscopic data previously reported for triisobutylalane and tris(2,4,4-trimethylpentyl)alane[5,9] which indicates that generally all trialkylalanes exhibiting alkyl branching β to aluminum are monomeric. Presumably, alkyl branching α to aluminum will in all cases produce monomeric trialkylalanes as reported for triisopropylalane[6] and tri-t-butylalane[10] in noncomplexing solvents.

Steric conditions involving the alkyl groups bonded to aluminum appear to be the dominant factor determining the degree of association of trialkylalanes. Examination of molecular models for the dimeric tri-n-alkylalanes demonstrates nicely that the n-alkyl groups can easily be arranged such that steric interactions involving the alkyl groups are largely nonexistent. Similar models for the more highly branched trialkylalanes show the steric interference of the alkyl groups to be progressively more difficult to minimize as the steric demands of the alkyl groups increase. Hence, diminished association as a consequence of steric factors nicely explains the experimentally observed data.

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* Equilibrium (1) or other equilibria involving disproportionation of trialkylalanes is essential for understanding the chemistry of these systems at elevated temperatures. Under the conditions of this study no olefins were observed. Hence, Equilibrium (1) or similar equilibria are not significant in determining the degree of association for the trialkylalanes.

Reactions of trialkylalanes are believed to proceed through the monomer which implies an equilibrium according to Equilibrium (2). The results of this study do not contrast this idea but simply imply something concerning the equilibrium position for Equilibrium (2). At the lowest concentrations examined in this study, the trialkylalanes were essentially dimeric (*i.e.*, the degree of association is at a maximum). Calculation of equilibrium constants (K_2) at these concentrations show minimum values of $\sim 10^2$–10^3. Such values are close to the values reported for triethylalane by Hoffman[5].

B. Dialkylalkoxyalanes

Experimental data obtained from the study of dialkylalkoxyalanes is presented in Table 2 and represented graphically in Fig. 2. Table 2 shows that data were obtained from systems having variously substituted alkyl and alkoxy groups bonded to aluminum. From this data and reliable literature data[5,14–16], generalizations concerning the factors which determine the degree of association for these systems are easily obtained.

Figure 2 demonstrates that generally the dialkylalkoxyalanes are dimeric in nature. In these systems there appears to be no systematic manner in which the ex-

TABLE 2

EBULLIOSCOPIC DATA FOR DIALKYLALKOXYALANES IN n-PENTANE

System studied	*Stoichiometric molality range examined*	*i value range obtained*	*i at infinite dilution*	*Number of determinations*
$(C_2H_5)_2Al(O\text{-}C_2H_5)$	0.038–1.97	2.01–2.14	2.03	9
$(C_2H_5)_2Al(O\text{-}n\text{-}C_6H_{13})$	0.044–1.14	1.99–2.07	2.02	8
$(C_2H_5)_2Al(O\text{-}n\text{-}C_8H_{17})$	0.077–1.01	2.07–2.19	2.14	9
$(C_2H_5)_2Al(O\text{-}i\text{-}C_4H_9)$	0.061–1.14	2.39–2.17	2.46	9
$(C_2H_5)_2Al(O\text{-}i\text{-}C_3H_7)$	0.091–1.11	2.24–2.21	2.26	7
$(C_2H_5)_2Al[O\text{-}CH_2CH(C_2H_5)(CH_2)_3CH_3]$	0.076–1.16	2.14–2.05	2.14	10
$(C_2H_5)_2Al(O\text{-}neo\text{-}C_5H_{11})$	0.092–0.407	2.16–1.92	2.08	4
$(i\text{-}C_4H_9)_2Al(O\text{-}i\text{-}C_4H_9)$	0.078–0.832	2.02–1.90	2.07	6
$(n\text{-}C_6H_{13})_2Al(O\text{-}n\text{-}C_6H_{13})$	0.067–0.316	1.88–1.80	1.84	6

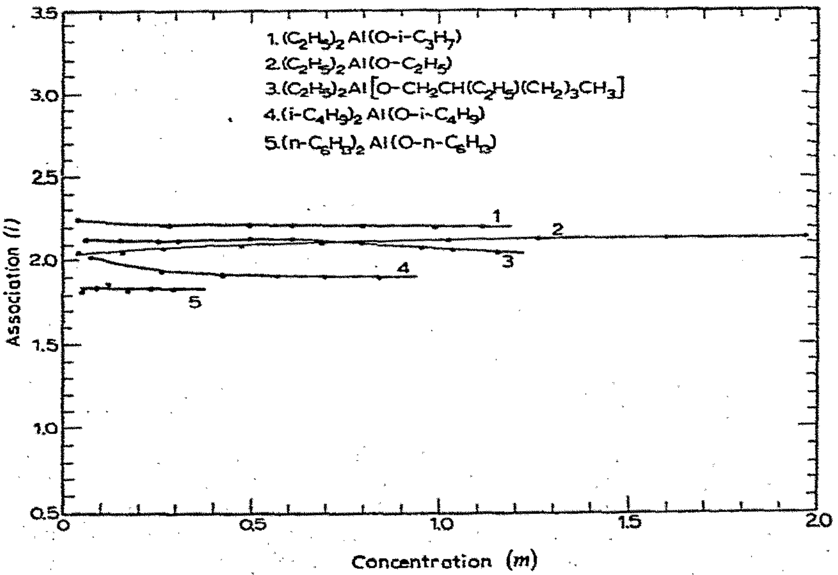

Fig. 2. Association of dialkylalkoxyalanes in n-pentane.

perimentally determined *i* values change as a consequence of variations in the substitution patterns of the alkyl and alkoxy groups bonded to aluminum. This generalization is consistent with literature reports for related systems[5], for systems such as $(C_2H_5)_2Al[OC(CH_3)_3]$, $[(CH_3)_2CHCH_2]_2Al[OC(CH_3)_3]$, and $(n\text{-}C_4H_9)_2Al[OC(CH_3)_3]$;[14] and for $(CH_3)_2Al[OC(CH_3)(C_6H_5)_2]$[16], all of which are reported to be dimeric.

Only the methoxydialkylalanes for which molecular weight data are available[5,15] appear to be associated beyond the dimeric state. The most thermodynamically stable form for these systems appears to be the trimer although ^{1}H NMR suggests that immediately after formation (methanolysis) the methoxides are also dimeric, being formed in a rate-controlled process[15]. Attempts to study the dialkylaluminum methoxides in the course of this study were curtailed by the insolubility of these systems in n-pentane.

Examination of the *i* value plots in Fig. 2 shows that within experimental error the individual *i* values are somewhat more internally consistent for the dialkylalkoxyalanes than for the trialkylalanes which indicates that the dialkylalkoxyalanes behave more ideally in solution than the trialkylalanes. In this respect these systems are classic.

The *i* value plots for the dialkylalkoxyalanes indicate that generally these systems are dimeric over a wide concentration range; and equilibria involving dimeric and other more or less associated species are not operative. Equilibria between the dialkylalkoxyalanes and disproportionation products produced according to Equation (5) appear to be nonexistent in noncomplexing solvents. Such findings are consistent with the literature report which stipulates that equilibria such as Equation

$$2\,R_2Al(OR') \rightleftharpoons R_3Al + RAl(OR')_2 \qquad (5)$$

(5) are important only under specialized conditions involving donar solvents[17].

C. Dialkoxyalkylalanes

To date no references have appeared which specify or imply anything concerning the molecular complexity of the dialkoxyalkylalanes. Very few references are made to these systems as a discrete or well-characterized class of compounds, although they are referred to as intermediates formed during direct oxidation processes[18].

The present study does not present the dialkoxyalkylalanes as a well-characterized class of compounds. However, on the basis of the molecular weight data presented, it can be said that the dialkoxyalkylalanes exist as a class of compounds and that the factors influencing the degree of association of these systems as observed experimentally in pentane solution were expected in view of similar trends apparent for the trialkoxyalanes[1-3].

Experimental molecular weight data obtained during the study of the dialkoxyalkylalanes is presented in Table 3 and represented graphically in Fig. 3. The structures of the alkyl and alkoxy groups bound to aluminum were varied systematically to determine the manner in which the degree of association varies as a consequence of these changes. Figure 3 shows that, as with the trialkylalanes, the most reliable molecular weight data is obtained under dilute conditions or preferably from extrapolation to infinite dilution. Examination of Fig. 3 shows that at infinite dilution the dialkoxyalkylalanes fall into three general categories: $i \cong 2$, $i \cong 3$, and $i \cong 4$.

TABLE 3

EBULLIOSCOPIC DATA FOR DIALKOXYALKYLALANES IN n-PENTANE

System studied	*Stoichiometric molality range examined*	*i value range obtained*	*i at infinite dilution*	*Number of determinations*
$(C_2H_5)Al(O\text{-}n\text{-}C_3H_7)_2$	0.059–0.865	4.13–3.72	4.20	7
$(C_2H_5)Al(O\text{-}n\text{-}C_4H_9)_2$	0.079–0.678	4.03–2.63	4.17	7
$(C_2H_5)Al(O\text{-}n\text{-}C_6H_{13})_2$	0.022–0.904	3.90–3.34	3.94	7
$(C_2H_5)Al(O\text{-}n\text{-}C_8H_{17})_2$	0.090–0.767	4.15–3.56	4.24	7
$(C_2H_5)Al(O\text{-}i\text{-}C_4H_9)_2$	0.251–1.275	3.94–3.76	3.97	6
$(C_2H_5)Al(O\text{-}i\text{-}C_3H_7)_2$	0.085–1.696	3.17–2.90	3.22	7
$(C_2H_5)Al[O\text{-}CH_2CH(C_2H_5)(CH_2)_3CH_3]_2$	0.046–1.716	3.76–3.37	3.80	5
$(C_2H_5)Al(O\text{-}neo\text{-}C_5H_{11})_2$	0.254–0.892	2.14–1.93	2.30	7
$(n\text{-}C_4H_9)Al(O\text{-}n\text{-}C_6H_{13})_2$	0.073–0.469	4.07–3.51	4.16	7
$(i\text{-}C_4H_9)Al(O\text{-}n\text{-}C_4H_9)_2$	0.030–0.916	3.79–3.40	3.82	7
$(i\text{-}C_4H_9)Al(O\text{-}i\text{-}C_4H_9)_2$	0.128–0.626	3.22–3.13	3.22	6
$(i\text{-}C_4H_9)Al(O\text{-}sec\text{-}C_4H_9)_2$	0.030–0.794	2.03–1.97	2.03	7
$(neo\text{-}C_5H_{11})Al(O\text{-}n\text{-}C_4H_9)_2$	0.058–0.494	3.08–3.01	3.07	5
$(n\text{-}C_6H_{13})Al(O\text{-}C_2H_5)_2$	0.034–0.461	3.14–3.28	3.10	5
$(n\text{-}C_6H_{13})Al(O\text{-}n\text{-}C_6H_{13})_2$	0.053–0.285	3.03–2.65	3.22	6
$(n\text{-}C_6H_{13})Al(O\text{-}i\text{-}C_4H_9)_2$	0.105–0.620	3.04–2.97	3.02	6
$(n\text{-}C_6H_{13})Al(O\text{-}sec\text{-}C_4H_9)_2$	0.084–0.598	2.22–2.16	2.20	7
$[CH_3(CH_2)_3CH(C_2H_5)CH_2]Al(O\text{-}i\text{-}C_4H_9)_2$	0.097–0.489	2.81–2.71	2.82	6
$[CH_3(CH_2)_3CH(C_2H_5)CH_2]Al(O\text{-}sec\text{-}C_4H_9)_2$	0.027–0.508	2.13–2.06	2.13	7

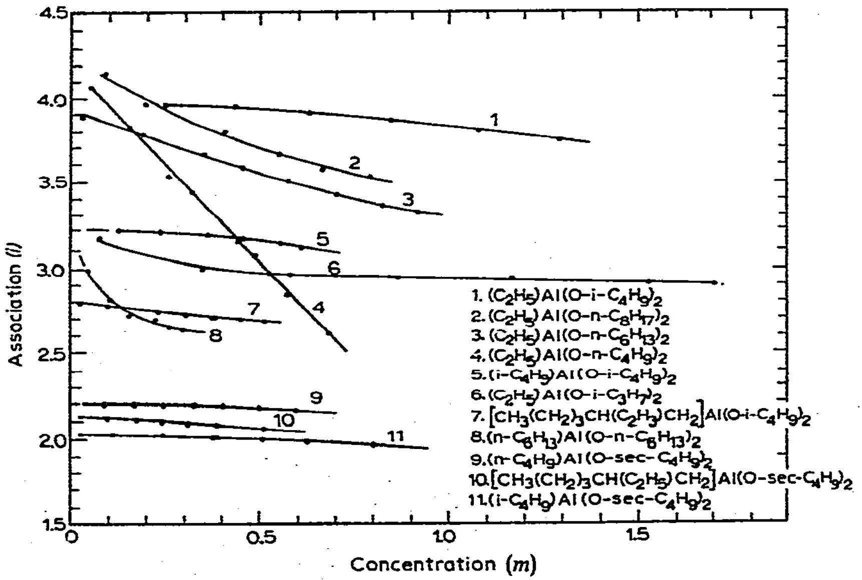

Fig. 3. Association of dialkoxyalkylalanes in n-pentane.

A survey of the molecular weight data presented for the dialkoxyalkylalanes shows that the representative i values for these systems decrease from an upper limiting value of 4 by nearly integer increments in a manner which is wholly consistent with steric limitations about aluminum. The degree of association appears to be a function of two variables, the substitution pattern of the alkoxy groups bound to aluminum and the substitution pattern, as well as the length, of the residual alkyl group bound to aluminum. What is unique concerning the ebullioscopic data presented for these systems is the regularity of the manner in which the degree of association changes as a consequence of changes in the structural features of the groups bound to aluminum. Such an observation indicates that these systems associate according to a principle briefly stated as follows: intermolecular association occurs in noncomplexing solvents to the maximum extent consistent with the combined steric requirements of the alkyl and alkoxy groups bound to aluminum.

An interesting feature of the molecular weight data for the dialkoxyalkylalanes is the apparent manner in which the ideality of the solutions appears to depend on the nature of the alkyl and alkoxy groups bound to aluminum. For dialkoxyalkylalanes having n-alkyl and n-alkoxy groups bonded to aluminum, the trend toward progressive nonideal behavior as a function of concentration is most pronounced. This behavior is characteristic of the tri-n-alkylalanes mentioned previously. In general, as the bulk (branching) of the alkyl and alkoxy groups bonded to aluminum increases, a trend toward more ideal behavior is apparent. A similar phenomenon has been observed during the ebullioscopic investigation of alkyl magnesium halides[12].

As with the tri-n-alkylalanes, the peculiar nature of the i value plots obtained experimentally for the dialkoxyalkylalanes is understandable only in terms of some form of nonideal behavior, not as a consequence of dissociative equilibria.

Further evidence indicating the absence of dissociative equilibria within the concentration ranges studied for these systems is provided by ^{1}H NMR studies. The ^{1}H NMR spectra of the dialkoxyalkylalanes examined in this study were in no case superimposed spectra arising from the respective dialkylalkoxyalanes and trialkoxyalanes. Examination of model compounds* by ^{1}H NMR was useful for demonstrating the absence of dissociative equilibria. Within experimental error, temperature dependent ^{1}H NMR investigations produced no noticeable spectral changes over a temperature range from 0 to 90° for the model compounds. Similarly, investigations at 37° for model systems over a concentration range from 0.04 to 9.00 molal produced no prominent spectral changes.

D. General conclusions concerning association of aliphatic organoaluminum compounds

During this study a survey of the structural factors which determine the degree of association for organoaluminum compounds was made. The survey showed an amazingly stringent relationship between structural factors of the alkyl and alkoxy groups bound to aluminum and the degree of association in compounds where they appear. Such relationships can be formulated into generalizations which may be used as a guide to predict the degree of association of such compounds in noncomplexing solvents without performing molecular weight determinations. Obviously, such generalizations should be used judiciously when predicting molecular weights and degrees of association for organoaluminum compounds since there are always "exceptions to the rule". However, it is felt that cautious application of the generalizations provided will give meaningful insight for anticipating the degree of intermolecular association of organoaluminum compounds having reasonably low formula weights.

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* Model compounds chosen for these studies were $(n\text{-}C_6H_{13})Al(O\text{-}n\text{-}C_6H_{13})_2$ and $(C_2H_5)Al(O\text{-}n\text{-}C_4H_9)_2$. These systems display the most apparent concentration dependent i value behavior.

Trialkylalanes

1. The degree of association for trialkylalanes appears to depend on the substitution pattern rather than the number of carbon atoms comprising the alkyl groups bound to aluminum.

2. Trialkylalanes which exhibit no branching of the alkyl groups bound to aluminum are in general dimeric ($i \cong 2$).

3. Trialkylalanes which exhibit branching of the alkyl groups bound to aluminum at the β positions by 1 or 2 additional alkyl groups are generally monomeric ($i \cong 1$).

4. Trialkylalanes which have aluminum bound to the secondary or tertiary alkyl groups (*i.e.*, single and double substitution on carbon α to aluminum) are generally monomeric ($i \cong 1$).

5. Trialkylalanes do not appear to participate in associative equilibria involving monomer and other more highly associated species in concentration dependent fashion under the conditions of this study.

Dialkylalkoxyalanes

1. The degree of association for the dialkylalkoxyalanes depends insignificantly on the substitution pattern or the number of carbon atoms in the alkyl and alkoxy groups bound to aluminum.

2. Dialkylalkoxyalanes formed by methanolysis of trimethylalanes and triethylalanes are trimeric ($i \cong 3$).

3. Dialkylalkoxyalanes other than methoxy derivatives are in general dimeric ($i \cong 2$).

4. Dialkylalkoxyalanes do not participate in associative equilibria involving dimeric and more or less highly associated species in concentration dependent fashion within the concentration ranges studied.

Dialkoxyalkylalanes

For systems having a residual ethyl group bound to aluminum:

1. If the alkoxy groups are composed of oxygen bound to an n-alkyl group, $i \cong 4$.

2. If the alkoxy groups are singly branched in positions $\beta, \cdots, \omega$ relative to oxygen, $i \cong 4$.

3. If the alkoxy groups are singly branched α to oxygen, $i \cong 3$.

4. If the alkoxy groups are doubly branched β to oxygen, $i \cong 2$.

For systems having a residual n-hexyl group bound to aluminum:

1. If the alkoxy groups are composed of oxygen bound to an *n*-alkyl group, $i \cong 3$.

2. If the alkoxy groups are singly branched β to oxygen, $i \cong 3$.

3. If the alkoxy groups are singly branched α to oxygen, $i \cong 2$.

For systems having a residual isobutyl or 2-ethylhexyl group bound to aluminum:

1. If the alkoxy groups are composed of oxygen bound to an n-alkyl group, $i \cong 4$.

2. If the alkoxy groups are singly branched in the α position, $i \cong 2$.

EXPERIMENTAL

Solvent preparation

Normal pentane (Phillips, 99 m/o) used as solvent in these experiments was acid washed and distilled (90% "center-cut") through a 1 inch by 2-foot glass helix-packed column. The solvent was stored in tightly sealed, amber glass bottles over 3A molecular sieves.

Source, analysis and handling of trialkylalanes

The trialkylalanes (Texas Alkyls or Ethyl Corporation) used in these experiments were analyzed for hydride and alkyl content (total activity) by titration with pyridine using phenazine as indicator. Aluminum analyses were performed by hydrochloric acid hydrolysis followed by complexiometric titration with cyclohexanediaminetetraacetic acid (Hexaver) using dithizone as indicator. When the total activity and aluminum analysis of the aluminum were within 5% and 0.5%, respectively, of the theoretical values, they were used without further questioning their composition.

The trialkylalanes, tri-n-octylalane and tris(2-ethylhexyl)alane were synthesized by conventional displacement reactions with triisobutylalane as substrate and appropriate olefins. Trineopentylalane was prepared according to the method of Pfohl[20].

Prior to chemical analysis, the neat trialkylalanes were in all cases transferred to all glass containers and stored under a dry argon atmosphere.

Preparation and chemical analysis of dialkylalkoxyalanes and dialkoxyalkylalanes

The dialkylalkoxyalanes and dialkoxyalkylalanes were in all cases freshly prepared by alcoholysis of the respective trialkylalanes prior to performing ebullioscopic experiments with them. The liberated hydrocarbons were removed by vacuum distillation.

Aliquots of the product were submitted for NMR analysis to determine the ratio of alkyl to alkoxy groups bound to aluminum. This method of analysis was favored in cases where the alkyl and alkoxy groups bound to aluminum contained six carbon atoms or less. Samples of organoaluminum compounds prepared in this way could also be analyzed to determine the ratio of alkyl to alkoxy groups bound to aluminum by acid hydrolysis of an aliquot of the sample solution and subjecting the liberated alkanes and alcohols to GLC analysis. The latter method of analysis was favored for cases in which the alkyl and alkoxy groups bound to aluminum contained six or more carbon atoms.

If the product was a mobile liquid, it was used neat for ebullioscopic studies. If the product was a viscous oil or a solid, weighed amounts of solvent and aluminum compound were mixed to produce a mobile liquid mixture.

Ebullioscopic equipment

A basic description of the type of equipment and accessories used in this investigation has been described previously by Ashby[4]. The ebullioscope so described was modified in the following manner. In order to facilitate smooth boiling while the system was in use, the bottom of the boiling chamber was modified to include several platinum pins which extended from the solution under investigation, through the bottom of the ebullioscope, and into the oil bath heating system. With the exception of 3 inches of the bottom of the boiling chamber and the condenser, the entire ebullioscope was fitted with a silvered Dewar jacket to help provide a constant thermal gradient within the system while in use.

Molecular weight determinations

Molecular weight studies were performed in n-pentane at 740 mmHg. Temperature measurements were made with a conventional differential Beckmann thermometer. Temperatures measured in this manner were considered accurate to 0.001°. No stem corrections were made for the exposed portions of the thermometer.

Equations and calculations

Equation (6) was derived from the Clapeyron–Clausius relationship with the assumption of an ideal but not necessarily a dilute solution[4].

$$X_s = 1 - exp \quad -\left(\frac{\Delta T_B M_1}{1000\, K_B}\right) \tag{6}$$

The terms are defined as follows: X_s = mole fraction of solute; ΔT_B = boiling point elevation; M_1 = molecular weight of solvent; K_B = the molal boiling point; elevation constant (2.34 for the system used at 740.0 mmHg). The necessity of this extended equation for the calculations has been described elsewhere[14,28].

Determination of K_B

Determination of the molal boiling point elevation constant, K_B, for use with a particular solvent-ebullioscope system was accomplished by operating the system with a preweighed amount of solvent and adding weighed quantities of a nonvolatile solute (n-pentadecane). The data obtained in this manner over the concentration range from 0 to 0.2 molal provided a straight-line plot whose slope was K_B. A least squares program to obtain the most reliable value for K_B was used. Values obtained for replicate determinations of K_B in this manner were within ±1.4% of the average value for n determinations.

The results of the experiments are calculated in terms of intermolecular solute association values called i values[4].

$$i = \frac{W_2 M_1}{W_1 M_2}\left[exp\left(\frac{1}{\Delta T_B M_1/1000\, K_B}\right) - 1\right] \tag{7}$$

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