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VAPOUR–LIQUID EQUILIBRIUM OF ORGANOALUMINIUM COMPOUNDS

I. VAPOUR PRESSURE OF METHYLALUMINIUM CHLORIDES

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Summary

The vapour pressures of dimethylaluminium chloride and methylaluminium dichloride were determined by the ebulliometric method. The results were approximated by the Antoine equation. The determination of the vapour pressures of ethylaluminium chlorides by the same method was impossible because of a rapid thermal decomposition.

Introduction

The data published on the vapour–liquid equilibrium of organoaluminium compounds are limited almost entirely to vapour pressures of pure compounds. Moreover, in many papers vapour-liquid investigations do not represent the main subject of the work, and there is no information about the technique applied and the accuracy of the results. Fic and Dvořák, describing results of the measurements of vapour pressures of triethylaluminium and diethylaluminium chloride [1], reviewed the data published in the literature for these compounds. The differences in boiling points under the same pressure reported by various authors reach the value of 19 K. There are only a few papers [2] concerning the vapour–liquid equilibria of binary systems containing organoaluminium compounds. With regard to these facts, the systematic investigations of vapour–liquid equilibria of organoaluminium compounds were initiated. The present paper deals with the results of vapour pressure measurements of pure methylaluminium chlorides; for these compounds there were no data found in the literature, excluding the bulletins of the Texas Alkyls and Ethyl Corporation.

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Experimental

Materials

Organoaluminium compounds were obtained by conventional methods from alkylaluminium sesquichlorides and purified by repeated distillation using a 0.5 m column filled with Fensky rings.

TABLE 1

VAPOUR PRESSURE DATA FOR METHYLALUMINIUM CHLORIDES

Series I				Series II	
t[°C]	p[Torr]	t[°C]	p[Torr]	t[°C]	p[Torr]
Me_2AlCl					
62.14	87.00	100.70	367.56	85.22	217.42
62.18	87.05	100.00	367.93	85.24	217.58
69.68	119.40	103.95	418.10	85.22	217.94
69.70	119.50	103.95	418.30	85.27	218.04
74.03	142.89	108.00	475.62 *	93.55	289.90
74.00	142.73	108.00	475.26 *	93.59	289.82
79.88	178.99	111.62	530.28	97.87	334.52
79.90	178.60	111.62	530.38	97.87	334.48
86.02	223.37	116.30	611.47	103.50	399.86
86.03	223.14	116.32	611.79	103.50	400.23
92.14	276.14	118.52	651.86	124.35	766.96
92.14	275.94	118.50	652.07	124.35	767.33
95.70	312.31	121.85	716.77		
95.72	312.42	121.85	716.74		
100.72	367.16				
$MeAlCl_2$					
98.10	109.23	131.71	350.26	100.16	119.31
98.25	109.99	131.76	350.68	100.24	119.84
98.40	110.39	135.15	388.48	109.03	164.72
98.40	110.93	135.20	388.87	109.07	165.28
98.48	111.45	138.75	433.58	119.00	232.45
98.65	112.35	138.78	433.92 *	119.06	232.40
98.80	112.73	142.59	482.60	126.73	299.23
99.00	113.31	142.68	483.20	126.81	300.12
100.50	120.16	147.08	549.92	131.87	349.91
100.43	120.93	147.13	550.36	131.94	350.21
103.08	132.70	151.54	618.58 *	141.92	472.62
103.25	133.49	151.60	618.28 *	142.00	473.13
111.45	178.72	150.86	617.75	149.24	579.28 *
111.53	179.40	154.40	683.08	149.24	579.40 *
115.64	205.82	154.30	683.04		
115.71	206.60	157.25	739.24		
123.23	267.28	157.30	739.04		
123.32	267.74	159.48	781.27		
127.16	305.03	159.50	780.61		
127.40	306.06				

Technique

The vapour pressure was measured by the ebulliometric method using a modified Świetosławski ebulliometer, constructed as reported [3]. There was no manostat in the system, and pressure stability was reached with a buffer container. Vapour pressure measurements were made with a mercury manometer equipped with a catetometer of ± 0.01 Torr resolution. Temperature was measured by mercury thermometers of 0.1 K resolution, previously calibrated. Readings were corrected according to standard methods [4].

Testing of the system

The experimental set-up was tested by measuring the vapour pressure of water. Nine values of temperatures (t_{exp}), obtained in the range of 200–760 Torr, were compared with the values calculated from the Antoine equation (t_{calc}) [5]. The standard deviation, $\Delta = [\Sigma(t_{\mathrm{calc}} - t_{\mathrm{exp}})^2/9]^{0.5}$, was 0.09°C, and was assumed to be satisfactory.

Measurements of vapour pressure of organoaluminium compounds

Before beginning the measurements the unit was attached to a vacuum line and repeatedly purged with purified argon. Organoaluminium compounds were injected with a syringe. Great care was taken with the determination of the plateau, i.e. the range of heating in which the temperature is constant. In the case of organoaluminium compounds the reflux from a cooler corresponding to the plateau was much higher than in the case of water, alcohol etc. This could be caused by the higher molecular weight and viscosity and low thermal conductivity of the compounds investigated, which makes proper heating of the thermometer socket difficult.

Results

Measurements of (p,t) values of each compound were carried in two series, I and II, in which the pressure was reduced and increased, respectively. Reproducibility between these series was taken as the criterion of thermal stability of the compounds investigated. In the case of Me_2AlCl and $MeAlCl_2$, boiling for more than 12 hours did not cause any significant decomposition. In the case of Et_2AlCl and $EtAlCl_2$ a rapid decomposition was observed, which made ebulliometric measurements impossible.

The results obtained for methylaluminium chlorides are listed in Table 1.

Discussion

Testing of thermal stability

Results from series I were divided into 3 temperature ranges and approximated by equation $\ln p = a + b/T$, using a least squares method. The equations obtained were subsequently used for calculation of boiling temperatures for series II, and these values were compared with the experimental ones. The differences of ± 0.2°C (without any trend) were assumed satisfactory as compared with the stability of the plateau (± 0.1°C).

Approximation by the Antoine equation

Pressure values (Torr) were approximated by the equation

$$\log_{10} p = A + B/(C + t)$$

according to a method described by Malanowski [3], with automatic rejection of large deviations. The following equations were obtained:

$$Me_2AlCl\text{: } \log_{10} p = 7.448133 - 1652.266/(237.934 + t) \quad (1)$$

(standard deviation $\Delta \bar{p} = 3.1062$ Torr, 39 values appeared to be consistent; values rejected are denoted in Table 1).

$$MeAlCl_2\text{: } \log_{10} p = 7.511030 - 1820.931/(234.822 + t) \quad (2)$$

(standard deviation $\Delta \bar{p} = 1.8513$ Torr, 48 values appeared to be consistent).
Better approximation by Antoine equation can be reached for smaller temperature intervals.

The values of the normal boiling temperatures calculated from the Antoine equation are as follows:

Me_2AlCl: $t(760\text{ Torr}) = 123.8°C$

$MeAlCl_2$: $t(760\text{ Torr}) = 158.4°C$

From eqs. 1 and 2 the molar entropy of vapourization can be calculated. The values of $\Delta S/R$ of 11.54 and 11.70 obtained for Me_2AlCl and $MeAlCl_2$, respectively, are in good agreement with the Trouton rule. The results prove that the compounds investigated are completely dimeric in both vapour and liquid states.

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