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THE DETERMINATION OF THE DENSITY OF A METHYLALUMINIUM DICHLORIDE–DIMETHYLALUMINIUM CHLORIDE MIXTURE AS A METHOD OF ANALYSIS

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SUMMARY

The density of methylaluminium dichloride–dimethylaluminium chloride was studied at various temperatures in relation to the percentage composition. Over the dimethylaluminium chloride concentration range 100–45% w/w the density varies linearly with the composition. If the density of a mixture of unknown composition is determined, a calibration curve enables the composition to be read with an accuracy of 0.25%. This determination is a simple, rapid and sufficiently accurate method of analysis.

Numerous methods are known for the analysis of organoaluminium compounds, starting with the classical procedure involving titrimetric determination of aluminium and halogen in an organoaluminium compound hydrolyzate with measurement of the amount of alkyl groups released in gaseous form during the hydrolysis, and recently supplemented by instrumental methods including conductometry, potentiometry, colorimetry, etc.[1]. All these procedures are time-consuming and often require the use of complex apparatus.

In the course of our investigations it was necessary to establish the contents of methylaluminium dichloride and dimethylaluminium chloride in a reaction mixture. The large number of determinations needed made it desirable to develop a simple and rapid analytical procedure. It was hoped to develop a method based on the difference between the densities of the two components of the mixture to be analyzed. Methylaluminium dichloride[2] is a solid with a density of 1.51 $g \cdot cm^{-3}$, whereas dimethylaluminium chloride[3] is a liquid with a density of 1.00 $g \cdot cm^{-3}$. A mixture of the two yields a solution that becomes saturated at about 60 mole% of the dichloride at room temperature.

The density was measured in relation to mixture composition at temperatures of 20, 30, 40 and 50°. Solutions of the required concentrations were prepared synthetically by mixing accurately weighed amounts of the pure components. The density was measured in a bulb with an outlet tube, 20 ml capacity, graduated in tenths of a milliliter. Changes in volume could be read to within 0.01 ml. The bulb was flushed with dry deoxygenated nitrogen, weighed, filled by means of a hypodermic syringe with the solution to be examined, and reweighed. The filled bulb was connected through an oil

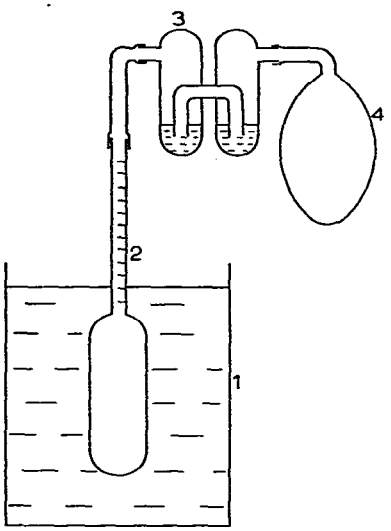

Fig. 1. The assembly for measuring the density of organoaluminium compounds. (1) Thermostat; (2) bulb containing an organoaluminium compound; (3) oil-filled washer; (4) pressure-levelling rubber balloon.

washer with a pressure-levelling balloon, placed in a thermostat (Fig. 1) and maintained at a temperature of 20° for 30 min (prolonged thermostatting resulted in no change of volume). The volume of the liquid was then read. The temperature was raised to 30°, the liquid thermostatted for 30 min, and the liquid volume read again. Analogous procedures were performed at temperatures of 40 and 50°. The density of the liquid was calculated by dividing the sample mass by the volume recorded.

The densities of the solutions containing 100, 90, 80, 70, 60, 50, 45 and 40% w/w of dimethylaluminium chloride were determined. Also, the percentage compositions of dimethylaluminium chloride solutions saturated with methylaluminium dichloride were studied at temperatures of 20, 30, 40 and 50°. A flask containing a solution of methylaluminium dichloride in dimethylaluminium chloride with crystals of the dichloride, was thermostatted for 24 h until the solid–liquid equilibrium became established. A sample of the supernatant liquid was then carefully withdrawn by means of a hypodermic syringe and its density measured by the method described above. Data are presented graphically in Fig. 2.

It is evident from the Figure that the density *vs.* composition plot is a straight line over the 100–45% dimethylaluminium chloride range at all temperatures investigated. The straight lines are approximately parallel at the given temperatures. To enable the lines to be precision plotted, the densities corresponding to dimethylaluminium chloride concentrations of 100 and 50% w/w are given in Table 1 for temperatures of 20, 30, 40 and 50°.

At dimethylaluminium chloride concentrations below 45% w/w, the lines bend towards higher densities which is presumably attributable to a condition close to the saturation state. The concentrations corresponding to the saturation states may lead to error. The close chemical affinity of the two components may have resulted in incomplete crystallization despite the protracted period of thermostatting, and the supernatant liquid may have contained suspended microcrystals which would

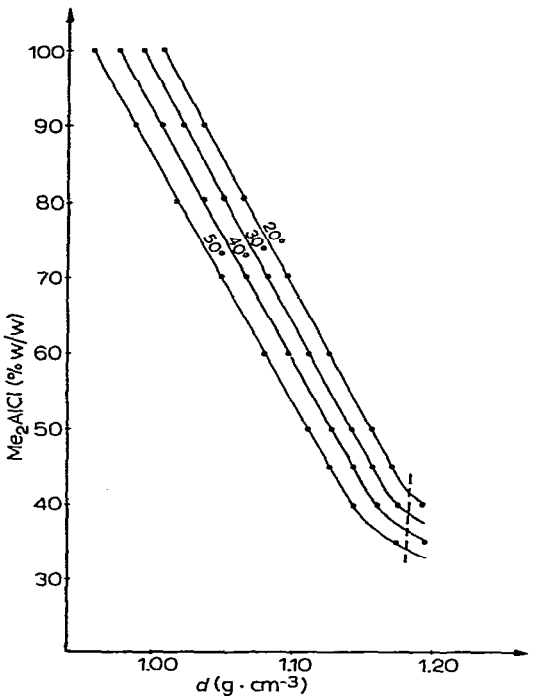

Fig. 2. The density (d) of Me_2AlCl–$MeAlCl_2$ mixtures in relation to composition. The dashed line indicates the saturation state.

TABLE 1

THE DENSITIES OF Me_2AlCl AND 50/50 Me_2AlCl–$MeAlCl_2$ AT VARIOUS TEMPERATURES

Temp. (°C)	Density ($g \cdot cm^{-3}$)	
	Me_2AlCl	$Me_2AlCl + MeAlCl_2$
20	1.0070	1.1560
30	0.9915	1.1415
40	0.9755	1.1270
50	0.9570	1.1100

interfere with the measurement and production of reproducible data. Nevertheless, the accompanying diagram prepared for dimethylaluminium chloride concentrations from 100 to 45% w/w (*i.e.*, to the saturation of the solution at room temperature) enables the composition of a mixture to be read to within 0.25%, provided its density is known or has been determined beforehand. With the aid of this diagram a straight line corresponding to a given ambient temperature can be constructed by interpolation and the measurement may be carried out with no thermostatting of the sample. The practical application of this method demonstrated its usefulness in laboratory work and permitted simple rapid and accurate determinations of the compositions of the mixtures investigated.

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