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## Density Data for Two Methylchlorosilanes

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Density data for dimethyldichlorosilane (DDS) and for methyltrichlorosilane (MTS), which were used several years ago to lay the foundation for a successful routine method to aid in controlling chlorosilane distillation, are given below. There appear to be no comparable earlier published data.

**Pure Compounds.**—As a by-product of painstaking distillation work done in 1943, the details of which are to be published later, the following densities (g./ml. at 25°) were obtained on chlorosilanes among the purest ever prepared here: for DDS, $1.066_3$; for MTS, $1.269_1$. The corresponding weight percentages of chlorine by hydrolysis were: DDS, $54.9_3$ *vs.* $54.9_5$ (theor.); MTS, $71.1_9$ *vs.* $71.1_7$ (theor.), the deviations from the theoretical being comparable with the possible uncertainty in the atomic weight of silicon.[1]

**Temperature Coefficients.**—For the interval 25–30°, dilatometric measurements on the best materials available from the pilot plant in 1944[2] yielded the following values for the change in density with temperature (g./ml./°C.): DDS, 0.00145; MTS, 0.00173. These precise results are in good agreement with older data (0.0015 and 0.0018, respectively) obtained on a Westphal balance.

The 50-ml. dilatometer was designed and manipulated to give a precision better than 0.005% in a density determination. Special techniques were required to mitigate the difficulty of handling the methylchlorosilanes, and the dilatometer itself did not change weight by more than a few tenths milligram—if at all—during the measurements.

**Volume Additivity.**—In order to establish whether any volume change on mixing DDS and MTS is negligible for purposes of routine control, the routine density-balance (to be described elsewhere) was used on DDS[2] and MTS[2], and on six solutions carefully prepared by weight therefrom. The measured densities are given in Table I alongside densities calculated for the solutions on the assumption of volume additivity.

TABLE I

VOLUME ADDITIVITY OF DDS AND MTS AT 27°

| Weight fraction DDS | Measured densities, g./ml. | Calculated densities, g./ml. |
|---|---|---|
| MTS | $1.259_3$ | .... |
| DDS | $1.061_8$ | .... |
| 0.81450 | $1.093_9$ | 1.0936 |
| .66014 | $1.121_7$ | 1.1216 |
| .42930 | $1.166_5$ | 1.1662 |
| .42930 | $1.165_9$ | 1.1662 |
| .29397 | $1.194_0$ | 1.1940 |
| .14036 | $1.227_5$ | 1.2273 |

The measured densities tend to exceed those calculated by an amount comparable with the experimental error; consequently, volume additivity could permissibly be assumed in the control work. The data in Table I indicate that this pair of methylchlorosilanes belongs among those for which volume additivity comes closest to being realized, which suggests that a thorough investigation of these and other chlorosilanes along lines laid down by Young[3] would be welcome.

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[1] Baxter, Guichard and Whytlaw-Gray, THIS JOURNAL, **69**, 731 (1947). The chlorine titrations were not of atomic weight precision. Correction of the final average chlorine contents for all conceivable sources of error would lower the percentages by 0.02; taking 28.10 as the atomic weight of silicon would produce the same change in the theoretical values. The density data have been corrected for all conceivable sources of error.

[2] The methylchlorosilanes used in the work on temperature coefficients and volume additivity were sufficiently pure for these purposes as the following data show. DDS, density at 25°, 1.065 g./ml.; wt. % Cl by hydrolysis, $54.7_2$, $54.6_4$. MTS, density at 25°, 1.263 g./ml.; wt. % Cl by hydrolysis, $70.6_4$, $70.6_9$.

[3] Young, "Distillation Principles and Processes," Macmillan and Co., Limited, London, England, 1922, pp. 31 *et seq.*

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## *p*-Bromobenzyl Bromide in the Identification of Some Aromatic Carboxylic Acids

BY B. A. FIEKERS AND E. M. DI GERONIMO

As part of a study of suitable derivatives for the identification of organic acids, *p*-bromobenzyl esters of benzoic acid, some of its derivatives and similar acids have been prepared and characterized in this Laboratory. The general preparation of these esters is given by the equation.

$$p\text{-BrC}_6\text{H}_4\text{CH}_2\text{Br} + \text{NaOCOR} \longrightarrow \text{NaBr} + p\text{-BrC}_6\text{H}_4\text{CH}_2\text{OCOR}$$

### Experimental

***p*-Bromobenzyl Bromide.**—This was prepared from *p*-bromotoluene by bromination of the side-chain, using ultraviolet light, quartzware and heat.[1] The solid product was purified by recrystallization from alcohol until a constant melting point (61.5°) was obtained.

**Preparation of the Esters.**—The sodium salt of the acid was formed by dissolving a slight excess of the acid in 5 ml. of 0.5 *M* sodium carbonate solution. The mixture was refluxed on a steam-bath and water was added sparingly, when necessary, until solution was complete. 1.25 g.

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[1] Weizmann and Patai, THIS JOURNAL, **68**, 150 (1946).