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Spectrophotometric Determination of Acetaldehyde in Mono-vinyl Acetate

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It is well known that in the polymerisation of mono-vinylacetate the presence of acetaldehyde decreases the molecular weight of the poly-vinylacetate obtained[1, 2]. Addition of acetaldehyde has even been used as a regulator for the viscosity of the end product[3]. It is accordingly of interest to have available reliable and sensitive methods for determination of acetaldehyde in vinyl acetate, if possible down to 0.1 g/l.

Physical methods of analysis are preferred to chemical methods because whenever vinyl acetate is brought into contact with water there is always the danger of saponification of the ester and subsequent increase in the aldehyde content.

Absorption in the ultraviolet region has been used by a German company for determination of acetaldehyde[4]. No details as to procedure, accuracy etc. were given, and it was also reported that another company found the method unreliable.

We have tested the method with the aid of a Beckman Spectrophotometer Model DU[5] and obtained an entirely satisfactory result. All measurements were made at room temperature with a cell thickness of 1.004 cm.

Vinyl acetate of commercial origin was distilled three times in a Podbielniak column modified by Skärblom and Linder[6]. The height of the column is 200 cm, and the fractionating efficiency corresponds to 30—35 theoretical plates. Fig. 1 shows the absorption curve for the original product and the different distillates. The optical density D is calculated from

$$D = -{}^{10}\log T/T_0$$

(T and T_0 transmission of sample and reference substance resp.)

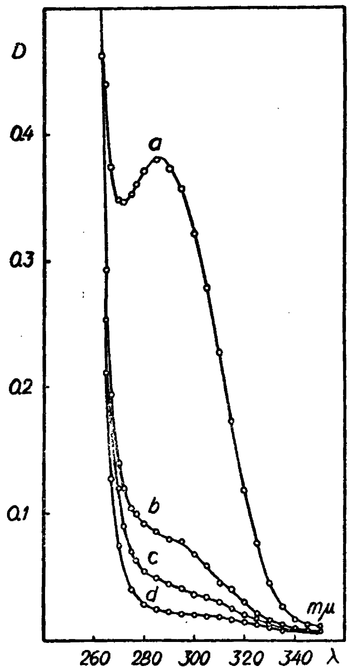

Fig. 1. Optical density D of mono-vinylacetate as function of wave-length. Distilled water was used as reference substance. Curve a obtained with the commercial product, curves b, c and d after single, double and triple distillations respectively.

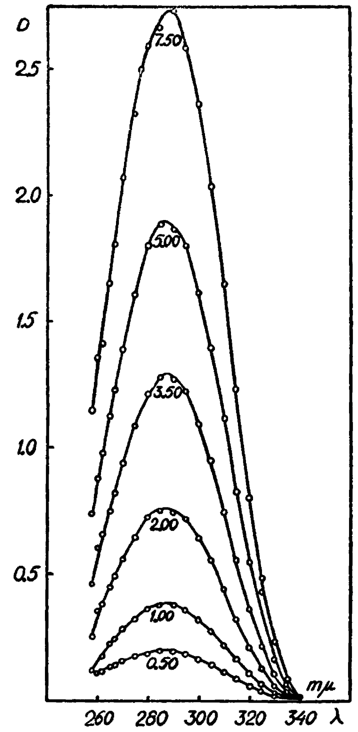

Fig. 2. Optical density D of acetaldehyde (conc. in g/l denoted for each curve) in mono-vinylacetate as function of wave-length. Triple distilled vinyl acetate (curve d in Fig. 1) used as reference substance.

Addition of different amounts of acetaldehyde gave the absorption curves in Fig. 2. From a similar series of curves the extinction at $\lambda = 287$ mμ (= position of the peak) plotted against concentration gave the curve in Fig. 3, which shows that the Lambert-Beer law is well fulfilled within the concentration interval 0—6 g/l. The fact that the point corresponding to the highest concentration falls below the straight line can easily be explained as experimental error, the transmission in this case being less than 1 %.

From the values of D the extinction coefficient ε (concentration in moles per liter, thickness of absorbing layer in cm) has been calculated in Table 1. The average is $\varepsilon = 17.3$.

Fig. 1 shows that at $\lambda = 287$ mμ even the triple distilled vinyl acetate has a certain absorption compared with distilled water. It is uncertain whether

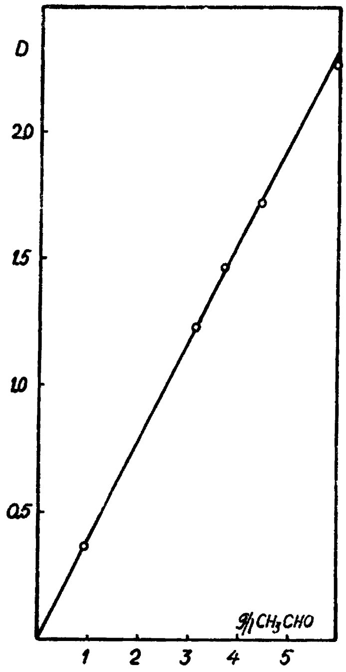

Fig. 3. Optical density D at λ = 287 mμ for acetaldehyde in vinyl acetate.

Table 1. Extinction coefficient ε calculated from experiments at different concentrations.

Conc. g/l	ε
0.94	17.3
3.13	17.3
3.72	17.4
4.46	17.0
5.95	(16.8)

this residual optical density should be ascribed to the absorption of vinyl acetate itself or to acetaldehyde still present in the liquid, but the latter alternative seems more probable. Previous investigations of the ultraviolet absorption spectrum of vinyl acetate [7, 8] were not continued beyond λ = 280 mμ. The maximum amount of acetaldehyde that can be present in the triple distilled product is 0.06 g/l. In another experiment double distillation resulted in a maximum amount of acetaldehyde = 0.09 g/l.

In order to test the reproducibility of the analysis different amounts of acetaldehyde were added to the distilled vinyl acetate. The result is seen in Table 2. The acid number, *i. e.*, mg KOH required for neutralisation per g of sample, was also determined. From the outset it was expected that the presence of acetic acid in the vinyl acetate should not interfere with the aldehyde analysis. Addition of acetic acid in two of the tests confirmed this. From the table we may draw the conclusion that the accuracy of the method is about 0.1 g/l. The minimum detectable amount is estimated to be a few thousands of a percent. It might be mentioned that some of the discrepancies in Table 2 can undoubtedly be ascribed to the difficulty of accurately preparing dilute solutions of an easily volatile solute like acetaldehyde.

Table 2. Analytical tests.

Conc. CH_3CHO in g/l		Acid number
Added	Found	
0.09	0.11	< 0.1
0.68	0.73	< 0.1
2.16	2.25	9.9
2.18	2.39	1.2
2.33	2.40	< 0.1
4.67	4.61	< 0.1

SUMMARY

A method for determining acetaldehyde in mono-vinylacetate down to a few thousands of a per cent by means of ultraviolet absorption is described. From the law of Lambert-Beer the extinction coefficient at $\lambda = 287$ mμ is calculated to be $\varepsilon = 17.3$ (conc. in moles per liter).

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REFERENCES

1. Blaikie, K. G., and Crozier, R. N. *Ind. Eng. Chem., Ind. Ed.* **28** (1936) 1155.
2. Skirrow, F. W. *Brit. Plastics* **10** (1939) 416, 507.
3. DeBell, J. M., Goggin, W. C., and Gloor, W. E. *German plastics practice.* Springfield, Mass. (1946) p. 106.

4. Rosenquist, E. N. *The production of mono-vinylacetate. F. I. A. T. Report* no. 860 (1946).
5. Cary, H. H., and Beckman, A. O. *J. Optical Soc. Am.* **31** (1941) 682.
6. Skärblom, K. I., and Linder, Å. *Tek. Tid.* **67** no. 7, *Kemi* (1937) 12.
7. Paist, W. D., Blout, E. R., Uhle, F. C., and Elderfield, R. C. *J. Org. Chem.* **6** (1941) 273.
8. Calvin, M., Magel, Th. T., and Hurd, C. D. *J. Am. Chem. Soc.* **63** (1941) 2174.

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