

Determination of Stearic Anhydride in the Presence of Isopropenyl Stearate

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Work is in progress in this laboratory to develop a commercially feasible process to make isopropenyl stearate (IPS) from stearic acid. Stearic anhydride is an undesirable reactor by-product. One constraint imposed by the process is that the stearic anhydride concentration be equal to, or less than, 2% by weight in the catalyst free product stream. The current method of determination for stearic anhydride, IR, is neither sufficiently accurate nor precise in this concentration range.

Johnson and Funk (1) reported a potentially suitable method for anhydride determination. They reacted morpholine with the anhydride and then back titrated the unreacted morpholine with HCl. They stated that ketene, diketene, and acid chlorides could interfere. The chemistry of isopropenyl stearate as an acylating agent is sufficiently similar to these compounds that it could be expected to in-

(1) J. B. Johnson and G. L. Funk, *Anal. Chem.*, **27**, 1464-5 (1955).

Table I. Determination of Exploratory Samples of St₂O^a in IPS^b and/or Stearic Acid

IPS	Weighed, g		Determined, g		Time on steam bath, min
	Stearic acid	St ₂ O	St ₂ O	St ₂ O	
5.01	...	0.21	0.21		12
5.00	...	0.59	0.62		12
5.03	...	0.05	0.10		12
5.02	0.01		12
5.02	...	0.28	0.33		15
5.06	0.50	0.28	0.39		15
...	0.51	...	0.00		15
5.02	0.02		15

^a Stearic anhydride. ^b Isopropenyl stearate.

Table II. Experimental Design 1 and Results—Butanol Based Reagents

	Design 1, grams		Results
	+1	-1	
A = IPS ^a	5.0	0	
B = Stearic acid	0.5	0	
C = St ₂ O ^b	0.3	0	
	Response, ml HCl	Variance	
1	47.4, 47.5		
A	46.6	2.26 ^d	
B	47.5	0.195 ^c	
C	46.5	2.05 ^d	
AB	46.2	0.165 ^c	
AC	45.8	0.0003	
BC	46.4	0.0378	
ABC	45.0	0.0078	

Error mean square =

$$\frac{\sum S^2(ABC, AC, BC, 2 \text{ blanks})}{4} = 0.093$$

^a Isopropenyl stearate. ^b Stearic anhydride. ^c $p \leq 0.05$. ^d $p \leq 0.01$.

terfere. Therefore, a study was made to determine whether this method could be used or adapted to accurately determine low concentrations of stearic anhydride in isopropenyl stearate. Several key questions had to be answered. Does the method give an accurate determination for stearic anhydride in the concentration range of 0–10% by weight? Does isopropenyl stearate interfere? Will stearic acid interfere?

EXPERIMENTAL

Simulated samples for determination were prepared so that the concentration range would be equal to that found in process efflux. A nominal sample size of 6 grams was chosen, yielding mixtures of one or more of the following: IPS (5 grams), stearic acid (0–0.5 gram), and stearic anhydride (0–0.6 gram).

The Johnson and Funk method was modified for use on stearic anhydride in IPS products. Fifty ml of 0.5N morpholine reagent were added to a sample of approximately 6 grams. A condenser was attached and the sample heated for 15 minutes on a steam bath. One hundred ml of methanol was added and titrations were made potentiometrically to a predetermined end point of pH 3.0.

Table III. Experimental Design 2 and Results—Methanol Based Reagents

	Design 2, grams	
	+1	-1
A = IPS ^a	5.0	0
B = Stearic acid	0.5	0
C = St ₂ O ^b	0.3	0
	Response, ml HCl	Variance
1	46.75, 46.85	
A	46.85	0.09
B	47.05	0.07
C	46.65	2.49 ^c
AB	46.05	0.015
AC	45.80	0.0003
BC	45.65	0.07
ABC	45.45	0.025

Error mean square =

$$\frac{\sum S^2(ABC, AB, AC, BC, 2 \text{ blanks})}{5} = 0.026$$

^a Isopropenyl stearate. ^b Stearic anhydride. ^c $p \leq 0.01$.

Table IV. Data Used to Establish Confidence Limits

IPS ^a	Weighed, g St ₂ O ^b	Determined, g St ₂ O ^b	Error, g (Weighed - determined)
5.052	0.0	-0.011	0.011
6.318	0.0	-0.011	0.011
5.946	0.0	0.006	0.006
5.474	0.0	0.0	0.0
5.624	0.088	0.146	-0.058
5.740	0.142	0.169	-0.027
6.065	0.188	0.194	-0.006
5.539	0.251	0.256	-0.005
6.158	0.294	0.315	-0.021
6.833	0.146	0.135	0.011
11.464	0.170	0.163	0.007
18.632	0.144	0.152	-0.008
0.0	0.156	0.149	0.007
0.0	0.144	0.118	0.026
0.0	0.155	0.130	0.025
0.0	0.0	0.007	-0.007
0.0	0.0	-0.016	0.016
0.0	0.0	0.007	-0.007
0.0	0.0	-0.0014	0.0014
0.0	0.0	-0.016	0.016
0.0	0.0	0.047	-0.047
0.0	0.0	-0.004	0.004
0.0	0.0	-0.024	0.024

^a Isopropenyl stearate. ^b Stearic anhydride.

RESULTS AND DISCUSSION

In initial trials, it was found that morpholine will react with stearic anhydride when Johnson and Funk's procedure is used. However, the reaction was very slow and unreacted anhydride remained after 24 hours at room temperature. In an attempt to accelerate the reaction, a group

of samples was heated on a steam bath. Their composition and determinations, shown in Table I, indicate that the morpholine reaction is complete in 15 minutes at an elevated temperature. It was noted that condensers are required to prevent loss of the morpholine during heating.

The reaction temperature on the steam bath is limited by the boiling point of the methanolic reagent (61 °C). Therefore, an attempt was made to further increase reaction rate by substituting butanol for methanol in each solution. This increased the solution boiling point to 78 °C. A 2³ factorial experimental design was made with the variables stearic anhydride, IPS, and stearic acid concentration. Titrations were made colorimetrically. Details of the design are shown in Table II. The results show a highly significant ($p \leq 0.01$) interference due to IPS, significant ($p \leq 0.05$) interference due to stearic acid, and significant interference attributable to the IPS-stearic acid interaction.

As this approach was unpromising, use of methanol was re-introduced and the above design was repeated. Actual samples from the process are colored, and prevent colorimetric titrations. Therefore, this design was analyzed by potentiometric titration. In order to facilitate the titration, ca. 100 cm³ of methanol is added after heating. The end point was taken as the inflection point on the curve. The details and results of the design are listed in Table III. The results indicate no significant interference.

To establish confidence limits for the determination, 23 data points were statistically determined. These data are

listed in Table IV. They include 3 samples containing only stearic anhydride, 4 samples with IPS and no stearic anhydride, 8 samples with both IPS and stearic anhydride, and 8 samples containing no IPS or stearic anhydride (blanks). The variances were pooled after it was determined that the variances of the 4 sets were not significantly different by pairs (F test, $p \leq 0.05$). The confidence limits were determined as ± 0.044 gram. For a nominal 6-gram sample of stearic anhydride in IPS this ± 0.044 gram stearic anhydride is equivalent to $\pm 0.73\%$. The mean of the pooled error data was not significantly different from 0.0 (by t -test).

CONCLUSIONS

The analytical method of Johnson and Funk, with the modifications described, can be used to measure stearic anhydride in isopropenyl stearate. The analysis, as modified, is not affected by IPS or stearic acid in the concentration range of 0–10% stearic anhydride. Analytical confidence limits of $\pm 0.73\%$ were found, which is considered acceptable precision.

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