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The Separation of Aliphatic Alcohols From Accompanying Hydrocarbons By Extraction With Aqueous Methanol

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I. Introduction

The more recent alcohol syntheses, such as the synol synthesis and the oxo process, always give a primary product consisting of alcohols and of accompanying hydrocarbons. In the oxo-process, the alcohols may be separated by distillation, provided that sufficiently well defined and narrow boiling components were used as initial raw material; but in the synol synthesis the alcohols are obtained in mixture with equally high boiling non-alcoholic components. Thus, in the synol synthesis, the separation of the alcohols is possible only by the following methods:

1. By chemically fixing the alcohols; this can be done by esterification, mostly with poly-basic acids such as boric-, arsenic-, adipic-, phthalic- and other acids, which give high boiling esters.

2. By physical separation methods, such as adsorption on silica gel; or by taking advantage of the greater solubility of the alcohols in organic solvents such as methanol, ethanol, acetone, etc.

After the preliminary experiments of Dr. Reisinger had established that aqueous methanol was a promising extracting-agent for the alcohols, it was decided to undertake a thorough study of the efficiency and capacity of the methanol extraction; this was to be done for the purpose of furnishing the basis for an eventually feasible technical process.

II. Experimental Bases

1. Solubility Of The Alcohols And Hydrocarbons In Aqueous Methanol

The alcohols in the low or intermediate boiling range, as compared to the hydrocarbons in the same range, are substantially more soluble in aqueous methanol. The synol fractions 120-170, 170-220, 220-270 and 270-320° were examined with particular care. The individual fractions were separated into alcohols and hydrocarbons by the boric acid method, and their solubility in aqueous methanol was determined individually. Figure 1 shows how many parts by volume (methanol-containing) of hydrocarbons or alcohols of the fraction 120-170° are left, undissolved, as upper layer with decreasing methanol concentration. It can easily be seen that the hydrocarbons (curve I) are already practically insoluble at methanol dilutions at which the alcohols (curve 2) are still completely dissolved. Both the alcohols and the hydrocarbons drop out almost entirely within a rather narrow concentration range. The alcohol curve at first exceeds the 100% boundary because the alcohols contain appreciable amounts of dissolved methanol. Now, the higher the fraction used for this study, the higher will be the methanol concentration at which the alcohols as well as the hydrocarbons are no longer soluble. (Unfortunately, the experimental details were destroyed by enemy action). Therefore, the wider the fraction, the flatter will be the slope of the curves.

A good separation of the alcohols from the hydrocarbons is to be expected only when the alcohols do not start dropping

out before a degree of dilution has been reached at which the hydrocarbons are already practically insoluble. This means that the components used initially cannot be of any great width if good results are to be achieved. It is for this reason that fractions of 50° width each were used. Furthermore the slope of the curve is the steeper, the greater the amount of solvent used (see below). The curves of Figure 1 were determined with the five-fold amount of solvent.

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2. Solubility Curve Of The Synol Products

If now a mixture containing one part alcohol and one part hydrocarbon is treated with aqueous methanol of decreasing concentration for the purpose of separating the hydrocarbons from the alcohols, one will not get a simple addition of the two curves (Fig. I, I and II) but rather, the curve becomes considerably flatter due to mutual solubilization effect (Fig. I, III). In other words, alcohols are still present in the separated hydrocarbon oil, and hydrocarbons are still present in the extract.

Figure II represents the course of the separation when the synol fraction 120-170°, which contains 56% alcohols, 2% esters, aldehydes, ketones, and 42% hydrocarbons, is treated with various different amounts of solvent.

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It is seen that when small quantities of solvent are used, there is hardly any fractional precipitation: at 42%, the

curve only shows a more or less sharply pronounced turning point, whereas at higher solvent-concentrations always....

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For this, it will be sufficient if an intermittent, two-stage counter current process in two graduated separation funnels is set up, as is shown schematically on the following page. The methanol has a turning point concentration (See Fig. II), so that in both cases 42% "neutral oil" are obtained. Whereas in case A the oil layer in the first separation funnel is higher than 100, in case B the oil layer decreases immediately. Correspondingly, the effect (in case A) is hardly better than in the co-current method, whereas in case B the extraction has become so selective that it fully meets all the requirements.

If, in case A, more than 2 stages in counter current are used, the alcohol content in the neutral oil will decrease a little more, but it reaches a certain limiting value over which one cannot pass; in contrast to this, when a three-fold amount of methanol is used in several stages, practically no alcohol at all is left in the neutral oil. These experiments have now shown that, with the synol fraction 120-170°, a two-fold amount of methanol is still barely sufficient.

For the higher synol fractions, the precipitation concentrations for the alcohols and for the hydrocarbons are closer and closer (and at higher methanol concentrations). Therefore,

Separation Funnel I			Separation Funnel II	
Fresh synol →	oil layer	→	oil layer	Neutr. oil product
Extraction product ←	extr. layer	←	extr. layer	Fresh methanol

After shaking and changing the layers 3-5 times according to this method, an equilibrium is reached, i.e. the quantities and concentrations in the 4 layers become constant.

The equilibrium conditions, with synol fraction 120-170° (42% neutral oil), are given below; in A. the methanol = the synol; in B., three times as much methanol is used.

	Separation Funnel I		Separation Funnel II	
A.	100 pts. synol oil (of which 56 pts. = 56% alcohols and 2 pts. = 2% esters and aldehydes) →	120 parts →	42 parts →	42 parts neutral oil (of which 7 pts. = 17% alcohols
	158 parts extract (of which 7 pts. = 12% of the oil hydrocarbons) ←	158 parts ←	175 parts ←	100 parts aq. methanol
B.	100 pts. synol oil (of which 56 pts. = 56% alcohol and 2 pts. = 2% esters and aldehydes) →	50 parts →	42 parts →	42 parts neutral oil (of which .1 part = .2% alcohols)
	358 parts extract (of which .1 parts = .2% of the oil hydrocarbons and 2 parts = 3% of the oil esters and aldehydes) ←	358 parts ←	308 parts ←	300 parts aq. methanol

these higher fractions require a still larger amount of solvent if the same results are to be obtained. The approximate required amounts and concentrations of aqueous methanol for the obtaining of 97% alcohols are summarized in the table below:

No.	Synol Fraction	Optimum Methanol Concentration In Vol.-%	Required No. of Parts of Aqueous Methanol for The Extraction of 1 Part Synol Oil
1	120-170°	68	2
2	170-220	76	3
3	220-270	81	6
4	270-320	85	10

For the preparation of alcohols with a 5-8% hydrocarbon concentration, a three fold amount of extracting agent will be sufficient for the 3rd fraction, whereas the 4th fraction will require a 5-fold amount.

When one is not dealing with extremely high or extremely low alcohol concentrations (above 50%?(almost illegible, Transl. or below 10%) in the synol product, both the quantity and the concentration of the methanol are so much less dependent on the alcohol content than on the boiling range, that the former can be practically disregarded. For the 4th fraction in the above table, the methanol extraction is probably without significance since the amount of methanol which has to be distilled is too great, i.e. the sharpness of separation too small. Only the extraction up to about 250° (i.e. up to the C_{12} alcohol) offers technical possibilities.

5. Extraction Of The Oxo-Alcohols

In the oxo process too, the alcohols are obtained in

mixture with hydrocarbons. However, the alcohols resulting from the synol synthesis have a chain length which is shorter, by several C-atoms, than that of the hydrocarbons from which they are to be separated; the alcohols obtained by the oxo reaction, on the other hand, are longer, by one C-atom, than the hydrocarbons formed in the same reaction. This means that the solubility differential is smaller, which in turn means that considerably greater amounts of solvent must be used if good separation is desired. (For the lower fractions, about double). Since the oxo-alcohols can, in general, be easily separated from the hydrocarbons by distillations - especially when one starts with narrow olefin cuts - the extraction method will, in most cases, not be required for these products.

6. Processing Of The Extract

The extract is broken down by distilling off the methanol in a column. Once the methanol has distilled, the liquid remaining in the still separates into two layers, one of alcohols and other one of water, which can be separated by mechanical means. When the methanol, mixed with water, is again used for the extraction, a relatively small reflux should be supplied to the column so that a little water and alcohols will go over but the energy cost is kept as low as possible. In actual practice, a reflux ratio of 1/3-3 will be sufficient, depending on the boiling range of the alcohol.

III. Practidal Operation Of The Extraction

1. Three-stage Apparatus

For the continuous extraction, a three-stage glass

apparatus, which is illustrated in Fig. III (Missing Transl., was used. The operation of this apparatus can be seen from this figure. The regulation of the amounts of synol and methanol to be fed into the unit can be done either by capillary tubes of different diameter or by coupled feed-pumps. The dosage in all the other stages is regulated by the apparatus itself, as follows: the mixing vessels are followed by settling containers which are in the form of Florentine flasks. The amounts of liquid leaving the settlers must therefore be fed into the next stage. The gear pumps which serve this purpose run so fast that they can carry more product than is actually fed to them. Since during this extraction there are always small amounts of iron hydroxide which precipitate (from rusty containers, etc.) which had been in colloidal suspension in the synol oil, a filter will be inserted in front of the pumps. The four containers at the top have the function of insuring a uniform feed to the mixers. The stopcocks on these containers remain completely open at all times, and are closed only when disturbances arise. The small unit with mixing vessels of one liter content each was already able to process over 1,000 liters of product in 24 hours. (The amount of alcohol which can be extracted per unit time decreases with increasing chain-length because 1) the stock consists to a greater extent of methanol, and 2) the synol product contains less alcohols.

The advantage of the multiple-stage unit is the good mixing and the extremely small amount of product holdup (Product-einsatz) especially when centrifuges are used instead of settlers.

The disadvantage is that many mechanically operated parts, such as pumps, mixers and centrifuges, are required.

With this apparatus, about 3 tons of synol products of different chain length were extracted. The neutral oil of the 120-170° fraction had an alcohol content less than 0.1%. In the fraction 170-220°, the alcohol content of the neutral oil was found to be about 0.3%. The alcohols were 97% pure. The other 3% consisted mainly of esters, ketones and aldehydes and could be removed to a great extent by hydrogenation with catalyst 1930 (1/2 Cr_2O_3, 1 ZnO? illegible, 1 CuO). The exact amount of hydrocarbons contained in the alcohols could not be established with certainty. For the fraction 120-170°, two counter-current stages are already sufficient. For the fractions above 220°, 4-5 stages are required.

2. Column With Packing

A counter-current column packed with Raschig rings has the following advantages as compared to a multiple stage apparat it has no mechanically moving parts, the construction costs are therefore smaller, and the operation is less subject to disturbances. On the other hand, the thorough and intimate mixing is not as good as with the mixing vessels. Experiments have established that a 1.5 m high Raschig ring column gives as good an extraction effect as a single co-current extraction in an extraction funnel. With a 4.5 m long column of 6.2 cm width and packed with 0.7 cm Raschig rings, approximately the same results were achieved as with the three-stage apparatus. However, it would not

require much additional effort to put up a 10 m column, thus increasing and further improving the selectivity. Capacity tests have established that, with a column of 30 cm^2 cross-section, a maximum liquid through put (synol + extracting agent) of almost 1,000 liters in 24 hours (=1.4 $l/cm^2/hr$) can be reached. It was further studied whether the separation level in the column should be kept in the upper or lower portion of the column. In order to obtain the purest possible alcohols, it appears to be preferable to keep the separation level in the upper portion; the oil-droplets in the methanol are smaller than the methanol droplets in the oil. However, the difference in degree of purity of the alcohols which were obtained was so small that one could achieve equally good results with the separation layer in the center of the column, where it is easiest to maintain.

However, there is another measure which is of great importance for the purity of the alcohols: the extract is slightly turbid, which means that it still contains some finely distributed neutral oil. Therefore, a "quieting zone" was fixed to the bottom of the column, the cross-section of which was 10 times as great (See Fig. 4); in this zone, the most finely emulsified oil droplets have time to climb back.

In Figure IV (missing Transl.) is also shown the method of operating the extraction continuously. The extract enters into a continuously operating distillation column. On top one withdraws the methanol, on the bottom the water and the alcohols. The latter are separated in a Florentine flask. The water and

the methanol are re-united. Possible losses and cnanges in concentratin are equalized by additions of water and/or methanol. The concentration is checked and controlled by density measurements. The water/methanol mixture re-enters the cycle. In Fig. V (missing Transl.) this cycle is represented in form of a flow-chart.

3. Summary Of The Results

Finally, we will gather all the data concerning the capacity of the extraction process and present them in a numerical table. The values were determined with the use of a 6 m column of 30 cm^2 cross-section, packed with Raschig rings of 0.7 cm diameter.

IV. Summary

On the basis of several definite fractions of the Oxynol alcohol process, the separability of alcohol/hydrocarbon mixtures by extraction with aqueous methanol of variable concentration, is described. Mixtures obtained from the oxo-synthesis are also included. Ways leading to an actual process were tested and described.

Signed:
/Dr. MEUSEL/

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Fraction	Chain Length Of Alcohols Contained In It	Approx. Amt. Of Alcohols In The Crude Synol Oil Wt. %	Optimum Methanol Concentration In %	Amt. of Extracting Agent Required for 1 Part Synol Oil (Parts)	Pure Alcohols Obtained Per cm^2 Column-Cross Section Per Hour (cm^3)	Amt. Of Methanol to Be Distilled In Order To Obtain 1 kg. Of Pure Alcohol In Liters (X)	Amt. Of Alcohol In The Neutral Oil Obtained In % (XX)	Non-alcoholic Content (esters, aldehydes, hydrocarbons) Of The Alcohol Obtained In %
120-170	5-7	56	68	2	265	2.4	0.1	3
170-220	7-10	48	76	3	170	4.7	0.3	3
220-270	10-13	40	81	6	80	12.2	0.6	3.5
270-320	13-16	29	85	10	38	29.5	1	3.5

(X) Without regard to the required reflux, which must be greater for the lower than for the higher fractions.

(XX) After removal of a trace of methanol by heating to almost the boiling point of the neutral oil.