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THE EFFECT OF PRESSURE UPON THE POLENSKE AND REICHERT- MEISSL VALUES.

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GENUINE butter fats analysed in the Government Chemical Laboratories, Nairobi, British East Africa, invariably give very low Polenske values, and the reason for this was made the subject of research.

When considering the explanation of the phenomenon, one of the first ideas to suggest itself was the possibility of the low atmospheric pressure affecting the composition of the distillate. Nairobi is situated at an altitude of about 5,500 feet above sea-level; the barometer generally read about 627 mm., and water boils at roughly 95° C.

In order to test this theory it was only necessary to devise a means of performing the Reichert-Meißl-Polenske distillation under different pressure conditions, and this was effected by attaching a Brühl jar to the receiver end of the condenser, and attaching to this jar a manometer, a bicycle valve and pump, and a Geryk vacuum pump.

All corks were carefully wired down and the lid of the Brühl jar secured, when pressures above that of the local atmosphere were required, by the use of clamps.

The only part of the standard apparatus which it was necessary or desirable to alter was the substitution of a 300 c.c. round-bottomed Jena flask, with neck cut down to the prescribed length, for the flat-bottomed flask normally used.

The butter fat used in these experiments was obtained from butter made in the laboratories.

Strict adherence to the prescribed conditions was observed in carrying out the observations, and it is unnecessary to describe here such a well-known process. The only points worth mentioning are that the times taken for distillation were a little over the twenty minutes—generally twenty-five minutes—that at very low pressures much difficulty was experienced in maintaining steady ebullition, and that one deviation from the usual procedure was made—i.e., the 110 c.c. distillate was agitated and allowed to remain a few hours before filtration and titration. The reason for this

deviation is that a perfectly limpid filtrate is not obtained often by the usual rapid method, with the probable result that a trace of insoluble acid is passing into the

In the case of the Reichert-Meissl curve the diminution of effect with increasing pressure suggested a logarithmic function, and trial was made of the following formula :

$$V = \frac{(v-K) \log P}{\log p} + K, \text{ when } K=10,$$

and although the agreement is not very close it enables a correction to be applied which will reduce the error to a negligible amount.

The agreement between the formulæ and the experimental determinations is shown in the table.

THEORETICAL CONSIDERATIONS.

That such simple empirical formulæ can express the relationship between pressure and Polenske and Reichert-Meissl values might lead one to suppose that some equally simple laws were involved. It is disappointing to find that no such simple explanation is forthcoming, and that the simplicity of the result under the complexity of the various factors involved in the performance of a Reichert-Meissl-Polenske distillation appears to be fortuitous.

The fundamental difference between the Polenske and Reichert-Meissl variations with pressure may be attributed to the fact that, as Regnault showed, non-miscible liquids vaporise independently of each other, and the proportions of each in the vapour phase have no relationship to the proportions present in the liquid phase, but are entirely dependent upon the ratio of their partial pressures and vapour densities,

$$\frac{w}{W} = \frac{d.p.}{D.P.} \text{ (Nauman),}$$

whereas in the case of miscible liquids the proportions of each present in the vapour phase have a relationship with the proportions in the liquid phase, but that relationship is greatly affected by attractions between like and unlike molecules. In the simplest case, the relationship may be represented thus :

$$\frac{x_1}{x_2} = C \frac{W_1}{W_2} \text{ (Brown),}$$

where x_1 and x_2 are the fractions vaporised, W_1 and W_2 the masses in the liquid phase, and C a constant not differing much from the ratio of the vapour pressures of the substances at the temperature of distillation. But this simple relationship between the composition of the vapour and liquid phases is only true of miscible liquids of closely related constitution, or of other mixtures when

$$P = \frac{mP_a + (100-m)P_b}{100} \text{ (Zawidski),}$$

and in the case of fatty acids and water the relationship does not hold good, particularly as butyric acid forms a maximum vapour pressure binary mixture.

To deduce the effect of pressure upon the proportions of soluble and non-soluble acids in the distillate from a knowledge of vapour pressures becomes hopelessly involved when it is remembered that in the R.M.P. mixture there exist—(1) water; (2) glycerol; (3) fatty acids of very low vapour pressures (non-volatile); (4) fatty acids of vapour pressures sufficient to yield a measurable mass in the distillate, (3) and (4)

being insoluble or only slightly soluble in water; (5) fatty acids of high vapour pressure, soluble in water.

The presence of the glycerol will reduce the partial pressure of the aqueous vapour, and its effect upon the partial pressures of the fatty acids will depend upon their solubility in glycerol. The fatty acids will constitute a series of miscible liquids, the relative proportions of which will affect the partial pressures of each constituent; while the non-miscibility, partial or complete miscibility, of the individuals of the series with water make the problem extremely complicated.

Molecules of all the fatty acids will occur in the distillate, and if the series form a mixture comparable with simple mixtures where

$$P = \frac{mP_a + (100 - m) P_b}{100},$$

then it is obvious that the proportions of the various fatty acids occurring in the liquid phase will affect the proportion occurring in the vapour phase (distillate), even though these various acids are not soluble in water. In other words, the Polenske acids must comprise oleic, stearic, palmitic, myristic, lauric, and probably capric (which has failed to dissolve in the R.M. acid and water) acids, in proportions depending to some extent upon their proportions in the liquid phase.

I am indebted to Prof. Sydney Young for pointing out that in the particular case of myristic acid and water the ratio of the partial pressures does actually increase in proportion to the total pressure when a simple mixture of these two substances is subject to experiment, but that with lauric acid the ratio of the partial pressures does not keep pace with the increase of total pressure. In my experiments it has been seen that the ratio of the partial pressures of the Polenske acid to that of water has increased in proportion to the increase in total pressure, precisely as would occur if water and myristic acid were distilled. The composition of the Polenske acids is not well known, but the composition of butter fat is as follows (Brown):

Glycerides of—					Per Cent.
Dihydroxystearic acid	1.04
Oleic acid	33.95
Stearic acid	1.91
Palmitic acid	40.51
Myristic acid	10.44
Lauric acid	2.73
Capric acid	0.34
Caprylic acid	0.53
Caproic acid	2.32
Butyric acid	6.23

The composition of the Polenske acids might be roughly deduced from a consideration of the vapour pressures of the above acids at the temperature of distillation and the molecular proportions in which they occur. The vapour pressure of lauric acid is something like two and a half times that of myristic acid, but there is present nearly four times as much myristic as lauric acid. The large proportion of palmitic acid must also contribute its quota to the Polenske acids, and in this case it is probable that the ratio of partial pressure of the acid to that of water would exceed

the ratio of total pressure, but, as was stated above, the behaviour of a mixture of a number of miscible substances cannot be predicted with accuracy, and it is remarkable that the experimental results should show that the mixture present in the R.M.P. process with a normal butter fat yields results at different pressures of such a simple character, and that these results should agree with what would occur if water and myristic acid alone were present.

As regards the Reichert-Meissl (soluble volatile acids), we may assume that they consist principally of butyric, caproic, caprylic, and possibly a portion of the capric acids.

It is difficult to predict anything from a knowledge of vapour pressures. Butyric acid forms a mixture of maximum vapour pressure of b.-pt. 99.2° (760 m.) containing 20 per cent. butyric acid (*vide* Young, "Fractional Distillation," p. 67). From this it might be expected that from 145 c.c. aqueous solution yielding 110 c.c. distillate the whole of the butyric acid would be obtained at most temperatures, and that the increase in R.M. figure at higher pressures and temperatures was to be attributed more to the increase in caproic and caprylic acids. It is unfortunate that the Kirschner figures were not obtained at the same time.

As was stated before, the relationship between the composition of vapour and liquid phases does in its simplest case approximate to

$$\frac{x_1}{x_2} = C \frac{W_1}{W_2},$$

when C is a constant not dissimilar to the ratio of the vapour pressures of the substances at the temperature of distillation. It is noteworthy that the ratio of the partial pressures of water and the lower fatty acids does not increase so rapidly as the temperature (and therefore total pressure) increases, as is the case with the higher fatty acids, and this fact alone explains why the R.M. figure cannot increase to the same extent as the Polenske when the distillation is performed at higher pressures (and temperatures), but no basis for a theoretical deduction of the empirical formula found by experiment exists.

CONCLUSIONS.

1. The Polenske value is a function of the pressure, and unless values are corrected to normal pressure serious errors are liable to be introduced.

With butter fat the relationship is as follows:

$$V = \frac{v(P - K)}{p - K}.$$

2. The Reichert-Meissl value is a logarithmic function of the pressure, and the errors introduced by ordinary variations in atmospheric pressure are quite small.

With butter fat the relationship is as follows:

$$V = \frac{(v - K) \log P}{\log p} + K.$$

Experiments are being conducted to ascertain the partial pressures of the several fatty acids with water, the partial pressures of various mixtures of acids and water, and the effect of glycerol upon these partial pressures.