Aqueous Isopropyl Alcohol for Extraction of Free Fatty Acids from Oils

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Liquid-liquid extraction of fatty acids from a vegetable oil is accomplished by aqueous isopropyl alcohol in the ratio of 1:1 in two-stage extractions at $30 \pm 2°C$. The mixtures studied contained 0 to 50% fatty acids in groundnut oil, and aqueous isopropyl alcohol solutions were of 75, 80, 85, 91, 95 and 99% concentrations. Phase separation depends on (i) the fatty acids content in the model mixture, and (ii) the concentration of aqueous isopropyl alcohol. Selective fatty acid separation and phase separation could be achieved by use of aqueous (75 and 80%) isopropyl alcohol over the whole range of fatty acid content in the model mixture.

Raw oils and fats produced from commercial lipid sources contain associated impurities. The major ones are phosphatides (gums), free fatty acids, partial glycerides and color bodies. Degumming and earth treatment leave behind fatty acids as the major impurity in the raw oil. Alkali refining and steam refining are used to remove the free acids. These processes are highly sophisticated, involving high energy inputs and costly machinery. Alkali refining also causes pollutants and consumes large volumes of chemicals while giving rise to by-products of low economic returns. Oils from corn and rice bran contain high amounts of free acids due to enzymic activity in the raw material. Such oils need special care during refining by any of the above processes. The present trend in the industry is to recover the products and the by-products with the least possible damage to the constituents, use of minimum energy and chemicals, avoidance of pollution and ecological problems and use of renewable resources. Extraction of fatty acids from raw oil at ambient temperature by solvents would meet the above goal. This approach has not drawn commercial attention. By use of suitable solvents or mixtures of solvents, free fatty acids could be separated from raw oils. References related to such extraction studies are limited (1–13). These are based on the use of solvents like methanol and ethanol. Harris (14) reported the extraction and simultaneous refining of cottonseed oil with aqueous isopropyl alcohol (IPA) at 30°C. Interest has revived recently in the use of IPA for the extraction of oil from oil-bearing materials (15–17) due to its low toxicity.

IPA can be made from renewable agricultural materials. The literature on this subject, however, leaves some areas unanswered. Some of these areas having impact on the process development are:

(a) Factors affecting the immiscible phase separation
(b) Selection of correct IPA concentration as extractant for effective separation of fatty acids from oil mixtures based on initial free acid concentration
(c) Composition of phases under the conditions studied.

Therefore, it becomes necessary to collect systematic data and establish some relation between the free acid content in the oil mixture and the concentration of the

IPA used. The present work evaluates the use of IPA concentrations of 75, 80, 85, 91, 95 and 99% for extraction of free acids from acid triglyceride mixtures containing 0 to 50% mixed free fatty acids and determines the parameters affecting the separation process.

EXPERIMENTAL

Materials and methods. Mixed fatty acids were prepared from refined groundnut oil by complete saponification and acidulation. Model mixtures (MM) containing the mixed fatty acids ranging from 0 to 50% in 5% intervals were made by blending mixed fatty acids with refined groundnut oil (w/w). Aqueous isopropyl alcohol (IPA) of 75, 80, 85, 91 and 95% (w/w) concentrations was made by blending the required quantity of water to distilled pure IPA.

The acid value (AV) of the MM's and the materials obtained during the extraction stages were determined in accordance with AOCS methods (18). Fatty acid contents in the MM's were calculated based on the AV.

Liquid-liquid extraction. The MMs containing 0 to 50% free acids were extracted with IPA of 75, 80, 85, 91, 95 and 99% concentrations in two stages in succession according to the procedure described below.

Weighed quantity of the pure oil or MM was mixed with IPA in the ratio 1:1 (w/w) at $30 \pm 2°C$ in a separatory funnel. The mixture was shaken vigorously by hand for five min and allowed to stand overnight undisturbed in order to permit immiscible phase separation. This resulted in two layers in many cases, while few MMs showed no separation at all. When separation of layers occurred, the lower layer was carefully drawn from the bottom into a second separatory funnel quantitatively leaving the top layer intact (IPA layer I). Fresh IPA of the same concentration and the quantity used in the previous stage was added to the second separatory funnel containing the lower layer. The extraction process was repeated as described earlier, and the mixture was allowed to separate into layers. The top layer (IPA layer 2) and the bottom oil layer 3 were quantitatively separated. These three layers were weighed. Analysis of the layers showed that IPA layers 1 and 2 contained a major quantity of the IPA used, mutually dissolved oil and the partitioned fatty acids when present in the MM. The bottom oil layer 3 contained the major quantity of oil, mutually dissolved IPA and residual partitioned fatty acids.

The IPA from these layers was removed by evaporation (the last traces under reduced pressure). The IPA in each layer was obtained from the initial and final weight difference. The dry materials left behind from IPA layers 1 and 2 and oil layer 3 were weighed as extract 1, extract 2 and reaffinate 2. These were analyzed for AV, and the free acid contents were calculated.

RESULTS AND DISCUSSION

The curves in Figure 1a show the trend quantitatively on the separation of IPA layers 1, 2 and the oil layer during the first and second extraction when neutral oil is mixed with different IPA concentrations. During the first

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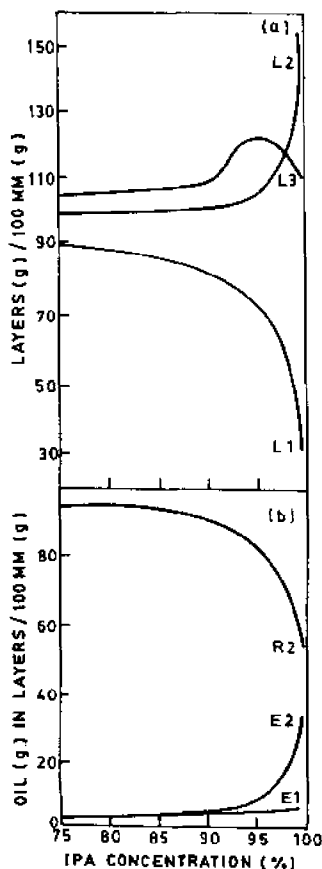[*] To whom correspondence should be addressed.

FIG. 1. Effect of concentration of IPA on pure oil extraction. (a) IPA layer from first stage extraction (L_1); IPA layer from second stage extraction (L_2); bottom oil layer 3 (L_3). (b) Neutral oil present in extract E_1 in L_1, extract E_2 in L_2 and raffinate R_2 in L_3.

FIG. 2. Variation of immiscible phase separability with simultaneous change of free acids percentage in MM and IPA concentration.

stage of separation, the layer 1 yield decreased with increased IPA concentration. A reversed trend occurred with the yield of layer 2. The difference in weight between the two layers widens with IPA of concentration 90% (IPA 90) and above.

The curves in Figure 1b show the amount of neutral oil present in extract 1, extract 2 and raffinate 2. The quantity of oil present in extract 1 and extract 2 is nearly the same when IPA 75 to 91 were used for extraction. Therefore, the difference in the layer weights of 1 and 2 is caused solely by additional IPA content in layer 2. Such a trend may be due to the ability of neutral oil to hold IPA due to mutual solubility at equilibrium during the first stage of separation. Once the two phases were equilibrated mutually with each other, subsequent amounts of each of the phases separated quantitatively. Further, it is to be noted that higher amounts of neutral oil appear in the IPA 95 and 99 layers, indicating that pure oil solubility increased with reduction in water content in the IPA. As the water content is increased, the aqueous IPA becomes relatively polar and the solubility of oil decreases and becomes nearly steady at IPA 91 to 75. This is to be taken into account to avoid the loss of neutral oil into IPA layer.

The curves in Figure 2 show the parameters that control the immiscibility of the IPA and oil layers, namely
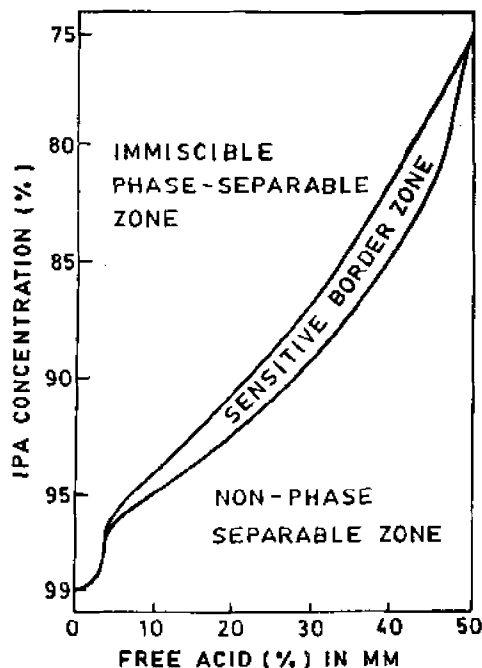
the immiscible separation boundary when (i) the free acid content is increased in the MMs, and (ii) the IPA concentration is increased. The area to the left (above the curve) is the zone where immiscible phase separation is feasible. This information guides the selection of correct IPA concentration based on the acid content in MM. The lower zone likewise is the homogeneous solution region that results when IPA is mixed with MM in the ratio 1:1 (w/w) at 30 ± 2°C. The success of any liquid-liquid separation process is dependent on such immiscible phase formation, and the homogeneous zone must be avoided.

Immiscible phases separated when pure oil (Fig. 1) was extracted with IPA 95 and 99. However, homogeneous solution appeared (Fig. 2) when free acid was present even at a low level of 5% in MM. Such a change in the physical behavior of the system may be attributed to the coupling effect exerted on IPA and the oil layers by the free acids that migrate into the IPA layer. It is also evident that the effect of the free acids as coupling agent, even at low levels, is enhanced by the high concentration of IPA. The presence of water in IPA is essential to bring about a progressive decoupling effect, leading to formation of immiscible phases at high levels of free acids in MM. Under these conditions IPA 75 and 80 (Fig. 2) serve the purpose.

Figure 3 shows quantitative yield patterns of IPA layers 1, 2 and the oil layer 3 based on the MM equal to 100 g. When various IPA's and MM's were subjected to extraction separations, IPA 99 and 95 resulted in homogeneous solutions. Therefore, these IPA concentrations should not be used for liquid-liquid separation of free acids from oil admixtures.

The pattern obtained for the IPA 75, 80, 85 and 91 is similar to Figure 1 with regards to IPA layers 1 and 2 and the oil layer 3. It is observed that the quantities of IPA layer 1 obtained were minimum with IPA 91 for all
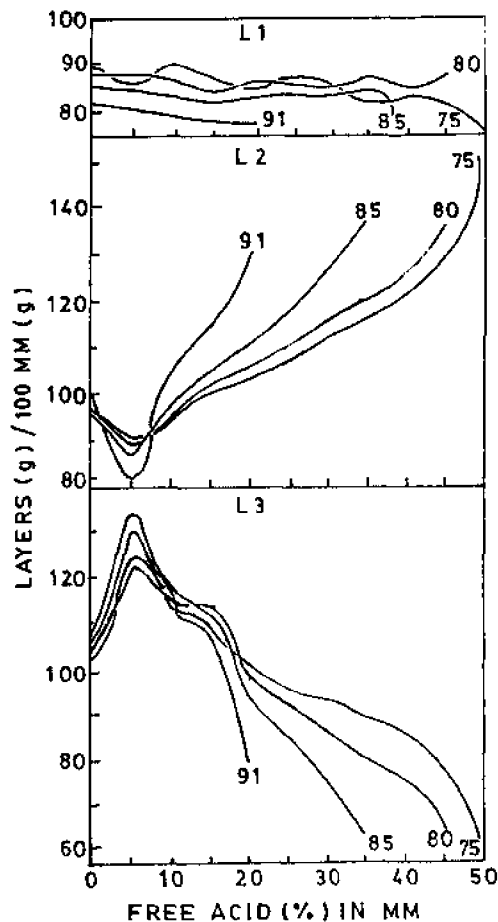
FIG. 3. Yield variation of L_1, L_2 and L_3 with simultaneous change of free acids percentage in MM and IPA concentration.
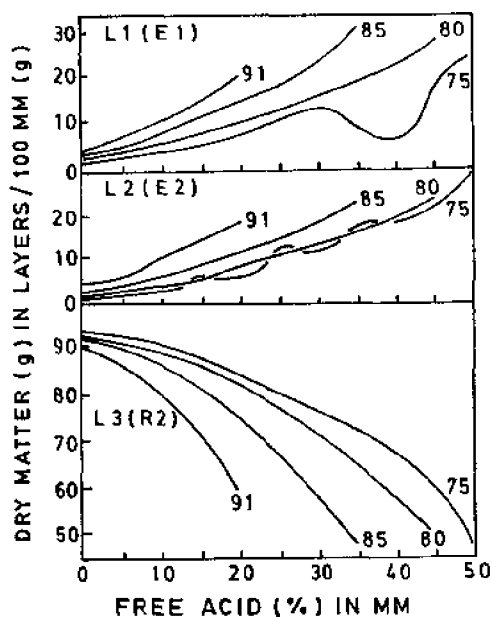

FIG. 4. Yield variation of dry matter E_1 (extract 1), E_2 (extract 2) and R_2 (raffinate) with the change in free acid percentage in MM and IPA concentration.

free acid levels and failed to give phase separation beyond 20% free acid in MM's. The IPA 75 and 80 gave immiscible phases at 50 and 45% free acid levels in MMs. Similar to the findings in Figure 1, the IPA layers 2 for all cases were higher and the layer yield decreased from IPA 91 to IPA 75.

The IPA free materials contained in the IPA layers 1 and 2 and the oil layer 3 are referred to as extract 1, extract 2 and raffinate 2 in Figure 4. Contrary to the earlier observations (Fig. 3) on the yields of the layers, the quantity of extract 1 obtained in the first stage of extraction is higher in all cases than the extract 2 obtained during the second extraction. Therefore, on comparing the extract and the layer quantities, it is obvious that during the first extraction the quantity of IPA appearing in layer 1 is low. This is due to IPA-equilibration with the MM. The increased bulk of layer 2 is due to IPA itself rather than to extract 2. The yields of extract 1 and 2 increased in all cases of IPA with the increase in free acid in MM. But the yield of extract 1 and 2 decreased with the decrease in concentration from IPA 91 to 75 for any one acid level in MM.

A slight variation occurred with IPA 75 extraction shown by an abnormal depression of curve when the free acid content varied between 30 and 40% in the MM
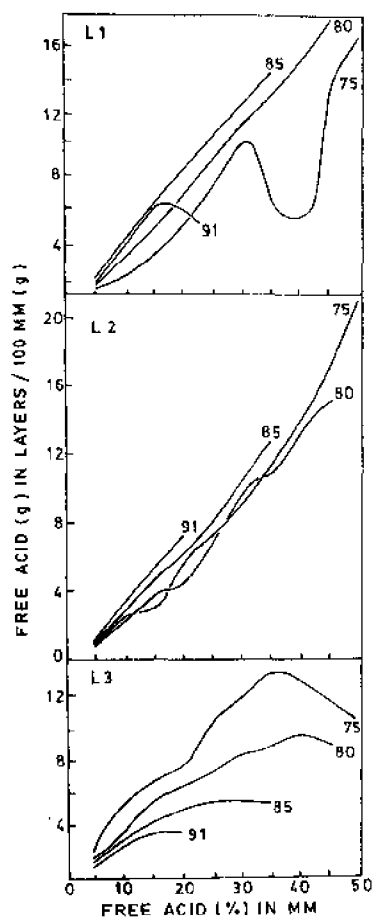

FIG. 5. Variation of weight of acid content in L_1, L_2 and L_3 with the change of free acids percentage in MM and IPA concentration.
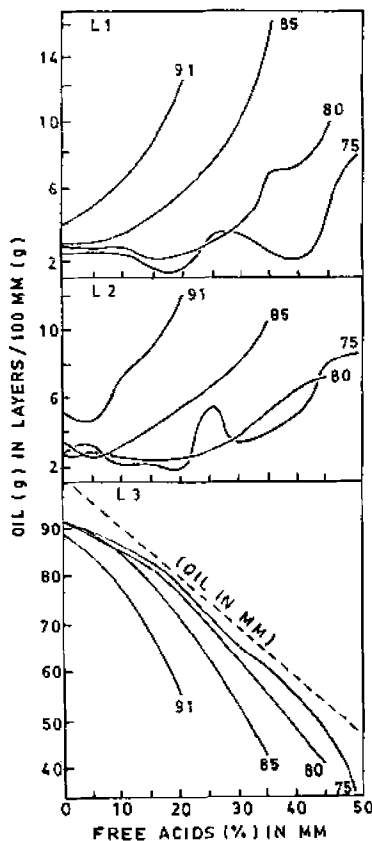
FIG. 6. Variation of weight of oil content in L₁, L₂ and L₃ with the change of free acids percentage in MM and IPA concentration.

FIG. 7. Free acid percentage in extracts E₁, E₂ and raffinate R₂ with the change of free acid percentage in MM and IPA concentration.

during the first stage of extraction. The IPA concentration affects the raffinate yields. The quantity of raffinate decreases from IPA 75 to IPA 91. Therefore, to get a higher raffinate yield, IPA 75 or 80 may be used. However, after making corrections for the free acid contents to the raffinates (MM), the yield is low and is not comparable with the values in Figure 1 obtained for pure oil extraction. A difference in the yields of the raffinate obtained during extractions with IPA in the absence (Fig. 1b) and in the presence (Fig. 4) of fatty acids is observed. This is due to mutual solubility effect of fatty acid extracted by IPA on neutral oil. This causes additional transfer of neutral oil from the raffinate layer to the IPA layer and a reduction in the yield of raffinate. Higher IPA concentrations aided higher amounts of oil transfer to the IPA layer for any one acid level in MM (Fig. 6).

Figures 5 and 6 quantitatively present the amounts of free acids and neutral oil contained, respectively, in the extract 1, 2 and raffinate 2 obtained from 100 g of the MMs. The weight of free acid in extract 1 and 2 increases with IPA 75, 80, 85 and 91, respectively. Thus, free acids extracted is high with high IPA concentration for any specified MM. These curves (Fig. 5) also show the effect of free acids present initially in the MM. The weight of free acids in the extract is high for the same IPA concentration when initial acid content in MM is high. Also, the free acids left in the raffinate are high when low IPA
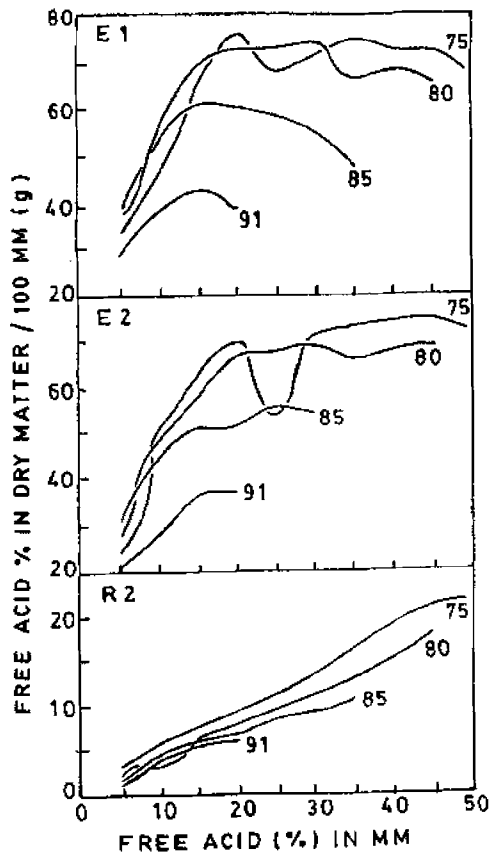
concentration is used for extraction. This implies the need for multistage extraction. An abnormal pattern of curve is observed with the extract 1 with IPA 75. Figure 6 pictures the neutral oil level in extract 1, 2 and raffinate. In both extracts it is noticed that the neutral oil content was lowest when IPA 75 and 80 were used and the initial free acid content in the MM influence the solubility of neutral oil. In the raffinate part (Fig. 6) the dotted line shows the weight of neutral oil in the respective MM's and the curves in the raffinate. The distance between the dotted line and curve indicates the loss of neutral oil. This is smallest when IPA 75 is used for extraction. IPA 80 gives a curve close to IPA 75, indicating interchangeability. Due to limitation of phase separation use of IPA 75 or 80 is recommended for extraction over 40% range of acids in MM.

Figure 7 brings out the selective nature and effect of water in IPA. This figure projects the quality of extract 1, 2 and raffinate 2. This makes a distinction between quantity and quality. The extracts for IPA 75 and 80 contain free acids above 70% when the MM contained acids just 20% initially. This segregation is highly selective and remarkable compared to IPA 85 and 91 which are low. It was shown that IPA 75 and 80 when used for extraction gave low yields by weight of extract 1 and 2 (Fig. 4) on 100 MM's basis, the acid content in these by weight was higher (Fig. 5) and neutral oil content low (Fig. 6). Thus, the selective separation of free acids is aided by low

IPA concentration. In the process development the values realized by the multiplication of quality and quantity play an important role. Therefore it is apparent that IPA 75 or 80, due to the selective nature of extraction of free acids, limited the extraction of neutral oil.

From the above findings it is recommended that the selection of correct concentration of IPA should be based on free acid content in MM; IPA 75 and 80% are selective over a wide range of acid levels. A multistage extraction based on these findings could result in an acid concentrate as a by-product and raw material for fatty acid production and also a raffinate suitable for refining. Such a liquid extraction process would satisfy the present trend in the industry on economic and ecological grounds.

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