TEMPERATURE DERIVATIVES OF VISCOSITY, DENSITY AND REFRACTIVE INDEX FOR THE WATER—ETHANOL SYSTEM

Part I.—Refractometric and Flow Activation Energy Charts for Dilute Aqueous Alcohol from 2% to 11% Alcohol and some Concentrated Ethanol Solutions

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A systematic study of the temperature derivatives of various physical properties of the water-ethanol system is being undertaken. The three important quantities, namely viscosity, refractive index and density are first taken up, and this communication presents data on the first derivative of refractive index (dn/dT) and viscosity (\(E_f = T^2 \frac{d \ln \eta}{dT}\)) for solutions at the two ends of the system, (i) those containing 2 percent to 11 percent ethanol by weight, as well as (ii) those containing 92 percent to 95 percent ethanol by weight.

It is found that the minima of (-dn/dT) nearly coincide with the jumps in activation energy \(E_f\), for viscous flow of the dilute ethanol solutions, and a tentative chart is prepared containing a series of graphs, each showing the variation of temperature for a particular jump (and minimum of -dn/dT) as the ethanol concentration varies from 2 percent to 11 percent by weight. A similar chart is shown for the maxima in (-dn/dT), and some anomalies are noted.

Similar refractometric measurements are given for 92 percent to 95 percent ethanol, where certain abrupt changes had previously been observed in the cyclic variations of activation energy. The growth of an 'anomalous' maximum and minimum is followed very readily on the dn/dT curves. Further measurements on dilute and concentrated ethanol are in progress.
X-RAY STUDIES OF THE IRON ORES FROM CHICHALI AREA OF THE KALABAGH ORE-FIELDS

The Analysis of the Component Mineral Phases

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A detailed X-ray analysis of the Chichali ore has been undertaken in order to determine its different constituent mineral phases. This study shows that the ore contains siderite, limonite and glauconite as its major constituent components. In some samples chamosite has also been detected. Thus this ore seems to be somewhat different from those of the Kutch-Khartop and Ziarat ores in composition, but perhaps the presence of glauconite in this ore may present much the same kind of problems for the successful recovery of iron as have been experienced with the other ores.

Introduction

In continuation of the earlier investigations 1-5 on the iron ore deposits of Pakistan, the studies of the ores from the Chichali area of the Kalabagh district have been undertaken in order to determine their mineralogical composition with a view to assess their workability in steel industries. Much attention has, in recent years, been focused on the iron ore resources of this country, and as a result, detailed investigations have been carried out on the ore reserves of the Kutch-Khartop area of the Kalabagh district and also of the Ziarat area of Quetta, which until a few years back appeared to be the main iron ore reserves of Pakistan. Since 1961, however, attention has been diverted towards the Chichali ore-field, the estimated reserves of which are over 213 million tons 6—much larger than either of the above mentioned ore resources—and are therefore of considerable importance for our potential steel industries.

The result of the investigations on the Kutch-Khartop ore have been reported in a series of papers. 1-4 These results have been of considerable value in the appreciation of the problems associated with the recovery of iron from these ores. The mean representative sample of this ore contains about 33.5% Fe, which is present in four different phases, namely haematite, siderite, limonite and chamosite. The first three of these phases are comparatively easily amenable to simple methods of reduction, but chamosite, which accounts for about 30% of the ore, is a ferruginous clay material, of composition 3(Mg,Fe)O.Al2O3. 2SiO2.3H2O and presents the main difficulties in the successful recovery of iron from these ores. The Ziarat ores 6 are essentially similar in composition, with the added disadvantage that these contain even lesser percentage of iron.

The Chichali ores, having on an average about 33% Fe, have become of considerable importance particularly because of their much higher estimated reserves, and attempts have therefore been made in this laboratory to determine their mineralogical composition with a view to assess their workability in steel industries.

Experimental

The X-ray methods have been used in the present study. Together with the mean representative sample, a few hand-picked samples were also studied in the hope that these may provide some information for the identification of particularly those phases that may be present in smaller quantities. The X-ray powder photographs of the mean and the hand-picked samples were taken using Cr-radiation with a 11.4 cm. diameter powder camera; the powder photographs of the mean sample were taken with filtered Cr-Kα radiation, the others being taken with unfiltered Cr-radiation. The d-values of the lines on the pattern of the mean sample together with the visual estimates of their intensities are reported in the first column of Table 1. A search through the A.S.T.M. X-ray data cards 7 shows that most of the lines of this pattern could be explained by the powder data of iron carbonate (FeCO3) and limonite (Fe2O3. H2O. nH2O). For confirmation, the powder patterns of these compounds were directly compared with the pattern of the mean sample: this showed satisfactory correspondence. The strongest line of iron carbonate, corresponding to d=2.8A° is outstandingly prominent on the mean pattern, indicating thereby that this phase is present in the ore in comparatively larger proportions than limonite. However, it is significant here to note (Fig. 1) that on almost all of the patterns of the hand-picked samples, except the one shown in the middle of Fig. 1 the line of d=2.8A° (indicated by *) is only just detectable, whereas the lines due to limonite appear much more prominently. Based on arguments similar to those made in the case of the Kutch-Khartop ores, 3 it seems most
ANGLE OF REPOSE AS FUNCTION OF THE PHYSICAL PROPERTIES AND THE PARTICLE-SIZE OF THE MATERIALS

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A correlation \( \tan \theta = K \varepsilon / dp \) \( \{1 - \varepsilon \} \) \( \theta, \varepsilon \) where \( \tan \theta \) is the tangent of the angle of repose \( \theta \) (static or dynamic), \( K \) is a constant, \( dp \) is the mean sieve particle-size and \( \varepsilon \) is the voidage fraction, is presented. Compared with other correlations, its application is simple and the results are accurate within a maximum error of \( \pm 3 \% \). It has also been shown that the tangent of the dynamic-angle is 1.126 times the static-angle over a specific grav-ity range of 1,3903...390.

**Introduction**

The work on the angle of repose dates back to French General Morin, who while working on trenches first realised its importance. Rankine \(^1\) later reproduced different values of the angle without giving the method of their determination. Since then much work on the variables such as the moisture, the particle-size, the physical properties and the methods of determination affecting the angle of repose, has been carried out.

Train \(^2\) has classified these methods as follows: (1) The fixed-funnel and the free standing cone. (2) The fixed-diameter cone and the funnel. (3) The tilting-box. (4) The rotating cylinder. (5) Free standing cone method as defined by Brown and Richards. \(^3\) Whatever is the method, it will be noted that there are always two angles of repose, one is called the static while the other is known as the dynamic angle. Franklin and Johanson and later Fowler and Wyatt \(^4\), \(^5\) have reported that the dynamic angle is 3 to 10 degrees smaller in value than the static angle of repose. According to the present work, it has been observed (discussed later) that the dynamic angle is greater than the static-angle by a few degrees.

The angle of repose also known as angle of friction, is a function of the physical properties and the characteristics of the granular materials used. Fowler and Chodziensker \(^6\) have expressed the angle as follows:

\[ \tan \theta = a/t^2 + b (R/d_{wa}) - c.P_t + d \quad (1) \]

This relationship though takes into account nearly all the known properties of the material, does not indicate whether the angle \( \theta \) is static or dynamic. Moreover, before making any use of the correlation, it is necessary to determine the shape-factor with the help of a modified Lea and Nurse apparatus \(^7\) and later making use of Carman's equa-

\[ \delta = a' (S + b'/a') (d + a''/a') + b'' - \frac{a'''}{a'} \quad (2) \]

where \( \delta \) = Sliding angle in degrees. \( S \) = ‘Standard-deviations’ of the mixed powders. \( d \) = Mean particle-diameter of the mixed particles. \( a, a', a'', b' \) and \( b'' \) are constants.

This equation is once again not very convenient to apply, as the values of the constants depending on the material will have to be determined before it could be of some practical utility.

The determination of the particle-size other than the sieve method is cumbersome and time consuming and so is the determination of shape factor and the surface roughness. There are a number of methods now available for finding out the particle-size of which the sieve method is the most convenient and rapid. Particle diameter may also be determined under microscope by a method outlined by Heywood. \(^10\)

Shape factors or coefficients may be determined using either Lea and Nurse apparatus (permeability method) and later Carman’s equation. The following relationship as proposed by Heywood \(^10\) may also be used for the same purpose:

\[ f = 1.57 + \frac{Q (ke/\eta)^{4/3}}{(n + 1)^n} \quad (3) \]

Surface roughness which is defined as the average depth between the particles constituting the surface, may be determined in the usual manner.
MOLECULAR COMPLEXES OF PICRIC ACID WITH AROMATIC HYDROCARBONS AND THEIR DERIVATIVES

Part I.—Association Constants of 1:1 Substituted Naphthalene-Picric Acid Complexes

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Interaction between aromatic nitro and polynitro compounds such as symmetrical trinitro—benzene, picric acid, picryl chloride etc. and aromatic hydrocarbons and their derivatives has been a subject of study by various physical methods. In the present investigation association constants of 1:1 complexes of Naphthalene, 1— and 2—methyl naphthalenes, 1— and 2—methoxy naphthalenes, 2—naphthol, 1—chloro and 1— and 2—bromo naphthalenes with picric acid have been determined in chloroform medium by partition method. These values have been utilised to compare the donor capacities of the compounds studied and the effect of the substituent groups on the stability of complexes. Also an attempt is made to throw light on the nature of interaction between the two components of the complex by studying the temperature dependence of their complexation.

Introduction

It has long been recognised that many aromatic hydrocarbons and some of their substitution products such as amines, phenols and ethers are capable of combining additively, in apparent violation of the classical rules of valency, with other organic compounds such as quinones, polynitro aromatic derivatives, maleic anhydrides and also with inorganic compounds such as sulphur dioxide, silver perchlorate and hydrogen halides. A large majority of these aromatic molecular complexes cannot be isolated in pure state as they dissociate very readily into their components in solution and therefore their existence has been recognised only through the investigation by physical methods of solutions or mixtures of their compounds. As the dissociation occurs in accordance with the law of mass action it was soon recognised that the evaluation of the equilibrium constants for the formation of these complexes in solution would provide a quantitative study of the extent of interaction between the components.

The comparative study of these complexes in solution has been made by various workers employing different methods such as Solubility Measurements, Cryoscopic Studies, Distribution Studies, Vapour Pressure Measurements, Melting-point Composition Diagram, Viscosity Measurements and the like. In recent years Spectrophotometric, Colorometric and Conductivity measurements have also been used. The determination of association constants of 1:1 picric acid complexes with certain hydrocarbons and their derivatives in chloroform solution by method of partition has recently been carried out in a series of investigations by Moore Shepherd and Goodal,1 Anderson and Hammick,2 Gardner and Stump3 etc. The method adopted by the author is the one used by Moore and coworkers and further refined and improved by the others already mentioned.

Experimental

Theory.—The method is based on the study of the distribution of picric acid between chloroform and water as influenced by the presence of varying amounts of aromatic substances in the chloroform phase. In the presence of the latter two effects serve, in opposition to each other, to alter the normal partition of picric acid between the two phases. The first effect corresponding to the formation of the complex in the chloroform layer causes an increase in the total concentration of picric acid in chloroform layer while the second effect due to salting out of picric acid from the chloroform phase by the uncomplexed aromatic material tends to lower its concentration in that phase. By determining the alteration in the concentrations of picric acid in two layers, the concentration of the complex formed in the chloroform phase can be calculated and hence the association constant of the interaction can be evaluated.

Consider the distribution of picric acid between water and chloroform, in the latter of which the concentration is P. Let an addition of an aromatic substance in concentration Z, soluble in chloroform, depress the concentration of picric acid to y by the amount (P—y). At the same time its concentration in chloroform is increased owing to interaction with the added substance to y1 by the amount (y1—P). Assuming that the two opposite effects are arithmetically additive, the experimentally observed picric acid concentration Y is given by:
FALL TIMES OF METEORITIC DUST IN THE UPPER ATMOSPHERE

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Based on Stokes’ law, calculations have been made to determine terminal velocities and fall times from various heights for meteor dust particles of different diameters. While, mean values of 1.8 x 10^{-4} g/cm sec for air viscosity and 5 g/cm3 for the density of meteoritic material have been used in the calculations, Cunningham’s correction has been applied to Stokes’ law to account for the molecular mean free path variation with height and its influence on fall times. It has been found that micrometeorites take varying times to reach the tropopause from different heights.

Introduction

Despite the critical dependence of the meteor hypothesis on settling rates for the particles presumed to influence rain yield from clouds, very few calculations on this parameter have been carried out. Bowen quoted rough estimates of 30 days for settling times from 30 km. to the earth’s surface of material in the 4-10μ size range but did not elaborate on this, even to the extent of giving expected densities. He recognized that under Stokes’ law conditions, the terminal velocity dependence on the square of the diameter would result in a wide spectrum but the basis of the theory required only a sharp “front” for the descending particles, this to be composed of the largest sizes. Here a major difficulty arises, for all estimates of meteor influx would limit the number of 8 micron diameter particles to fewer than one per cubic metre for an entire shower, and considerably longer delay times would be involved if the more numerous 2-5μ particles were required by the theory. Alternatively, Bowen used the evidence from noctilucent clouds at 70-90 km. altitude as evidence that meteor dust particles—assumed to be responsible for the water vapour nucleation and cloud formation at this level—were in fact more numerous than otherwise indicated, but this greater height would also result in increased delay times for settling.

In support of Bowen’s theory, Rosinski and Pierrard postulated that the vaporization of larger meteors in the 80-110 km. region would produce by coagulation many micron-sized particles per unit volume, and that this process was the source of ice nucleating material. They made no calculations of settling rates, but through comparison of meteor shower and rainfall anomaly dates, arrived at delay times varying from 40 to 65 days.

Buddhur carried out calculations of terminal velocities for meteor particles at different heights up to 100 km. As he assumed Stokes’ law behaviour without any consideration of the molecular mean free path variation with height and its influence on settling rates, his data are of little value. Because of the confused nature of the subject, the obtaining of more reasonable estimates of fall times would appear to be important; inasmuch as it is only against those estimates found by assuming the upper atmosphere to be stable, stationary medium, that one can discuss the influence of stratospheric winds and turbulence on this settling.

Basis of the Procedure

Published measurements of the terminal velocity, \( V_t \), of natural particles were treated as experimental determination for each type of particles of drag coefficient, \( C \), over a range of Reynolds number, \( Re \)

\[
C = \frac{2mg}{\sigma V^2 A} \quad \text{and} \quad Re = \frac{D V}{\eta}
\]

where \( m \) is the mass, \( D \) is the diameter and \( A \) is the cross sectional area of the particle; \( \sigma \) is the density of the air; \( \eta \) is the dynamic viscosity of the air and \( g \) is the acceleration due to gravity. If \( \varphi \) is the density of the particle, then

\[
V_t = \frac{gD^2 (p-\varphi)}{18\eta} = V_{st}
\]

which is Stokes’ law. This law is applicable to particles with diameters between approximately 1 and 50μ and generally \( \varphi \) may be neglected.

Equation (1) can be used to determine rough terminal velocities and settling times from various heights for particles of different diameters. A mean value for the gravitational acceleration of 970 cm./sec² may be regarded as reasonable as it changes but little with height. Air viscosity is practically independent of pressure over the range considered here and as its variation with temperature is relatively small—about 30 percent.
THE 5-AND 8-IODINATION OF QUINOLINE AND SOME OF ITS DERIVATIVES

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Quinoline (0.3 mole) and silver sulphate (0.2 mole) in 98 percent sulphuric acid at 150-200°C., and iodine (0.2 mole) give 5-iodoquinoline (20 percent), 8-iodoquinoline (18 percent) and 5,8-diodoquinoline (35 percent), the approximate proportions were determined from the products isolated. With an excess of quinoline, moniodoquinolines predominate and with silver sulphate and iodine in excess, 5,8-diodoquinoline is the major product. 5-iodo and 8-dideoquinolines are similarly iodinated to form 5,8-diodoquinoline. It is considered that the positively-charged iodinium ion (I⁺) and the protonated form of the bases are the principal species involved in the initial and the subsequent iodination. Such reactions should form convenient preparative routes to mono and diiodination of quinoline.

Experimental

Quinoline was purified through chlorozincate or phosphate. The purified material had b.p. 236°/760 mm., m.p. -19°C. Iodine, sulphuric acid and silver sulphate were of analytical grade. Iodoquinolines required as reference substances were prepared by standard methods. The data concerning the prepared iodoquinolines and their derivatives are shown in Table 1; their properties are in good agreement with values recorded in the literature.

Method of Iodination.—In principle the method is that of Derbyshire and Waters and was modified according to requirements of the reactions. The base quinoline or its derivative and an appropriate quantity of silver sulphate were dissolved in concentrated sulphuric acid and heated to 150-200°C. About one equivalent of iodine relative to silver sulphate was gradually added with thorough shaking, in about an hour time. After filtration of the resultant silver iodide precipitate the filtrate and the washings were treated with sodium sulphite solution containing crushed ice to 5 percent remove any free iodine. The reaction mixture was then basified, extracted with solvent or steam-distilled and worked up suitably.

(a) Preparation of 5-and 8-iodoquinoline.—Quinoline (33 g.) and silver sulphate (16.5 g.) in sulphuric acid (98%, 100 ml.) at 150-200°C were allowed to react with iodine (6.5 g.) added small quantity at a time. The reaction was indicated by the appearance of silver iodide precipitate and was complete in an hour. The filtered reaction mixture was poured into ice-cold sodium sulphate solution, basified and steam-distilled. The ether extract of the steam distillate was dried and fractionally distilled in vacuum. After removal of the excess of quinoline the residue was redissolved in sulphuric acid. The solution was treated with sodium hydroxide, 5-iodoquinoline was precipita-
CHEMICAL CONSTITUENTS OF CORYDALIS STEWARTII FEDDE

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Three alkaloids provisionally named and formulated as (a) Corydine, C_{11}H_{17}O_4N, m.p. 290-92° (dec.), (b) Corydine, C_{17}H_{17}O_4N, m.p. 199-200° and (c) Corydine, C_{19}H_{17}O_3N, m.p. 181-82° have been isolated from Corydalis stewartii Fedde. Besides, a saturated alcohol C_{30}H_{63}O, m.p. 76-77° has also been obtained from the fatty portion.

Corydalis stewartii Fedde, locally called mamiri, is a small annual herb belonging to the family "Fumariaceae". It is found growing by shady road-sides and in forests at Murree and the Gallies during the monsoon. It also occurs, in fair quantities, in Kaghan valley, Azad Kashmir, Dir and Swat States. The juice of the plant is used by local people in the treatment of eye diseases. The plant was taken up for investigation as no work on it has so far been reported in literature. As a result of the present work, it has been possible to isolate three alkaloids provisionally named as (a) Corydine, (b) Corydine, and (c) Corydine which, on the basis of elemental analysis and molecular weight determinations have been assigned the formulae:

(a) Corydine, C_{11}H_{17}O_4N, m.p. 290-92° (dec.).
(b) Corydine, C_{17}H_{17}O_4N, m.p. 199-200° and
(c) Corydine, C_{19}H_{17}O_3N, m.p. 181-82°.

All the three alkaloids were found to contain methylene dioxy group and the tertiary nitrogen. The purity of the bases was established by the technique of T.I.C. The results of the combustion analysis correspond very closely with the molecular formula assigned to corydine. Molecular weight determination by titration with perchloric acid in non-aqueous medium gave the value of 405, which is double the calculated figure. Further work to decide whether the formula of corydine exists as such or as (C_{17}H_{17}O_4N)_2 is in hand.

The petroleum ether-soluble fraction yielded a colourless crystalline alcohol provisionally named as Corydanol, m.p. 76-77°, formulated as C_{20}H_{43}O on the basis of combustion analysis and molecular weight determination. It did not decolourise potassium permanganate or bromine, gave negative Leibermann-Burchard test, indicating its non-steroidal character and lack of unsaturation. The acetyl derivative melted at 37-38°.

Further studies on the characterisation of these constituents are in progress.

Experimental

The plants were collected in the month of July from Dunga Galli and immediately after collection were cut into 1-2 cm. bits and repeatedly percolated with 95 percent ethyl alcohol until the extract gave a negative test for alkaloids. The combined extracts were first concentrated in a cyclone evaporator and then under reduced pressure to a thick syrupy consistency. The residue was macerated with dilute acetic acid (10 percent) until free from alkaloids. The acid-soluble fraction was basified with dilute ammonia (10 percent) and extracted with ethyl acetate. The residue obtained on removal of the solvent under reduced pressure, was extracted with chloroform and the chloroform-insoluble residue was dissolved in alcohol, treated with activated charcoal, filtered and concentrated. On keeping, colourless shining plates of corydine were obtained m.p. 280-85° (dec.). (yield 0.04 percent). This fraction, on repeated crystallisation from hot methyl alcohol, finally melted at 290-92° (dec.).

It was also observed that, on treatment of the original ethyl acetate extract with activated charcoal, corydine was selectively absorbed and could be separated by treatment with hot methanol.

The chloroform-soluble fraction after washing and drying over anhydrous sodium sulphate was concentrated and an equal volume of methyl alcohol added when corydine crystallised out as colourless thick rectangular plates m.p. 190-95° (yield 0.096 percent). On further crystallisation from the same solvent, it finally melted at 199-200°. The mother liquor, on further concentration and keeping, yielded fresh crop of crystals. Fractional crystallisation from methyl alcohol and chloro-

Melting points were taken in J.W. Fower's electrical melting point apparatus. Micro analysis was done by A. Bernhardt 433, Mulheim (Ruhr), West Germany. Infra-red was taken on Beckmann IR-5 Spectrophotometer.
Chemical Constituents of Euphorbia Royleana Boiss*  

Part II  

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3,3'-Dimethoxy ellagic acid, succinic acid, and an unidentified compound C_{19}H_{16}O_{7} containing a number of ester groups have been isolated from Euphorbia royleana Boiss.

A systematic study of the chemical constituents of Euphorbeaacea is being carried out and the latex of Euphorbia royleana Boiss. has already been shown to contain euphol, cycloecualenol and a novel triterpenoidal alcohol in the previous communication. The present work deals with a detailed study on the juice of the plant which had not been investigated so far.

The scheme given in Fig. 1 was followed in the isolation of various constituents of Euphorbia royleana reported in this communication.

Fig. 1.

Compound C.—C_{4}H_{6}O_{4}, m.p. 186-187° is soluble in water and crystallises as needles. It decomposes aqueous sodium bicarbonate. Its infra-red spectrum (KBr) shows the presence of carboxylic groups 3560 cm.⁻¹, 1750-1700 cm.⁻¹ and 900 cm.⁻¹. The compound on titration against standard alkali proved to be dibasic. The infra-red spectrum is superimposable on that of succinic acid.² Mixed melting point with an authentic sample of succinic acid was unpressed.

Compound B.—C_{16}H_{16}O_{5}, m.p. 335-336 (dec.) pale yellow needles, is insoluble in bichromate but is soluble in cold dilute alkalies giving yellow solution from which it can be regenerated on acidification. It absorbs in the infra-red spectrum (KBr) at 1735 cm.⁻¹ (lactone), at 3450 cm.⁻¹ (hydroxyl) and at 1108 cm.⁻¹ (ether). The compound was methylated with diazomethane to a product insoluble in cold dilute alkalies showing the absence of phenolic groups. The infra-red spectrum of the methylated product was identical in all details with that of tetramethoxy ellagic acid.³ The compound was acetylated to give an acetate ⁴ as yellow needles m.p. 298-300 — insoluble in cold dilute alkalies. The data, therefore, indicate that compound B is 3,3'-dimethoxy-4,4’dihydroxy diphenic acid di lactone which can also be called as 3,3'-dimethoxy ellagic acid (also isolated from Euphorbia formosana Hay).⁴ The identity of the compounds was further confirmed by comparison with a sample synthesised in the Laboratories. Ellagic acid was prepared according to Nierenstein ⁵ and acetylated.⁶ The resultant tetraacetate was converted to 3,3'-dimethyl ether of ellagic as described by Jurand.⁷ The IR Spectra of the synthetic and the compound B were identical in all details. Mixed melting point also showed no depression.

Compound A.—Tentative formula C_{19}H_{16}O_{7}, mp. 181-182°, white rhombic crystals, is soluble in chloroform, ethyl acetate, acetone and most of the organic solvents, but insoluble in cold dilute alkalies or mineral acids. In the IR spectrum (CCl₄) it displays bands at 1210 and 1239 cm⁻¹ (ester), doublet at 1700 and 1730 cm⁻¹ (carbonyl and ester carbonyl) and at 1100 cm⁻¹ (ether). The band at 1700 cm⁻¹ disappears on reduction with sodium borohydride while bands at 1210 cm⁻¹, 1700 cm⁻¹, 1730 cm⁻¹ disappear on reduction with lithium aluminium hydride. The molecular formula of the compound shows sufficient unsaturation but it remains unaffected by bromine in carbon tetrachloride solution. There

* While this work was in progress Sharma et al. isolated taraxerol and ellagic acid from its stem and flowers. (R. C. Sharma, A. Zaman and A.R. Kidwai, Ind. J. Chem., 2, 234 (1964)).
TRITERPENOIDS I. THE SAPOGENINS OF FAGONIA CRETICA LINN.  
(ZYGOPHYLLACEAE)

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The water soluble sapoines, which are present in Fagonia cretica in high concentration, have been extracted and hydrolysed into a mixture of sapogenins and sugars. Among the five sugars found in the hydrolysate, four have been identified as glucose, rhamnose, xylose and arabinose. From the mixture of sapogenins, two pure, well-crystalline sapogenins, provisionally named as Fagogenin and Genin-A, have been isolated. The molecular formulae of Fagogenin and Genin-A have been found to be $C_{30}H_{48}O_{4}$ and $C_{29}H_{46}O_{5}$ respectively and the former has been characterised by preparation of its diacetate and dibenzoyl ether. Spectroscopic studies on both the compounds have been made and the oxygen functions of Fagogenin have been determined. Fagogenin has been found to contain a lactone and two hydroxyl groups in addition to, at least, one double bond.

Fagonia cretica Linn., a small green spiny under-shrub which grows throughout North Western India, Sind, the Punjab, and the southern provinces of the Western Peninsula, is reputed in the indigenous system of medicine as a tonic, lebrifuge and prophylactic against smallpox. It has also been used in the treatment of dropsy. As literature search showed that no chemical work has hitherto been done on this plant, and also because its aqueous extract has been recently claimed by some of the physicians of the Unani Tib as useful in the treatment of certain types of cancer, it was considered of interest to undertake a chemical investigation of the plant.

As a result of the present investigations, it has been found that the plant contains water soluble sapoines in high concentration. On hydrolysis with dilute acid, the sapoines yielded a crude mixture of sapogenins, the major portion (ca. 60%) of which was alkali soluble, thus indicating the presence of one or more acid sapogenins in the mixture. From the neutral portion, we have isolated a pure crystalline sapogenin which we have named provisionally “Fagogenin”.

With acetic anhydride in pyridine at room temperature, Fagogenin gave a diacetate, $C_{34}H_{32}O_{6}$, which crystallised from ethanol-water or, better, from ether in the form of colourless, glistening needles, m. p. 243°, $[x]_{D}^2 + 50.10^\circ$. The infra-red spectrum of the diacetate in KBr showed strong bands at 1733 cm$^{-1}$ (shoulder at 1742 cm$^{-1}$) and 1248 cm$^{-1}$ (ester) but no OH absorption. Whilst Fagogenin itself gave no colour with tetranitromethane, the diacetate gave a strong yellow colour with this reagent indicating the presence of a carbon-carbon double bond which is evidently of the unreactive type present in triterpenes.

With benzoyl chloride in presence of pyridine, Fagogenin yielded a dibenzoate, $C_{34}H_{32}O_{6}$, which crystallised from benzene-petroleum ether in the form of clusters of white leaflets, m. p. 264-4°, $[x]_{D}^2 + 100.62^\circ$. The infra-red spectrum of the dibenzoate in KBr showed a doublet at 1582 and 1600 cm$^{-1}$ (aromatic) and strong bands at 1733 (C=O of benzoate), 1712, 1267 and 1110 cm$^{-1}$. The last two bands are due to C-O stretching vibration of the $C_{6}H_{4}COO$-group.

The formation of the diacetate and the dibenzoate and, at the same time, the absence of any OH absorption in their infra-red spectra, prove that Fagogenin contains only two hydroxyl groups.

Fagogenin did not give an oxime, a semicarbazone or a D.N.P. derivative even on refluxing with the ketonic reagents for 2-3 hours. On refluxing with 10 percent ethanolic potash for 3 hours, neither did it produce any acid. But when it was refluxed with 10 percent KOH in diethylene glycol for 3 hours, an acid was obtained in a very low yield proving that Fagogenin contained an ester.
DETERMINATION OF NITROGEN IN ORGANIC COMPOUNDS

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The determination of nitrogen in nitro, nitroso and azo compounds is described. The compounds are digested with sucrose and sulphuric acid in a sealed tube. The digest is passed through two columns of anion-exchange resin, placed one above the other. The upper column contains the resin in the hydroxide form and the lower in the iodide form.

Introduction

A novel method for the determination of ammoniacal nitrogen in organic compounds was described recently. The method employs sealed tube digestion of the compounds and the conversion, through ion-exchange resin, of ammonium sulphate to ammonium iodide which is then determined by the Leipert amplification procedure.

A similar determination of nitrogen in the nitro, nitroso and azo compounds will enhance the applicability of the method provided the oxidized nitrogen is reduced with an agent which does not interfere subsequently. Metallic reductants such as stannous chloride, titanous chloride, zinc and hydrochloric acid, etc. cannot be used as they interfere with the subsequent column operations. However sucrose or glucose which leave no residue on digestion with sulphuric acid have already been effectively used for the determination of these forms of nitrogen. In the present studies sucrose (5-6 mg) as reductant has, therefore, been used in addition to the reagents already reported. The recovery of nitrogen in NO₂, NO and -N=N- compounds is correct within ±0.3%.

Experimental

Reagents.—1. Ion-Exchange Resin:

Grind A.R. grade, strongly basic anion-exchange resin, Amberlite IRA-400(Cl) (Rohm & Hass Co. Ltd., Philadelphia, U.S.A.) to -40 mesh and +85 mesh. Treat it with 500 ml. of 2N H₂SO₄ and then wash it with water till free from the acid. Convert the resin to the hydroxide form by treating it with 1 litre of 2N NaOH. Wash it on a sintered glass funnel with deionized water till free from alkali. Convert 60 g. of this resin to the iodide form by treating it with 250 ml. of 2N potassium iodide. Wash it with deionized water till it is free from the excess of potassium iodide.

2. Sucrose A.R.
3. Concentrated sulphuric acid (E. Merck), G.R.
4. Bromine solution:

Dissolve 100 g. of potassium acetate in 1 litre of glacial acetic acid then add 4 ml. of M.A.R. bromine.

5. Formic acid 98-100 percent.
6. Sulphuric acid 2N.
7. Sodium thiosulphate solution 0.02N.
8. Starch indicator solution.
9. Deionised water: Deionise distilled water by passing it through a bed of Bio-deminolite.

Apparatus

1. Digestion tubes: Thick walled pyrex glass tubes (10 x 100 mm.) size.
2. 1 ml. graduated pipette.
3. Heating Block.5

An electrically heated thermostatically controlled dural block with 8 holes to accommodate sealed digestion tubes.

4. Transfer pipette containing 2 ml. glass bulb in the stem.
5. Ion-exchange columns:

Fit together two air condensers 25 x 1.4 cm. each with B₁₅ ground glass joints. Fill the upper column with the hydroxide resin and the lower column with the iodide to give a bed of 19 cm. in each column. Fit the upper column with 75 ml. pear-shaped funnel with B₁₅ ground glass joint to serve as a wash water reservoir.

Experimental

(1) Digestion.—Weigh 1-1.5 mg. of an organic compound and (4-5 mg.) of sucrose into a clean digestion tube. Add 0.1 ml. of concentrated
COMPLEXOMETRIC ESTIMATION OF MICROGRAM AMOUNTS OF COPPER USING E.D.T.A.

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Microgram amounts of copper can be determined by titration against a standard EDTA solution using pyridine and potassium thiocyanate as an indicator at pH 5.2. Bromobenzene is used to enhance the sharpness of the end point. At the end point the colour change is from green to colourless which can be readily detected visually. At least as 25 μg of copper in 25 ml solution can be estimated. Citrate, pyrophosphate, thiosulphate and oxalate interfere in the presence of interfering cations modified procedures such as masking, solvent extraction and Lead Collector separation procedure give accurate results.

Introduction
A number of methods have been used for the titrimetric determination of copper with EDTA. They employ some indicator and give satisfactory results up to milligram quantities of copper. Ansbacher, Remington and Culp have employed modified Bazzio’s method for the colorimetric determination of copper. In this method copper (II) is precipitated by means of pyridine (Py) and thiocyanate as a green inner-complex of the composition, [Cu(Py)₂₂(CNS)₂]. The precipitate is extracted with bromobenzene from the aqueous phase and concentration of copper determined colorimetrically. Accurate results are obtained for 50-150 μg of copper. It was thought of interest to investigate the copper (II), pyridine and thiocyanate reaction for estimating microgram amounts of copper by a titrimetric method using EDTA (disodium salt) with a view to develop a rapid, convenient and accurate volumetric method for the said purpose.

Principle of the Method.—Copper forms a green coloured complex with pyridine and thiocyanate (CNS) which reacts with EDTA at ~90°C, giving a light blue solution. Hence, copper can be titrated against EDTA using pyridine and potassium thiocyanate as an indicator. The use of bromobenzene gives a sharp end point as in this solvent copper-pyridine-thiocyanate complex is highly soluble and trace amounts of unreacted copper-complex gives intense colour in bromobenzene. The titration is continued to the point till bromobenzene layer becomes colourless.

Experimental

Reagents.—All reagents used were either A.R. grade or extra pure (E. Merk).

Standard Copper (II) Solution.—A stock solution of CuCl₂·2H₂O, of 99.89 purity, was prepared by dissolving 8.4337 g. of the salt in 1-litre distilled water. Solutions of desired concentrations varying from 1000 μg to 1 μg Cu/ml. were obtained by diluting an aliquot of the stock solution with water.

Standard EDTA (Disodium Salt) Solution.—A stock solution of EDTA of about 0.005 M was prepared and standardised against Calcium Carbonate using Eriochrome Black T indicator. Solutions ranging from 1x10⁻³ to 5x10⁻⁶M in strength were prepared by diluting the stock solution.

HCl-Acetate Buffer of pH 5.2.—It was prepared by mixing 200 ml of N-Na A c and 40 ml of N-HCl and making the volume to 1 litre with distilled water.

Potassium Thiocyanate.—A 10% solution (w/v) of KCNS was prepared.

Colorimeter: For photometric titrations Karl Kolb “Lichtelektrisches Kolorimeter Modell VI” with a cell of 1 ml. capacity was used.

Effect of pH

Effect of pH on the detectability of copper is shown in Table 1. The optimum pH for this determination is 5.2.

Procedure in Absence of Interfering Substances

A known volume of copper solution containing 5 to 3000 μg copper was taken in a conical flask (50 ml) and different volumes of pyridine and 10 percent KCNS solution were added, followed by buffer solution of pH 5.2. The volume of solution was made upto 25 ml., heated to 90°C and standard EDTA was added from a micro burette until the green colour precipitate had almost completely disappeared. Bromobenzene (0.5 ml) was added and the titration continued till bromobenzene layer had become colourless. The end point was noted visually and photome-
ACTIVATION EFFECTS OF MAGNETISM ON REDUCED NICKEL SUPPORTED ON METALLIC OXIDES*

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A study was made of the magnetic susceptibility of the various metallic oxides used with varying quantities of nickel supported on them. It was shown that there is an increasing amount of evidence in favour of a direct relationship between the magnetic susceptibilities of the supports and their catalytic activities. An attempt was made to study the nature of the reduced nickel on the supports by the carbon monoxide chemisorption method, electron microscope and X-ray diffraction.

Several workers, notably Winger, and Kalcher and Teller have investigated a possible relationship between magnetism and catalysis. No single mechanism can possibly explain all catalytic activities, but catalysis and magnetic properties are often found together. In some cases, such as the ortho-para hydrogen conversion, there is a direct relationship between the activity of the catalyst and its magnetic moments. In others, the magnetic properties of a catalyst can be made use of in the determination of its structure. Diamagnetic gases do not catalyse, but diamagnetic solids such as charcoal are excellent catalysts. The heterogeneous ortho-para hydrogen conversion on paramagnetic oxides has been studied by Taylor and Diamond. The effect is marked in that a 6 hours contact with diamagnetic lanthanum oxide produced only 17 percent conversion, whereas less than three minutes contact with strongly paramagnetic gadolinium oxide produced nearly 100 percent conversion. This experiment is impressive because of the striking similarity in all the chemical as well as physical properties of these oxides. This magneto-catalytic effect was confirmed by Forestier and Selwood.

Conflicting reports, however, appear from time to time in the literature. For instance Olmer failed to find any relationship between the catalytic activities of iron, nickel and cobalt and their magnetic properties. Ogawa, on the other hand, claimed that the ortho-para conversion of hydrogen on a ferromagnetic catalyst is retarded by the magnetisation of the catalyst. The question as to whether there is an effect of a magnetic field on the reaction velocity and the chemical equilibrium has also been discussed by Bhatnagar and Mathur.

Elements which show strong catalytic activity can be related more or less directly to their magnetic properties, d-band character and unpaired electrons. In recent years, Maxted has pointed out that there exists considerable evidence that the catalytic activity is related to the d-band deficiency. In other words, the catalytic activity is proportional to the degree to which d-orbitals are filled with paired electrons. This is confirmed further by the observation that the poisons for such catalysts are substances which eliminate the d-band deficiency by contributing electrons. Such substances are atoms or groups having free electron pairs in the valency shell; metals with half filled or completely filled d-band or compounds with unsaturated bonds. An example can be cited in the poisoning action of dimethyl sulphide on palladium, which causes a decrease of paramagnetism, owing to the filling of the partially unoccupied d-band of the metal of electrons from the free pair in the sulphide.

The purpose of the present work was to use magnetic susceptibility measurements to study the structure of supported nickel and to relate the magnetic data to actual catalytic activity, as far as possible.

Preparation of Supports

Nickel supported on zirconia, thoria, titania and lanthanum oxide were prepared as follows:

The general experimental method of preparing reduced nickel on various oxide supports as laid down in detail in a previous publication was followed. A fixed amount of support (4.5 g) was taken in a narrow glass vessel and to this was added a varying amount of nickel formate (0.25 g to 4.5 g) dissolved in aqueous ammonia (0.88M). Ammonia was slowly boiled off the sample accompanied by vigorous shaking in order to ensure a thorough impregnation of nickel formate on the metallic oxide. It was dried overnight (12 to 14 hours) in an oven at 65°. The sample was then reduced under a current of hydrogen at 280° for

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*This work was done by the author in the Department of Physical and Inorganic Chemistry, University of Bristol, England.

*All temperatures are in degrees centigrade unless stated otherwise.
BIOCHEMICAL AND NUTRITIONAL STUDIES ON EAST PAKISTAN FRUITS

Part II.—Differential Mechanism of Ripening of Ordinary Variety and (Unripe Green Sweet) Variety of Mangoes (Mangifera indica)

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The differential mechanism of ripening of local ordinary varieties of mangoes has been investigated by measurement of the changes in titratable acidity, reducing and non-reducing sugars and the dehydrogenase activities at different stages of their growth up to ripening and comparison against the values of the same for Kanchamitha variety which is sweet even in the green stage. The results show gradual increase of acidity in every part of the ordinary mango with the progress of growth upto maturity and then a decline of the above value when the mango ripens. This fall in acidity is associated with the formation of both reducing and non-reducing sugars and the elaboration of dehydrogenase activities. In the case of Kanchamitha variety, even in its unripe condition the acidity is low in association with more contents of sugars and more activity of the dehydrogenases. The significance of these results in the above varieties of mangoes has been discussed in the light of the two different mechanisms operating in the process of ripening of mangoes.

Introduction

In East Pakistan different varieties of mangoes are grown every year in sufficient quantities. But in the humid tropic atmospheric conditions of the region a large fraction of the total product get spoiled due to overripening and ultimate fermentative breakdown of sugars. In order to develop preservation techniques, it is necessary to have complete information about the actual mechanism of the process of ripening for each individual variety of mango. This necessitates the study of the formation of acids, gradual breakdown of acids with simultaneous formation of sugar and finally the fermentative breakdown of sugar to alcohol, and also of the different enzyme systems which are involved in the whole chain of the above reactions. Though the overall reaction in each variety may be of the same nature, the period of onset of some enzyme systems in one variety pertaining to ripening process may be different from the other or the pathway of activities of some enzyme systems may differ from variety to variety. This possibility has been shown by Qudrat-i-Khuda, De and Khan in their work on the ripening of two opposite varieties of banana,—one "Amrit Sagar" (Gross Mitchell) and the other vegetable variety where it was shown that the dehydrogenase activity develops in the "Amrit Sagar" variety with gradual formation of sugars during ripening whereas this is completely absent in the vegetable variety which, even on storage for a long period, does not show any formation of sugar. It is quite possible, therefore, that similar differences might also exist in different varieties of mangoes which show different degrees of sweetness and flavour after ripening. With this possibility in view, the present work has been undertaken to investigate the mechanism of ripening of one local variety of mango by study of the changes of its acidity, sugar content and the dehydrogenase activities and by their comparison against the similar values of another variety which is sweet even in unripe green stage and locally called the Kanchamitha Variety. (Kancha means green unripe and Mitha means Sweet)*

Work carried out on some important varieties of mangoes grown in India are reported in the literature and most of this work refers to the difference in the acidity and sugar contents in green and ripe mangoes. But no attempts have been made to correlate these differences with the activities of some dehydrogenases, kinase etc. which may actually help to judge the differential characteristics of the various varieties with respect to the formation of acids and sugars in unripe and ripe conditions. In the present investigation attempts have been made in this direction by simultaneous study of the activities of dehydrogenases in green and ripe conditions.

Experimental

The tree of the mango of the local Desi variety was selected from the laboratory garden and the fruits were collected at regular intervals from the smallest edible stage until maturity and ripeness. The sizes of the fruits at each stage of collection were measured and these are expressed as length and breadth in cm. and the averages of large number of fruits collected at each stage are shown in the Table. These were then segmented with glass edge into four fractions—(a) skin, (b) flesh or marrow (c) seed and (d) the seed cover.

*This variety is grown in East Pakistan and West Bengal and mentioned by Ganguly et al. on Marketing of Mangoes in India—Agri. Marketing Ser., 77 38-45 (1958) and also referred to in Wealth of India, C.S.I.R., New Delhi, Raw Materials Vol. VI (I-M), p. 270.
ELECTROLYTIC PREPARATION OF COPPER CARBONATE

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(Received March 3, 1964)

Electrolytic preparation of basic copper carbonates has been studied. The electrolysis was carried out both with a mixture of sodium sulphate and sodium carbonate or sodium sulphate alone with the incorporation of CO₂, using copper electrodes or lead as cathode. The maximum current efficiency (98 percent) was obtained with the concentration of 60 g. per litre Na₂SO₄ and at a current density of 13.5 amp./ft². 'Thur' (salinity) being abundantly available containing sodium sulphate 25-30 percent, Na₂CO₃, 12-15 percent and NaCl 5-7 percent provided the electrolyte. Copper sulphate was prepared by dissolving the basic carbonate obtained from the above process in dilute sulphuric acid and crystallized out.

Basic copper carbonate (Azurite, 2CuCO₃, Cu(OH)₂, or Malachite, CuCO₃Cu(OH)₂) which finds a market as such, has been prepared by a number of investigators employing a variety of methods. The most important work already done being, (i) Alexander Wacker's Method: a copper gauze is immersed in a saturated solution of sodium chloride and shaken with oxygen and CO₂ at 2 atmospheric pressure, to give a precipitate of basic CuCO₃ containing 1 percent Cu₂O,CuCl₂, (ii) Copper is treated with oxygen in the presence of an ammoniacal solution of (NH₄)₂ CO₃ or NH₄HCO₃, (iii) Howard's Electrolytic Process: a solution containing NaHCO₃ or any other salt providing CO₂ and NaClO₃ is electrolyzed in the presence of a copper anode.

The conversion of electrolytic copper carbonate to copper sulphate by treatment with H₂SO₄ ensures the purity of the product. In addition, this process is much more convenient as compared to the conventional methods, i.e., treating copper scrap or ore with H₂SO₄. This chemical finds an extensive application in textile and leather industries but the complete absence of metallic sulphates and free acid is a prerequisite.

Experimental

Electrolytic basic copper carbonates form the starting material for the preparation of CuSO₄.5H₂O. Copper carbonates best suited for the above preparation are either azurite or malachite (2CuCO₃, Cu(OH)₂ or CuCO₃Cu(OH)₂). Both of these were prepared by continuous as well as batch processes.

Preparation of Electrolytic Basic Copper Carbonate.—Continuous Process: Electrolytic copper carbonates were prepared by electrolyzing a solution containing Na₂SO₄ as electrolyte, using copper electrodes or copper anode and lead cathode, while CO₂ was passed during electrolysis. Copper ions at the anode react with sulphate ions of the electrolyte to give copper sulphate, whereas sodium ions discharged at the cathode form NaOH, which eventually gets converted to Na₂CO₃ in the presence of CO₂. Sodium carbonate and copper sulphate so generated react together to form basic copper carbonate, i.e., azurite or malachite, regenerating Na₂SO₄ in the solution.

A series of experiments was carried out to establish most appropriate conditions for the efficient electrolysis, by varying composition and concentration of the electrolyte at various current densities.

1. Variation of Current Efficiency* with Concentration.—Aliquots of different concentrations of the electrolyte were electrolyzed in the presence of CO₂ at a constant current density of 13.5 amp./ft² and current efficiencies calculated in each case.

2. Variation of Current Efficiency with Current Density.—Taking the concentration 60 g./L. (Expt. 1, Table 1) as the optimum, the current efficiency was measured at various values of C.D. (Table 2).

The investigation covered a range of C.D. from 13.5 to 25.5 amp./ft². Current efficiency was high up to 98 percent at a C.D. of 13.5 amp./ft² but it decreased with the increase in C.D. (Fig. 1).

Instead of using CO₂ for the formation of basic copper carbonate, experiments were conducted with Na₂CO₃ in the electrolyte. The object in view was to explore the possibilities of utilizing 'Thur' which is abundantly available in saline areas of West Pakistan. The average analysis of 0.5 ton of 'Thur' collected from large area near village Chung, Tehsil Lahore, is Na₂SO₄, 25-30%; Na₂CO₃, 12-15% and NaCl, 5-7%. Since the composition of 'Thur' has been found to vary from place to place, the experiments were

*In the following text, the current efficiency, current density and weight g./litre are abbreviated to C.E., C.D. and g./L.
TURPENTINE OIL-BASED CHEMICALS

Part I.—A new Method for the Production of Terpin Hydrate

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A systematic study of the production conditions for terpin hydrate has been carried out. The application of either benzene- or toluene sulphonic acid has advantageously eliminated the use of sulphuric acid in the existing processes. In contrast to sulphuric acid, the sulphonic acids do not require the presence of additional emulsifiers and the maintenance of costly conditions of low temperature and inert atmosphere. The yield of the hydrate with ether acid is also always higher than that obtained with sulphuric acid.

Introduction

Terpin hydrate is an important intermediary product in the manufacture of commercial terpineol. It is also used in the pharmaceutical preparations to inhibit cough and expectoration in chronic bronchitis, and is administered in an elixir. Terpin hydrate, terpineol and pine oil are obtained as a result of hydration of \( \alpha \)-and \( \beta \)-pinenes (I and II), generally occurring in different quantities, in turpentine oils. cis-Terpin hydrate (III) can be obtained quite readily in the crystalline form when turpentine oil is allowed to react with sulphuric acid under controlled conditions. In one of the methods, the reactants are vigorously shaken for periods extending well over ninety hours. The resulting crystalline terpin hydrate is separated from the reaction mixture by centrifuging and washing with dilute ammonia and water in order to remove the adhering acid and the unreacted oil. In the modified methods, sulphuric acid is used again but in the presence of various emulsifying agents such as gelatine and gums, sulphonates and sulphonic acids. There is, however, no obvious improvement in the yield of the product.

Since concentrated sulphuric acid is basically a dehydrating agent, its use in this reaction always requires the adoption of special measures which include slow dropwise addition of the acid, maintenance of low temperature and continuous vigorous stirring of the reactants. Another condition is to keep the reactants under an inert atmosphere. A little rise in temperature, for instance, results in the polymerisation of turpentine oil and in the formation of other undesirable side-products, thereby affecting the yield of terpin hydrate.

The maintenance of these conditions, particularly of low temperature and inert atmosphere in sulphuric acid hydration, is obviously a costly as well as tedious step. Its elimination, therefore, would considerably simplify the procedure for the production of terpin hydrate. A successful attempt has been made to prepare terpin hydrate from Pinus longifolia turpentine oil at room temperatures (16-35⁰), by replacing sulphuric acid with benzene-or toluene sulphonic acid which acts simultaneously as a mild hydrating as well as emulsifying agent.

In this paper, the production conditions for terpin hydrate with the sulphonic acids have been described.

Materials and Methods

Materials.—Turpentine oil: Turpentine oil, Grade I, obtained from the Jallo Rosin and Turpentine Factory, was employed in these studies.

Acids and Sulphates: The various acids and sulphates were of commercial grade.

Reaction Vessel.—The conversion of the turpentine oil pinenes into terpin hydrate was carried out in a 3-litre stainless steel drum which had a removable lid. The drum when mounted on its horizontal axis could be revolved with an electric motor at 40 r.p.m.

Procedure

500 g. of the turpentine oil and known amounts of the hydrating agents particulars of which are recorded in the Results were placed in the reaction vessel. The lid of the vessel was closed tightly and the reactants were thoroughly shaken for
EVALUATION OF ANTIFIREOL—A FOAM FIRE FIGHTING COMPOSITION

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Antifireol has been tested for its stability, compression ratio, density, drainage of liquid and the throwing range. Commercially available foam compositions have also been tested for a comparative study.

Introduction

Chemical foams have been known for a long time to be very useful as fire extinguishers. They act in many different ways e.g., (1) by enveloping the fire with an atmosphere of carbon dioxide which reduces the supply of oxygen; (2) by generating steam from the liquid draining from the foam which again restricts the access of oxygen; (3) by depositing a layer of chemicals which acts as a barrier between the burning material and air and (4) by absorbing heat from the burning material thus imparting a cooling effect. Antifireol has been developed in these laboratories and bears quite a few advantages over the commercially available compositions.

The ingredients are a mixture of soluble and insoluble carbonates which, when mixed with a solution of aluminium sulphate, sets in two types of reactions: one involving the soluble carbonates or bicarbonates results in an instantaneous evolution of carbon dioxide and the other is a slow one with the insoluble carbonates which keeps on reacting even after the first reaction has ceased. This gives a two-fold advantage: one is the production of dense foam, sodium bicarbonate alone does not produce thick foams and the other is the added stability to the foam. The last named property is due to the slow reaction.

The stability of foam may be dependent upon two different phenomena. (1) The rate of drainage of liquid from the foam and (2) the rate of breakdown of the foam. If a good stabiliser is at hand, the rate of drainage is not affected by the breakdown of foam. In estimating the stability of the foams particular attention has been directed towards determining the time required for the collapse of the foam to half the initial volume and to find out the drainage of the liquid from the foam. The other tests required for the evaluation of a fire fighting composition are the density of foam, the compression ratio, the range covered when the foam is expelled through the nozzle of a two-gallon container and the effectiveness in extinguishing the fire. Laboratory studies were carried out for all of these tests except the last named for which only the field test was undertaken.

Experimental

Tests were carried out by preparing two sets of solutions. The acidic solution was poured into the alkaline solution by means of a delivery tube in a way that its tip reached the lower most portion of the funnel thus ensuring complete admixture of the two solutions. For estimating the drainage time the tests were carried out in a large separating funnel with a conical base. The drained liquid was collected and measured at regular intervals. The stability and compression ratio tests were performed in large graduated cylinders. The volume of the foam was noted at regular intervals. For the measurement of the density, the weight of a definite volume of foam from the field tests and also from the laboratory tests was noted. The range of the throw of the foam was found by performing a series of tests on solutions prepared according to the directions. A two-gallon container was used for the purpose.

Results

Six commercial foam compositions were tested in order to compare with the results of Antifireol. Most of these compositions have been imported from abroad. It was thought that some of these samples got deteriorated due to long storage and hence the results on Antifireol were checked by exposing it to air for three months. Very little, if any, deterioration had occurred. This is attributed to the excellent property of the stabiliser and the insoluble carbonates which are known to act as desiccants.

Table 1 shows the throwing range and density of foams and Table 2 gives the drainage of liquid from the foam. The volume occupied by the foam and the compression ratio are given in Tables 3 and 4. By observing the volume of the foam at regular intervals, it is found that only 1,
AN AGRO-PEDOLOGIC STUDY OF THE SOILS OF SYLHET FOOTHILLS, EAST PAKISTAN

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The present investigation deals with the agro-pedologic study of the soils occurring in a portion of the foothills of Sylhet, the major tea-growing area in East Pakistan. The N-P, and K status of the soils was studied on horizon basis to find out the pattern of distribution of these elements.

Introduction

The locality wherefrom the present soils have been collected is the major tea-growing region of East Pakistan. With the growing need for the expansion of tea plantation in the country, it was assumed that an investigation on the elements of major agronomic importance, i.e., nitrogen, phosphorus and potassium might prove helpful to land-users. In this paper an attempt has been made to study the profile distribution of the different forms of N-P-K to assess their interplay in plant nutrition on the one hand and the influence they exert on the pedogenic characteristics of the soils on the other.

Materials and Methods

The soil samples were collected on a natural horizon basis from a portion of the foothills of Sylhet which are situated at a distance of 180 miles north-east of Dacca. The area under investigation covers about 30 sq. miles. It consists of conspicuous hills and valleys which have a Lang's rain factor of 225.67 and presents an ideal condition for the production of tea. The climate of the region is wet, monsoonic, and the annual rainfall is about 200". On the hill tops the major portion is occupied by mixed deciduous forest and a small portion is under tea plantation. In the valley region rice is the main crop. Native grass also covers a considerable area.

From six soil profiles 29 soil samples were collected for laboratory study. The soil types were tentatively named after their surface texture and locality names as follows:

Hill Soils.—(1) Salia Sandy Loam (Salia SL), (2) Mughlipara Fine Sandy Loam (Mughlipara FSL), and (3) Lackatooarah Loamy Sand (Lackatooarah LS).

Valley Soils.—(1) Nacksapara Silty Clay Loam (Nacksapara SCL), (2) Khakurpara Silty Clay (Khakurpara SC), and (3) Salehpur Silty Loam (Salehpur SL).

Different forms of nitrogen, phosphorus and potassium were determined. For the estimation of ammoniacal and nitrate nitrogens Piper's methods were followed. The percentage of organic nitrogen was obtained by subtracting inorganic nitrogen from total nitrogen.

Available phosphorus (0.002N H₂SO₄-soluble) was determined by Troup's method, modified by Lynch, Davis and Mc Naught. Inorganic (0.2N H₂SO₄-soluble), organic, sesquioxide-bond (acidoxalate-soluble) and aluminium-bound (2.5 percent CH₃COOH-soluble) phosphorus were determined by the methods given by Mattson et al. Iron-bound phosphorus was obtained by deducting aluminium-bound phosphorus from the sesquioxide-bound phosphorus.

Available potassium was determined by Dyer's method. For the determination of total and adsorbed potash, Piper's was followed. Fixed potassium in soil and clay was obtained by deducting both available and adsorbed K₂O from the total K₂O on soil and clay respectively. Fixed K₂O in non-colloid fraction was obtained by deducting fixed K₂O in clay from the fixed K₂O in soil. Organic carbon was determined by Piper's method.

Results and Discussion

Relationship Among Available N-P and K.—It is nowadays a universally known fact that there
SHORT COMMUNICATION

UTILIZATION OF D.D.T. WASTE FOR THE SYNTHESIS OF 5-CHLORO-7-IODO-8-HYDROXYQUINOLINE AMOEBCIDE FROM P-DICHLOROBENZENE

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EFFECT OF HEAT ON PETKOLINS – CHLORINATED PESTICIDES, UNDER ATMOSPHERIC CONDITIONS

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