COMPARATIVE MEASUREMENTS OF THE TEMPERATURE DERIVATIVES OF VISCOSITY, DENSITY AND REFRACTIVE INDEX OF PURE LIQUIDS AND SOLUTIONS

Part I.—Some Dilatometric Measurements on Ethylene Glycol at Intervals of 1°C. to 2°C. in the Range of 20°C. to 80°C.

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Recent work on analysis of the temperature variations of coefficient of dilatation, \( \alpha \), and new measurements on refractive index of water\(^7 \) have shown good correlation with previously reported jumps in activation energy, \( E_r \). In order to elucidate further the physical basis for such behaviour, similar measurements have been made on coefficient of dilatation \( \alpha = \frac{I \Delta V}{V_o \Delta T} \) of ethylene glycol in the range of 20°-80°C., with temperature intervals \( \Delta T = 1°-2° \) C. A large dilatometer with a calibrated capillary is used, in which a change of 1°C. produces a change of about 40 mm. in the level. With temperature control within 0.002 to 0.005°C., an accuracy of 1 in 400 in \( \alpha \) is attainable.

The temperature variation of \( \alpha \) shows a nicely undulating regular graph from 30°C. to 75°C., and the mean graph of two sets of measurements exhibits a peak-to-peak amplitude of about 1.2×10\(^{-5} \) with a period of 4° to 6°C. The majority of the minima in \( \alpha \) correspond closely (within \( \pm 1°C. \)) with sharp jumps in \( E_r/J \) for ethylene glycol. Some extra minima are also found at 42°, 56° and 67°C., each of which is in the middle of a long "flat" i.e. constant region of \( E_r/J \). Further work on other liquids and solutions is planned.
THE ACTIVITY COEFFICIENTS OF SULPHURIC ACID IN ACETONE-WATER MIXTURES

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The work on the activity coefficient of \( \text{H}_2\text{SO}_4 \) in acetone-water mixture was conducted on the cell: Pt, H\(_2\) (1 atm.) | \( \text{H}_2\text{SO}_4 \) (m), acetone \((X\%)\), \( \text{H}_2\text{O} \) \((100-X\%)\) | \( \text{H}_2\text{SO}_4 \) | Hg. The electromotive forces were measured at eleven different molalities ranging from 0.5 to 1.00 m at \( 32 \pm 0.05^\circ\text{C} \). To find the standard potentials, extrapolation method was used. Better extrapolation was obtained by plotting \( \Delta E \) against the square root of molality, as described by Land and Crockford.\(^1\) where \( \Delta E \) is the difference between the measured c.m.f. for various acid molalities for a given acetone-water mixture and the corresponding values of Hamed and Hamer\(^2\) in water corrected to \( 32^\circ\text{C} \). Standard potentials were obtained by subtracting \( \Delta E \) at zero molality from the standard potential of water at \( 32^\circ\text{C} \), and the values found were 0.5674, 0.5572, 0.5651 and 0.4654 volt at \( 32^\circ\text{C} \) for 5, 10, 20 and 40\% acetone, respectively. The mean ion activity coefficients were calculated with the help of the equation:

\[
E = E^0 - \frac{3 RT}{2F} \ln \left( \frac{4 \sqrt{3}}{\pi} \ m \ \gamma_{\text{aq}} \right)
\]

and the values were found to be lower than those in aqueous solutions at the corresponding molalities.

**Introduction**

Moore and Felsing\(^3\) attempted to measure the electromotive forces on the cell: H\(_2\) (Pt.) | H\(_2\)Cl | AgCl | Ag, using 10\% acetone in water as the solvent. They were unable to get steady and reversible hydrogen electrode in the medium using platinum electrodes coated with platinum black. D. Feakins and C.M. French\(^4\) investigated the same cell and claimed stability and reproducibility of the electrode when a bare platinum electrode is used. They reported that the surface should be cleaned by polishing the electrode (e.g. by rubbing it with an abrasive or with round end of a glass rod) or by treatment with 50\% aqua regia or preferably by a combination of these two methods. It is evident that rigid control of several conditions is necessary to obtain a steady and reversible hydrogen electrode in the acetone-water mixtures. The present investigation was designed to find the requisite conditions for a steady and reproducible hydrogen electrode in the said solvent when hydrochloric acid is replaced by sulphuric acid. Consequently the cell under investigation was

Pt, H\(_2\) (1 atm.) | \( \text{H}_2\text{SO}_4 \) (m), acetone \((X\%)\), \( \text{H}_2\text{O} \) \((100-X\%)\) | \( \text{H}_2\text{SO}_4 \) | Hg.

However a considerable data about the activity coefficients of sulphuric acid in water-organic solvents (except acetone) is available in literature. The worth mentioning work in this connection is of Y.S. Przeborowski, V.G. Georgievski and N.D. Filippova,\(^5\) Shibata and Oda,\(^6\) McDougall Blumer,\(^7\) Crockford and Wideman,\(^8\) Land and and Crockford\(^2\) and French and Hussain.\(^9\)

**Experimental**

Materials.—100\% sulphuric acid was obtained by adding a calculated quantity of oleum (containing 65\% free SO\(_3\)) to concentrated sulphuric acid as described by Lange.\(^10\) On account of the hygroscopic nature of the acid, it was considered desirable to prepare it frequently in small quantities for the experimental work.

Analar acetone was further purified by shaking it with silver oxide, then filtered, dried over freshly ignited potassium carbonate and distilled through an efficient fractionating column as described by Werner.\(^11\) The middle fraction thus obtained was used.

Analar mercury supplied by the B.D.H. was further purified by passing repeatedly through dilute nitric acid column containing mercurous nitrate and subsequently distilled under vacuum.

Mercurous sulphate needed for the preparation of the electrode was prepared by adding mercurous nitrate in water containing a few drops of concentrated nitric acid and the resulting solution was poured into electrically stirred dilute (1 to 6\%) sulphuric acid. Mercurous sulphate thus obtained was preserved in 3M. \( \text{H}_2\text{SO}_4 \) until used.

For the purification of hydrogen and for the preparation of hydrogen electrode the procedure adopted was the same as already described by F. Hussain and S.S. Haque.\(^12\)

Mercury-mercurous sulphate electrode was obtained by the method used by French and Hussain.\(^9\)
EVALUATION OF SOME WEST PAKISTAN CLAYS

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Twenty-seven clay samples from different regions of West Pakistan have been studied. The tests include chemical analysis, infrared absorption analysis, plasticity, water of plasticity, drying and firing behaviour including shrinkage, water absorption, and colour. The majority of these clays have been found suitable for different uses in the ceramic industry.

Introduction

Clay deposits have been reported to occur all over West Pakistan; very little is, however, known about the extent and quality of these deposits. The scanty and scattered information hitherto available of West Pakistan clay deposits was recently reported by Kazmi and Safdar. The present work was, therefore, undertaken to provide relevant information on the physico-chemical characteristics of West Pakistan clays, and to determine their suitability for different uses in the ceramic industry.

Twenty-seven clay samples were collected from the various ceramic raw material suppliers and lease-owners. Insufficient information is available regarding the geology and the magnitude of these clay deposits. Since most of these samples were obtained from suppliers, it is assumed that in all cases the deposits are commercially exploitable. They were subjected to a number of physical and chemical determinations including chemical analysis, infra-red absorption analysis, plasticity, water of plasticity, slaking nature and drying and firing behaviour. These tests are of considerable importance to a clay worker. However, further work on differential thermal analysis, X-ray studies, particle size analysis and dehydroxylation studies is in progress and the results will be communicated later.

Experimental

Methods.—The raw colour of clays and the visible impurities like quartz, sand and other gritty materials present therein, were observed by visual examination.

Slaking Nature of clays was determined by immersing an approximately one-inch cube of crude clay lump in distilled water in a beaker. The slaking behaviour was recorded as quick, slow or non-slaking. The raw colour, visible impurities and the slaking nature of these clays are given in Table 1.

Chemical Analysis was carried out, on duplicate samples using the ASTM methods for clay analysis. Presence of free lime (calcium carbonate) was detected by dropping dilute hydrochloric acid on several representative pieces of the dried material. Any effervescence was taken as an indication of the presence of calcium carbonate. The absence of any effervescence was indicative of the absence of free lime.

The Pyrometric Cone Equivalent (PCE) was calculated from the chemical analysis according to the Schuens formula:

\[ \text{Seger Cone} = \frac{113 + \text{Al}_2\text{O}_3 - \text{RO}}{4.48} \]

This method is reported to have an accuracy of + one cone for clays containing 20-50 percent alumina. The results of chemical analyses, along with the-alumina, silica ratio and the PCE for each clay are presented in Table 2.

Infra-Red Absorption Analysis was conducted with a double-beam Beckman Spectrophotometer, Model IR5A. The samples, for infra-red absorption analysis, having particle diameters smaller than 5 microns, were prepared according to the Hunt and Turner method.

Plasticity was noted by the hand-feel method by mixing 120 mesh clay sample with an adequate amount of distilled water to form a mass suitable for plastic pressing between the fingers; it was recorded as good, fair, moderate or poor.

The test pieces for the determination of other physical properties were prepared by hand-pressing the same plastic clay mass used for noting plasticity, in a steel mould to form straight and smooth rectangular bars of \(7" \times 1" \times 1"\) size, free from air bubbles and voids. The test pieces were marked with two parallel crossed lines 14 cm. apart for shrinkage measurements.

Drying Linear Shrinkage was calculated in the usual way by measuring the difference of the shrinkage marks after drying at 110°C. Fired linear shrinkage at 1000°, 1100°, 1150°, 1200°, 1250°, 1300°, and 1350°C. was similarly measured and calculated on the dry-length basis of the test pieces.
A STUDY OF A SWAT KAOLINITE

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A recently discovered Swat clay has been studied with a view to determine the physical properties like plasticity, water of plasticity, drying and firing shrinkage, water absorption and reflectance; and chemical analysis, differential thermal analysis, infra-red absorption analysis, spectrographic analysis and pyrometric cone equivalent. Results indicate it to be a kaolinite of an excellent quality suitable for making high grade ceramics and porcelain, paper making and various miscellaneous industries.

In view of the scanty and scattered information hitherto available on Pakistani glass and ceramics raw materials, the West Regional Laboratories, P.C.S.I.R., Lahore, in collaboration with other Laboratories, have undertaken a comprehensive programme of evaluating indigenous raw materials. Previous work on the clay resources of West Pakistan has already been reported.

This communication is in continuation of this project and is based on the study of a Swat clay. The clay deposit occurs in villages Shah Deri and Shalhan, P.O. Bewlay, approximately 13 miles north-west of Mingora (Swat State), and is at a distance of about 8 miles from the Swat river. The samples have been taken from surface outcrops in this area. It is believed that the deposits are fairiy extensive and occur in various stages of weathering from the parent rock. Geological information is not at present available and the Minerals Division of the North Regional Laboratories, P.C.S.I.R., Peshawar, are shortly undertaking a geological survey of this deposit.

Experimental

Physical properties namely, plasticity, water of plasticity, specific gravity, drying and firing shrinkage at different temperatures and chemical compositions were determined by methods previously described. The particle size distribution in the sub-sieve range was determined by the Andreasen pipette method, pH was determined after agitating a 1:2 clay water suspension for 30 minutes and using a Cambridge pH meter, brightness of the -300 mesh fraction of washed clay was measured on a photo volt Reflection Meter, Model 610, samples for infra-red absorption analysis were prepared by the Hunt and Turner method, pyrometric cone equivalent was determined according to ASTM methods and differential Thermal Analysis was carried out by using calcined alumina as inert material. Before making the D.T.A. run of the raw clay, larger pieces of quartz and felspar were removed by hand picking. PCE in °C. was also calculated from the chemical analysis according to the equation:

\[
PCE = \frac{360 + Al_2O_3 - RO}{0.228}\ 
\]

Washing of the raw clay was carried out in the following way:

500 g. of -60 mesh B.S. clay was mixed with 1.5 litre of tap water in an enamel bucket. The clay-water mixture was thoroughly hand-blunged for 30 minutes and then stirred mechanically to ensure the thorough dispersion of clay particles. The mixture was allowed to stand for about 15 minutes to permit coarse impurities to settle down. The top suspension was then passed through a 200 mesh B.S. sieve into another basin and allowed to settle down. The supernatant water was decanted and the sedimented clay was oven-dried at 110°C. The washed clay thus obtained was weighed and the percent yield was calculated.

Results and Discussion

Chemical Composition and PCE.—From Table 1, it may be seen that the alumina/silica ratio of both raw and washed clay is nearly the same as for theoretical kaolinite.

The only colour imparting oxide present in raw clay is Fe₂O₃ to the extent of 0.525%. Most of this is associated with the quartz and felspar and is reduced to 0.095% by beneficiation. Both the raw and the washed clay are white-firing.

The raw clay has a total flux content of about 10%, including 9.15% of CaO, which contributes to its low PCE. value (Orton Cone 23°, 1595°C.).
ELECTROLYTIC POLISHING OF ALUMINIUM

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A new electrolyte for electrolytic polishing of aluminium has been developed. The polishing is accomplished under controlled conditions in a mixture of sodium hydroxide, metaphosphoric acid and glycerine. A bright and glistening surface is developed after three to four minutes. Sulphuric acid can be used for subsequent anodizing.

Polishing brings about bright and smooth finish on metal surfaces. Metal surface, which might ordinarily appear even, is not so in actual fact. It consists of depressions and elevations, better known as valleys and hills. The object of polishing is evidently to cut down these hills to the level of valleys.

Three different methods have been and are being practised to achieve this object. The first and the oldest is the mechanical method that involves the cutting of hills of the surface with the help of a bob (fine grinder) revolving at a high speed. On close examination, however, it has been found that the hills are not cut down but are mostly flowed down in the valleys by the high pressure of the bob. Moreover, in mechanical polishing the surface is imbedded with the abrasive particles and acquires a greyish tinge in its appearance. In order to remove these defects, a second method known as chemical polishing was developed. The metal surface is dipped in a chemical or a mixture of chemicals which causes preferential corrosion of the hills of the surface and renders the surface smooth and polished. It is difficult, however, to control the corrosion and carry out the process successfully. This difficulty was overcome by a third method which is known as electrolytic method of polishing. In this method, the surface to be polished is made the anode in a suitable bath. When direct current is passed for a few minutes, the surface becomes bright and smooth.

The preferential attack on the so-called hills has been explained by various workers on the basis of the layer formation theory, although it is not found to be applicable in all cases. Jacquet first developed this process as early as 1933 for the electropolishing of copper using a mixture of acetic anhydride and perchloric acid as the electrolyte. Later on, several new electrolytes were introduced by other workers for a number of metals and alloys like brass, bronze, all types of steel, nickel, nickel-silver alloys, monel metal, nichrome, zinc, magnesium and aluminium.

Electrolytic polishing finds wide application in industry and research. In the early stages, metal surfaces were electropolished mainly for microscopic examination. Such polishing was regarded of much value as it did not disturb the crystalline structure of the metal. Later on, however, electropolishing acquired importance also in case of irregularly shaped articles where mechanical polishing is inapplicable.

When aluminium is exposed to air, a thin film of aluminium oxide is readily formed on the surface which protects further corrosion of the metal. Evidently the degree of protection can be augmented by increasing the thickness of oxide film. The process for increasing the thickness of aluminium oxide layer electrolytically is called anodizing. However, during anodizing, the original shine of aluminium surface is much reduced if the article has already been polished chemically or mechanically. This drawback is overcome to a large extent if the surface is electropolished before anodizing.

Interest in the study of the process was evoked by the fact that aluminium utensils are a common house-holder item in an average Pakistani home. To impart to them a permanent brightness in different shades, increased hardness and other desirable characteristics would certainly add to their presentability and acceptance. The process, in itself, is a simple one; aluminium surface, electropolished and anodized, is the pre-requisite in a number of decorative industries where the metal constitutes the main raw material for the finished goods.

It has been observed during the present studies that aluminium articles anodized in sulphuric acid bath under different conditions were not able to maintain the original brightness which had already been obtained mechanically or chemically. The present investigations were also directed towards the elimination of the dullness developed during anodizing.

Experimental

Materials.—1. Aluminium strips of 99.9% purity. Their surface area varied from 2 sq. inches to 8 sq. inches. They served as anode.
Some technological aspects of the chlorination of Daudkhel 'gasoline'

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'Gasoline', a waste industrial product from ammonium sulphate industry, has been chlorinated to obtain a pesticide named as Makrolin. Chlorine gas-rates when increased from 50 to 150 litres/hr./250 ml. of the 'gasoline', lower the first-stage chlorination period from 1.192 to 0.634 hours but do not appear to have any effect on the second-stage of chlorination. Caustic soda when used in 0.5 to 4 percent concentration lowers the overall period of chlorination from 44 to 22 hours. Higher concentration namely 5 to 10 percent do not further reduce the chlorination period. Catalytic chlorination in presence of anhydrous ferric-chloride (0.2 g./FeC1250 ml. of the partly chlorinated 'gasoline') has been found useful in reducing the overall chlorination period down to 24 hours. The aqueous phase separated after the chlorination contains about 20-30 g. of hydrochloric acid per 100 ml. of the solution which can be used as pickling-agent.

Introduction

At Daudkhel ammonium sulphate plant, water gas is produced by the gasification of low grade sulphuraceous coals. Along with it cracked volatile matter is carried over which when condensed yields a pale yellow oily product named as 'gasoline'. Gasoline, having specific gravity of about 0.8 g./cc. and b.p. range 60—200° C., is a mixture of unsaturated aliphatic and aromatic hydrocarbons. Since it contains 3-5 percent of sulphur, mostly in the form of thioethers, 'gasoline' cannot be used as a motor fuel. But by chlorinating 'Gasoline' a useful application has been found as a pesticide. Direct chlorination did not prove successful because it resulted in the formation of a thick resinous material due to the formation of chloro-sulphur compounds known to have polymerising effect on hydroaromatic bodies. This difficulty has been overcome by making use of oxidative chlorination i.e. chlorination in presence of hypochlorite solution. Since the gas-rate, concentration of caustic soda and a number of metal catalysts have a pronounced effect on the overall period of chlorination, the present work has been restricted to the study of these variables. The new pesticide developed has been named Makrolin which compares favourably with D.D.T. in its insecticidal values, and copper naphthenate and colloidal copper in its fungicidal properties.

Experimental

Apparatus and Procedure.—The chlorination apparatus which consists of a number of vertical condensers arranged in a row is shown in Fig. 1.
SOME USEFUL PRODUCTS BASED ON EPOXY RESINS

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Some useful industrial and engineering materials like high temperature anticorrosion linings, universal flooring for chemical plants, grinding stones and fire resistant coatings on wood have been made from epoxy resins. Steel and iron have been metallized with Zn, Sn and Al using new technique based on these resins.

An epoxy resin is generally a product of the reaction between epichlorohydrin and bisphenol-A. The product is called an epoxide or epoxy resin because of the existence in the polymer of a carbon-oxygen chemical arrangement known as an epoxide group or an oxirane ring shown in the following manner:

\[
\begin{array}{c}
\text{C} \\
\text{O} \\
\text{C}
\end{array}
\]

Most of the epoxide resins at present available have the following general structure:

\[
\text{CH}_3
\]

These resins are liquid or solid, depending upon the degree of polymerisation, indicated by refractive index.

Epoxy resins, as such, are useless thermoplastic materials. To convert them into useful products, they are hardened or cured by condensing with anhydrides of polybasic acids, like phthalic anhydride, alkaline curing agents such as polyamines or compounds containing active hydrogen atoms.

Unlike the condensations leading to polyesters and polyamides, in which one water molecule is split out of the product, the epoxide condensation proceeds by opening cyclic structures which then combine to form chains. Since end groups are not lost, there is little volume change on condensation; furthermore, no water removal is involved. These two inherent properties are primarily responsible for the rapid growth in the use of these resins in recent years. They find application in many fields of industry and technology on account of their high strength, excellent adhesion, outstanding insulating properties and chemical resistance.

Uptil now, no work appears to have been done in Pakistan on epoxy resins. In view of the versatility of these resins and the multifarious uses to which they can be put with success, no country can ignore their development for long. Because of the availability of glycerine and acetone in the country now, it was considered desirable to start work on these useful resins.

Epoxy resins of different properties have been prepared by changing the proportion of the reactants. The low molecular wt. epoxies can be prepared by taking epichlorohydrin in large excess. Some of the epichlorohydrin reacts with bisphenol-A while the rest provides the medium for the condensation of the reactants. After the completion of condensation, the excess epichlorohydrin is recovered by distillation in vacuum. In case of high molecular wt. and solid resins, only the calculated quantity of epichlorohydrin is taken for condensation. Thus, solid resins with melting point up to 150°C have been prepared. Resins of low viscosities have been used without expensive solvents in high temperature coatings, fire-proof coatings and in metallizing steel. High viscosity resins were found to be satisfactory for their high chemical resistance. These resins in combination with phenol-formaldehyde and some suitable fillers have been used in the production of lining material which can be applied within the factory by an ordinary operator. High viscosity resins have also proved useful for the production of universal flooring for chemical industry.

Experimental

Epoxy Resin.—In a 2 lit. four-necked flask equipped with thermometer, reflux condenser and mechanical stirrer were placed 228 g.5 of 2,2-bis (4-hydroxy phenyl propane) and 925 g. of epichlorohydrin. The flask was heated in a water bath. 82 g. of NaOH (10% solution) were added in ten equal instalments. After the addition of NaOH, the reaction flask was heated for another hour at a temperature of 95°C. with constant stirring. The reaction being exothermic,
ORGANIC PEROXIDES

Part VIII.—Reactions of Dibenzoyl Peroxide and t-Butyl Perbenzoate with Grignard Reagents and Phenyllithium

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Dibenzoyl peroxide and t-butyl perbenzoate are allowed to react with phenyllithium and several Grignard reagents. The yields of benzoyloxy substitution by these Grignard reagents varied between 15–44%. Phenyllithium appeared to be markedly inferior for similar substitution.

As an alternative to our previous method for introducing the benzoyloxy group into aromatic nuclei, the reaction of benzoyl peroxide with aromatic magnesium/lithium compounds has been studied:

$$\text{RMgX} + (\text{PhCOO})_2 \rightarrow \text{PhCOOR} + \text{PhCO}_2 \text{MgX} \quad (1)$$

$$\text{RLi} + (\text{PhCOO})_2 \rightarrow \text{PhCOOR} + \text{PhCO}_2 \text{Li} \quad (2)$$

Gilman and Adams reported a 30% yield of phenyl benzoate from the reaction of phenylmagnesium bromide with dibenzoyl peroxide. We have obtained 15–44% yields of benzoate esters from four different Grignard reagents. The yield of phenyl benzoate decreased when the reaction of phenylmagnesium bromide with peroxide took place in the presence of additional magnesium bromide.

**Table 1.**—**Yields from Reactions of Dibenzoyl Peroxide with Grignard Reagents RMgBr.**

<table>
<thead>
<tr>
<th>R</th>
<th>Yields of ester (%)</th>
<th>Yield of benzoic acid (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-Butyl</td>
<td>20</td>
<td>80</td>
</tr>
<tr>
<td>Cyclohexyl</td>
<td>44</td>
<td>71</td>
</tr>
<tr>
<td>Phenyl</td>
<td>23</td>
<td>72</td>
</tr>
<tr>
<td>p-Biphenyl</td>
<td>15</td>
<td>51</td>
</tr>
</tbody>
</table>

*Based on equation 1. + Based on: $\text{Br}_2\text{O}_2 \rightarrow 2\text{BrOH}$.  

This finding and the high yields of benzoic acid have since received an explanation from the work of Lowesson and Yang, who found that Grignard reagent may react in two different ways:

1. to give benzoate ester and benzoic acid:

$$\text{R}_2\text{Mg} + 2(\text{PhCOO})_2 \rightarrow 2\text{PhCOOR} + (\text{PhCOO})_2 \text{Mg} \quad (3)$$

From this reaction the maximum yield of benzoic acid (based on $(\text{PhCOO})_2 \rightarrow 2\text{PhCO}_2 \text{H}$) can only be 50%.

2. to give alkyl or aryl bromide and benzoic acid (maximum yield, 100%):

$$2\text{MgBr}_2 + 2(\text{PhCOO})_2 \rightarrow 2\text{Mg(OCP)}_2 \text{Ph}_2 + 2\text{Br}_2 \quad (4)$$

$$2\text{Br}_2 + \text{R}_2\text{Mg} \rightarrow 2\text{RBr} + \text{MgBr}_2 \quad (5)$$

$$\text{MgBr}_2 + \text{R}_2\text{Mg} + 2(\text{PhCOO})_2 \rightarrow 2\text{Mg(OCP)}_2 \text{Ph}_2 + 2\text{RBr} \quad (6)$$

Thus the result with cyclohexylmagnesium bromide (Table 1) indicates that in this case reaction 3 and reaction 6 are of almost equal importance, while that with n-butylmagnesium bromide indicates that with this reagent reaction 6 becomes more important than reaction 3.

It was thought that with phenylmagnesium chloride reactions 4 and 5 might not take place, and that the yield of phenyl benzoate might consequently be increased; in fact, it decreased to 17%. The reaction of phenylmagnesium iodide and of butylmagnesium chloride with benzoyl peroxide failed to yield any benzoate esters.

Because organolithium compounds are frequently easier to prepare than organomagnesium compounds, a few experiments were carried out...
ANATOMICAL CHARACTERS DIFFERENTIATING CRAWLING LARVAE OF MALE AND FEMALE LAC INSECTS

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A lac crop depends entirely on the presence of females in the generation. The body outlines of the two sexes in the crawling larval stage shows a difference. This requires morphological or anatomical characters to confirm sex differentiation. The lac insects have two brachial plates as a feature special to them. In the centre of this structure is a cluster of pores secreting wax. These pores are on the two brachia number 14 in the female, and 7 in the male larva. This anatomical finding confirms the observation that the female larva secretes more soft wax filaments than does the male.

Of all species of lac insects that are cultivated the Sind lac insect, Lakshadina sindica, Mahdi shows the greatest sex-ratio variability. The lac crops differ in quantity and the main contributing factor seems to be the sex-ratio in the generation, favourable to the female when the crop happens to be good. It is therefore necessary to identify the sex of the crawling larvae just settled on a twig, in order to forecast the crop the generation would produce. In actual practice what can be done as a convenient measure would be to place a sample of a twig infected with lac and determine the sex ratio by the difference in outline of the larval bodies. Such a method was first communicated by Mahdihassan and later confirmed by Negi. It is strange that no other author has added further observations on this vital problem. Above all if there be any doubt that the sex of the larva in its first stage has been rightly determined there is no morphological feature to decide the point. It is this crucial problem that forms the basis of the observations reported here.

Fig. 1 represents the male crawling larva, treated with alkali and finally stained with fuchsin, but is seen lying on its back. The anterior portion of the body, below the head, and on each side of the body margin, shows two thick chitinous plates. These are brachia, a structure peculiar to lac insects, and associated with the major spiracies. The insect (Fig. 1) is seen from below so that the brachium to our left actually represents the one which was on the right side of the insect body. The posterior end of the body shows six anal ring hairs forming a sort of brush; further two long Major Apical Hairs; and finally on each side a bidental appendage seen as dark markings. None of these features characterize the sex. But the brachium does. The brachia of Fig. 1 are enlarged in Fig. 2. The peripheral margin shows tactile hairs, represented here as pin holes, numbering five, which have also been partly numbered in Fig. 2. The brachial plate contains in the centre a group of pores from which filaments of soft wax arise. In Fig. 2 the insect’s right brachium contains as a central cluster four pores while the other only three. The total number of central pores is therefore seven in the young male larva.

Fig. 3 represents the anterior portion of another male larva, but seen dorsally. Its brachia are enlarged in Fig. 4, and show again, three central
EARLY DEVELOPMENTAL STAGES OF LEPTODIUS EXERATUS (MILNE EDWARDS)

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(Received December 28, 1963.)

Early development stages of Leptodius exeratus, reared in the laboratory have been described. Stages of egg till the time of hatching have also been studied. Prezoea, first zoea and second zoea have been illustrated and described.

1. Introduction

Three species of Leptodius occurring in the Karachi area are: L. exeratus (Milne Edwards) L. crossimanus (Milne Edwards) L. euglyptus quadrirrinosus (Chhapgar). Leptodius exeratus is very common and found on the shores having loose pebbles and stones. There is no record of any previous work done on the life history of this species from this area.

2. Materials and Method

Leptodius exeratus occurs commonly at low water under loose stones. Berried females were obtained from under the stones which were submerged even at low tide. Specimens were carried to the laboratory in sea water and transferred to glass aquaria. The berried crabs may be classified into four groups: (i) Early stage in which eggs are very small and mostly of yellowish colour (ii) Medium stage in which eggs are more developed and become pale or light brown (iii) Mature stage, in which the eggs become well developed having black spot in the middle. (iv) Spent stage, in this stage the eggs rupture by the movement of the abdomen of female crab and the prezoeal come-out. It was not always easy to distinguish between the four types except the last one which is more clearly marked out due to the colour and black spots. On September 3rd, the majority of the female crabs were berried of first stage and on October 15th large numbers were found 'spent'. In the same way from April 14th to June 20th there was a large proportion of early and medium stages. Reference to previous work reveals that females become mature with carapace width of approximately 11 mm. The size at which sexual maturity is attained in male has not been ascertained definitely.

The female crabs of spent stage were reared in glass aquaria. Since there was no arrangement of circulation of sea water it was changed every 24 hours. It is observed that female crabs of spent stage do not feed at all in the aquarium. The larvae upon hatching swim to the surface of water. They were removed with a pipette and placed in large beakers of freshly obtained sea water, stirred with an electrically operated propeller for aeration.

The larvae were examined every twelve hours and, when any change was observed, some of them were preserved in 70% alcohol. Dead material and sloughed skins were removed or the active larvae transferred to a fresh container already supplied with fresh sea water with some phytoplankton. Fume spent in each stage varies and depends considerably on the relative abundance of food, temperature and salinity of the water and on other factors.

The eggs hatched, while still attached to abdomen, into prezoeal which do not swim or move actively except for a little movement of the abdomen. This stage lasts about two to three hours. The first zoea stage, in favourable conditions lasts from two to three days and during this stage larva grows in size. It moults, and becomes second zoea. This stage lasts from four to five days.

3. Early Developmental Stages

Eggs.—In the early stage the eggs are 0.82 mm. in diameter. In this stage two layers are quite clear (Plate I, Fig. 1). Mature egg is 1.0 mm. in diameter and the eye spot is quite distinct (Plate I, Fig. 2). Pigments are formed and two layers of the egg seem more prominent. The egg of spent stage measured 1.44 mm. in diameter and is the most developed stage of the eggs. (Plate I, Fig. 3). At this stage the outer wall of the egg ruptures by jerks of the abdomen of the female crab and the first and second maxillipeds emerge; eyes are quite prominent and the abdominal segments can be demarcated.

Prezoea.—Prezoea is obtained from the spent state; it measures 1.04 mm. in breadth and 2.3 mm. in length; breadth of telson is 0.54 mm. Telson is not forked and does not bear any hair
PESTICIDAL POTENTIALITY OF PETKOLIN IN COMPARISON WITH OTHER CHLORINATED INSECTICIDES

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Pesticidal action of Petkolin, a petroleum based chlorinated insecticide, has been studied by using topical application method against cockroaches and house flies. The LD$_{50}$ was found to be in the range of 64 to 96 micrograms per cockroach and 8 to 20 micrograms per fly. Against mosquito larvae, LC$_{50}$ was in the range of 5 to 8 p.p.m. and LC$_{95}$ in the range of 8.5 to 15 p.p.m. Petkolin was more toxic than Makrolin against house flies and mosquito larvae, but less toxic against cockroaches.

**Introduction**

In continuation of earlier work on the pesticidal action of Makrolin by Ashrafi et al., a series of pesticidal products, obtained through the chlorination of indigenous and foreign petroleum cuts by Siddiqui and Qureshi, have been tested to evaluate their insecticidal action. As a result of these co-operative studies it has been found that the chlorination of certain fractions of both indigenous and imported petroleum furnishes products which are toxic to insects. Out of these, the two products obtained through the chlorination of petroleum cuts in the boiling range of 35-155°C, and named as Petkolin-A and Petkolin-S, have been found more toxic to insects than others.

The insects used were cockroaches (*Periplaneta americana*), house flies (*Musca domestica*) and mosquito larvae (*Aedes aegypti*).

**Materials and Methods**

The topical application method has been used for testing the insecticides. The different concentrations ranging from 0.1 to 5% of Petkolin, Makrolin and DDT (Technical) were prepared in acetone. In case of cockroaches 10 µl and for house flies 1.2 µl of each concentration were applied topically. Cockroaches and house flies of known age were used and each experiment was run in triplicate. Thirty cockroaches and seventy-five flies were exposed against each concentration. The percent mortalities were calculated by using Abbott's formula and LD$_{50}$, LC$_{50}$ and LC$_{95}$ values were calculated by probit analysis.

For testing the larvicidal action, 0.31 ml. of each concentration was used to spread a 10µm thick film on the surface of water. The total quantity of water used was 1500 ml. in which 20 mosquito larvae of known age were released. A detailed account of the method has already been described by Ashrafi et al.

**Results**

*Cockroaches.*—Mortalities obtained with different concentrations of Petkolin have been shown in Fig. 1, and calculated LD$_{50}$ values along with those of Makrolin and DDT are given in Table 1.

![Fig. 1. Showing the percent mortalities of cockroaches against percent concentration of Petkolin.](image-url)
PHARMACOLOGY OF THE CRUDE EXTRACT OF ANONA SQUAMOSA, (SHARIFA)

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The pharmacology and toxicology of the water soluble portion of the alcoholic extract of the leaves of Anona squamosa (Sharifa) has been studied. The extract was found to stimulate the isolated rabbit heart, relax the isolated rabbit duodenum and raise the blood pressure of anaesthetised animals. It also caused a contraction of the nictitating membrane of the cat. The actions were very similar to those produced by adrenaline. Adrenergic blocking agents like dibenamine and ergotamine completely blocked and reversed the pressor response of the extract.

The results indicate that the active substance is very similar to adrenaline in its pharmacological actions.

Introduction

Anona squamosa Linn., is an indigenous plant belonging to the family Anonaceae and is commonly known as "SHARIFA". Various preparations made from its leaves and seeds have been described to possess anthelmintic and insecticidal properties. In indigenous medicine decoction of Sharifa leaves has also been used in cases of cardiovascular collapse. Santos et al studied the chemistry of the extract of the leaves and seeds and found gum, resins, oils and an alkaloid "Anonaine", both in the leaves and the seeds. The pharmacological activity of the crude extract of the leaves as well as that of the alkaloid "Anonaine" has not so far been described. The paper deals with the pharmacology and toxicology of the water soluble portion of the alcoholic extract of Sharifa leaves.

Preparation of Extract

Fresh, undried leaves were weighed, cut into small pieces and percolated with alcohol for seven days. Percolation was repeated three times, and the alcohol was removed in vacuo at 40°C. The extract was treated with petroleum ether and the semisolid mass was taken up in distilled water. This pale strawcoloured solution with a pH of 5-6 was found to be active.

Pharmacology

The pharmacology of the extract was studied on the following preparations:

1. Isolated Rabbit Heart.—Langendorff isolated heart preparation was set up according to the method of Burns. Mc Ewan's solution was used for perfusion. Contractions of the heart were recorded on the smoked drum.

2. Isolated Rabbit Duodenum.—A piece of rabbit duodenum was perfused in oxygenated Tyrode's solution at 37°C. Contractions were recorded on smoked drum by a frontal writing lever.

3. Blood Pressure of Dog.—Dogs were anaesthetised with a dose of Pentothal 15 mg./kg. combined with Gendaroal 25 mg./kg. given i.v. followed by an injection of Sodium Gendaroal 75 mg./kg. given intraperitoneally.

4. Blood Pressure of Cat.—Normal cats were anaesthetised with Gendaroal 1 mg./kg. intraperitoneally. Blood pressure was recorded from the carotid artery and the drugs were injected into the femoral vein. In certain experiments the contractions of the nictitating membrane were recorded by a frontal writing lever on smoked drum.

The above studies were repeated on three "reserpinised" cats. Reserpine was injected intraperitoneally in a dose of 1 mg./kg. b.w. on the first day, 2 mg./kg. b.w. on the second day and 3 mg./kg. b.w. on the third day. Experiments were done on the fourth day. Contractions of the nictitating membrane were also recorded.

5. Rat Blood Pressure.—Adult male rats were anaesthetised with chloralose 15 mg./kg. body weight given intraperitoneally. Blood pressure was recorded with a mercury manometer from the carotid artery. Injections were given via cannulated jugular vein.

Results

1. Isolated Rabbit Heart.—The extract was injected through a polythene cannula opening near the coronary artery into the perfusion fluid. A dose of 0.1 ml. produced a sharp rise in the amplitude and the rate of the heart. The contractions of the heart returned to normal after about 2 minutes. These responses were very closely matched by a dose of 0.5 µg of adrenaline given in a similar way (Fig. 1). The response
SHORT COMMUNICATION

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PROTEOLYTIC DECOMPOSITION OF FISH MUSCLE PROTEINS UNDER DIFFERENT CONDITIONS

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(Received January 01, 1964)
METHOD OF DETECTION OF PIRICULARIA ORYZAE AND HELMINTHOSPORIUM ORYZAE, ON MALT AGAR*

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