microbalance with a pyknometer of 25 ml capacity. The refractive indices were measured by a Pulfrich refractometer for sodium-D line. Chemicals used were of reputed make, purified and redistilled before use. The experimental values were reproducible within limits of reasonable experimental error so as not to affect the calculated values of g_{ab} (table 1).

It is expected that the two dissimilar molecules in the mixture form microheterogeneous clusters that vary in composition over the entire concentration range of the components in the mixture. The magnitude of g_{ab} reflects at least qualitatively the relative arrangement of these dissimilar molecules in those clusters. When the dissimilar molecules align in the same direction (co-operative angular correlation) they are said to form α-clusters and the value of g_{ab} comes out to be greater than unity. Alignment in opposition (destruction of angular correlation) results in formation of β-clusters for which the value of g_{ab} is less than unity. A perusal of table 1 indicates that β-clusters appear to be predominant in all the mixtures studied. The alcohol molecules in the pure state are arranged in homogeneous clusters of atleast three molecules[6]. There are molecular size holes or voids[7,8] in such structures. But the toluene molecules have no such clustering tendency. As the concentration of alcohol increases, some of the toluene molecules go to fill the voids in alcohol structure while maintaining anti-parallel alignment. This is manifested by gradual decrease in the value of g_{ab} reaching a minimum somewhere in the mid-range. Apparently, the α-clusters are predominant over clusters in these cases.

In mixtures (not reported here) of toluene with non-associated liquids such as chlorobenzene, methylbenzoate, ethyl benzoate, the value of g_{ab} comes out close to unity indicating no tendency for clustering of dissimilar molecules in such binary mixtures.

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EXTRACTIVE SPECTROPHOTOMETRIC DETERMINATION OF TRACE AMOUNTS OF PALLADIUM WITH BENZYLDI-METHYLPHENYLAMMONIUM CHLORIDE

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BENZYLDIMETHYLPHENYLAMMONIUM chloride, a quaternary ammonium salt possesses considerable potentiality to find application as a reagent for the determination of a number of metal ions when present in trace amounts in solution. Use of this reagent for detection of large anions, viz CrO_4^{2-}, $S_4O_6^{2-}$, $[Fe(CN)_6]^{3-}$, $[Fe(CN)_6]^{4-}$, and I^- and for the spectrophotometric determination of Co(II), Fe(III), Cu(II), Mo(V) and Bi(III) has been reported[1-3]. In this paper, we present a method for the extractive spectrophotometric determination of palladium in microamounts using benzyldimethylphenylammonium chloride as the reagent and 1,2-dichloroethane as the solvent for extraction.

Absorbance was measured with a Hilger Uvispek photoelectric spectrophotometer in matched quartz cells of 1 cm optical path.

Standard solution

A stock solution was prepared by dissolving Palladium(II) chloride (Johnson Matthey, London) in distilled water containing a few drops of HCl and was standardized by the known method[4]. Test solutions of lower concentration were prepared by appropriate dilution of the stock.

Reagents

The reagent, benzyldimethylphenylammonium chloride was prepared by mixing equimolar amounts of benzyl chloride and dimethylaniline and allowing the mixture to stand until a crystallisation was effected. The solid after washing with acetone was recrystallized from alcohol.

A 0.01 M (0.24%) aqueous solution of benzyldi-

methylphenylammonium chloride and a freshly prepared 5% aqueous solution of A.R. potassium iodide were used as reagents. Solutions of 0.2 M acetic acid and 0.2 M sodium acetate were prepared to constitute the required buffer.

Standard solutions of diverse ions were prepared from their chloride, nitrate or sulphate, or from sodium, potassium or ammonium salts.

Recommended procedure

An aliquot of the palladium solution containing 5–160 μg of palladium was made upto 5 ml with water and acetate buffer so that the pH was between 3.4 and 5.8. To this, 1 ml each of the solutions of potassium iodide and benzyldimethylphenylammonium chloride followed by 5 ml of 1,2-dichloroethane was added. The resulting mixture was shaken for two minutes and the organic layer was separated. Absorbance of the extract was measured at 450 nm against the pure solvent. Amounts of palladium in unknown solutions were calculated from the standard calibration curve.

When potassium iodide is added to a neutral (or slightly acidic) solution containing a small amount of palladium, a reddish-brown colouration due to the formation of tetraiodopalladium(II) ion is produced which is not extractable into 1,2-dichloroethane. An aqueous solution of benzyldimethylphenylammonium chloride (QCl) forms a reddish brown precipitate with tetraiodopalladium(II) ion- the precipitate being an ion-association complex of the type $[Q^+]_2$ $[PdI_4{}_-]^{2-}$, which is completely extractable into 1,2-dichloroethane. The extract has maximum absorption at 450 nm and obeys Beer's law over the concentration range of 1–32 μg palladium per ml. The reagent blank has no absorption at this wave-length. Molar absorptivity and Sandell's sensitivity are 0.534 $\times 10^4$ 1 mole^{-1} cm^{-1} and 0.02 μg/cm^2 respectively. The standard deviation and coefficient of variation of the absorbance was found to be 0.003 and 0.6% respectively for 50 μg of palladium. The colour of the complex is stable for more than 72 hr.

The complex exhibited constant and maximum absorbance in the pH range 1.1—8.0. Sodium acetate-hydrochloric acid mixture was used to maintain lower pH values, acetate buffer was used for the pH range 3.4–5.8 and potassium dihydrogen phosphate—sodium hydroxide buffer was used for higher pH values. It was observed that the pH range 3.4–5.8 was most suitable for complete extraction because the interference due to diverse ions was minimum. If the pH is below 1.1, addition of potassium iodide resulted in the precipitation of black palladium iodide and the

reagent blank was found to possess some absorption at 450 nm due to liberation of iodine. In the pH range 1.1–8.0, the reagent blank was devoid of any absorption at 450 nm and the absorbance of the extract could be measured by taking the pure solvent as the reference.

The concentration of the potassium iodide solution employed had to be maintained between 1% and 12.5%. Use of a solution below 1% concentration gave low absorbance of the extract while that with concentration beyond 12.5% produced a coloured blank which absorbed considerably at 450 nm.

The effect of varying reagent concentration was also studied. A 0.24% (0.01 M) solution of benzyldimethylphenylammonium chloride was preferred, since the use of a solution with concentration below 0.15% gave low absorbance while the increased concentration produced no significant effect upon the absorbance.

The effect of foreign ions was studied by adding different amounts of foreign ions to 50 μg of palladium and then determining palladium by recommended procedure. It was found that Co(II), Ni(II), Ag(I), Au(III), Zn(II), Cd(II), Hg(II), V(V), Cr(III & VI), Mn(II), As(III), Sb(III), W(VI), Pb(II), F$^-$, Br$^-$, SO$_3^{2-}$, NO$_3^-$, SCN$^-$, ClO$_4^-$, C$_2$O$_4^{2-}$, citrate and tartrate ions even in amounts five times that of palladium did not interfere, and a good recovery of palladium (within 4% error in microgram level) was achieved. Equal amounts of Cu(II), Bi(III), Pt(IV), S$_2$O$_3^{2-}$ and MnO$_4^-$ interfered. Although Fe(III) and Mo(VI) did not interfere when present in equal amounts, their presence in five fold excess produced appreciable interference.

Interference due to Cu(II) and Bi(III) could be checked by using EDTA as masking agent. Effect of MnO$_4^-$ was overcome by reducing it with oxalic acid before the addition of potassium iodide. Fe(III) and Mo(VI) were rendered innocuous by the addition of ammonium fluoride.

The method thus proved to be simple and rapid, and yet provided excellent recovery of palladium in trace concentration in the presence of most of the common ions. The merit of the method is its high degree of precision and accuracy as is evident from the standard deviation and coefficient of variation in the absorbance for 50 μg of palladium.

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A NOTE ON THE ANTIINFLAMMATORY ACTIVITY OF BERGENIN

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BERGENIN, a gluco isocoumarin isolated from the flowers of *Peltophorum pterocarpum* Backer ex. K. Heyne (Fam. Leguminosae)[1] has been investigated for antiinflammatory activity by the carrageenin induced rat paw *oedema*[2].

Albino rats of either sex (130–150 g) were used as experimental animals. The animals were given food and water *ad libitum* both before and during the experiment and maintained at room temperature. The test compound suspended in sterile water to give the desired concentration, was administered to three different groups of rats (5 rats in each group) at doses of 60 mg/kg BW, 120 mg/kg BW and 240 mg/kg BW and the reference drug—phenyl butazone was given to a group at a dose of 100 mg/kg BW.

A solution of carrageenin (1% W/V, 0.1 ml) was injected into the sub-planter tissue of one of the hind feet. The paw volume was measured immediately after injecting carrageenin and again after 3 hr by the Plethysmometric method[3]. The results were expressed as increase in foot volume in ml over the initial volume (table 1).

From these results it is clear that bergenin produces a dose dependent inhibition of carrageenin induced rat paw oedema. Its potency is maximum at higher doses, comparable to that of the reference drug viz. phenyl-butazone. This test offers a significant predictive value for its clinical usefulness.

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Table 1 *Effect of phenyl butazone and bergenin on carrageenin induced rat paw oedema.*

Treatment	Dose mg/kg BW	Mean increase in paw volume $\pm$ S.E. (ml)	% inhibition
Control	—	0.28 ± 0.01	—
Phenyl butazone	100	0.08 ± 0.01	72.6
	60	0.16 ± 0.01	44.1
Bergenin	120	0.13 ± 0.01	53.6
	240	0.09 ± 0.01	65.5

ISOLATION OF PHYTOSTEROLS FROM SUGARCANE PRESS MUD AND MICROBIAL CONVERSION OF THE PHYTOSTEROLS TO 17-KETOSTEROIDS

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THE sugarcane press mud is a waste material of sugar industries. It contains a number of valuable materials like wax and lipids which have commercial potential[1]. It has been suggested that phytosterol in the press mud may serve as a potential source of sterol for production of biologically active steroids[2]. In this communication, the isolation of phytosterols alongwith wax and lipids from press mud and microbial conversion of the phytosterols to androst-4-ene-3,17-dione (AD) and androsta-1,4-diene-3,17-dione (ADD) which can serve as intermediates in the synthesis of steroid hormones are described.

Benzene extraction of the dried sugarcane press mud (obtained from Assam Cooperative Sugar Mills Ltd.,