Investigation on the extraction of molybdenum(VI)5-chloro-7-iodo-8-quinolinol/5,7-diiodo-8-quinolinol into *N*-butanol and its analytical application

J. Chem. Research (S), 2002, 258–259
J. Chem. Research (M), 2002, 0662–0680

L. Ramadevi

Department of Chemistry, RVR & JC College of Engineering, Chowdavaram, Chandramoulipuram, Guntur-522 019(A.P.), India

A simple extraction-spectrophotometric method has been developed for determining 5,7-diiodo-8-quinolinol(diiodoquin/DIQH)5-chloro-7-iodo-8-quinolinol(clioquinol/ClQH) in pills and ointments and also important observations were made in deducing the composition of the extracted species.

Keywords: diiodoquin, clioquinol

Halogenated derivatives, diiodoquin(DIQH) and clioquinol(CIQH) have been widely used as chemotherapeutic agents possessing antiamebic, antiprotozoal and antimicrobial properties.[1,2] The extraction of yellow complexes Mo_2L_2[5]/NaL[6] into benzene/alcohol has provided a method for the assay of clioquinol in drugs and ointments. The author now reports a simple extraction–spectrophotometric method for determining diiodoquin and clioquinol in pharmaceutical preparations using excess molybdenum(VI) as reagent and also the composition of the extracted species under metal excess and ligand excess condition.

The absorption spectrum of an *n*-butanol extract of DIQH/CIQH from excess molybdenum(VI) solutions shows absorption maxima at 410 nm with molar absorptivities 3.52×10^3 and 3.16×10^3 mol^{-1} lit cm^{-1} respectively. Absorbance of the species were stable for more than 4 hrs. A one fold excess of Mo(VI) reagent was suitable for the analytical determination. The optimum acidity was larger than indicated by pH 3.5 and up to 1.5M H_2SO_4. Beer's law is obeyed up to a maximum concentration of 119.04 and 106.40 µg/ml respectively for DIQH and CIQH. Pharmaceutical sample solutions were prepared by dissolving accurately-weighed amounts of powdered tablet or cream in 2.75M sulfuric acid in 100ml volumetric flask. An aliquot of the test solution was employed in the place of a standard. The amount of pure compound in the aliquot was read from the calibration graph constructed for DIQH and CIQH separately. Common excipients used in tablets and the base in ointments did not interfere.

The composition of the coloured species, determined using Job's method of continuous variation and mole ratio method indicated the formation of 1:1 complexes. However, it is observed that there is a change in absorption spectra with increase of ligand concentration. A series of solutions of *n*-butanol extracts were prepared with different ratios of DIQH/CIQH keeping Mo(VI) concentration constant. The absorption spectra of each of these extracts were measured against respective blanks. The spectra show the presence of an isosbestic point at around 450nm(diiodoquin) and 440 nm (clioquinol) which seem to be consistent with the author's expectation of the formation of the two metal complexes with metal to ligand ratios of 1:1 and 1:2. No further change in absorption spectrum after a certain ligand excess is indicative of the completeness of ML_2 formation. However, in experiments done using excess Mo(VI) as chromogenic reagent for recovering the ligand in a coloured form extracted into n-butanol, it is observed that with a slight excess of Mo(VI) over that needed for the 1:1 complex formation under the optimum pH condition, the recovery is complete. This is in contrast to the behaviour in experiments using increased concentration of diiodoquin/clioquinol. In both types of experiments, the absorbances were measured against appropriate excess reagent blank and accordingly the different trends observed cannot be attributed to analytical factors or errors.

The usual extraction equilibrium studies using metal ion, pH and excess reagent as variants to determine the composition of the extracted species could not be adopted as the metal from the aqueous phase was extracted completely, even with only a slight excess of the ligand as reagent. The change in the absorbance of the extracted species with increased ligand reagent concentration may therefore have to be looked upon as a change in the chemical composition of the species by the interaction with excess ligand through a reaction that may be conveniently described as an organic phase reaction.

Assuming that the 1:1 complex is formed and extracted completely at the stoichiometric ratio of metal to ligand in the extraction system, the author has adopted the following procedure to determine the composition of the higher complex from the equilibrium of reaction in the organic phase under conditions of constant pH.

$$(ML)_0 + (X\text{-}1)HL_0 \rightleftharpoons (ML_x)_0 + (X\text{-}1)H^+ \qquad (1)$$

The absorbance of the organic extracts were measured at 410nm at various DIQH/CIQH concentrations. The absorbance at the 1:1 point in each of the curves is taken to represent $(ML)_0$ concentration ($A_{initial}$). The limiting absorbance value (A_{final}) in the curve at higher ligand concentration is taken to represent the concentration of the higher complex (ML_x) when the whole metal exists in this form. Both $A_{initial}$ and A_{final} are constant as long as the metal ion concentration in the experiment is constant. Intermediate absorbances (A) were accordingly considered to be sum of contributed absorbances of ML and ML_x. Assuming the additive property of the absorbances of the two complexes, the contributions of the respective complexes for absorbance were calculated with the help of the following derived expressions.

$$A_{ML} = \left[\frac{A_{final} - A}{A_{final} - A_{initial}}\right] A_{initial} \qquad (2)$$

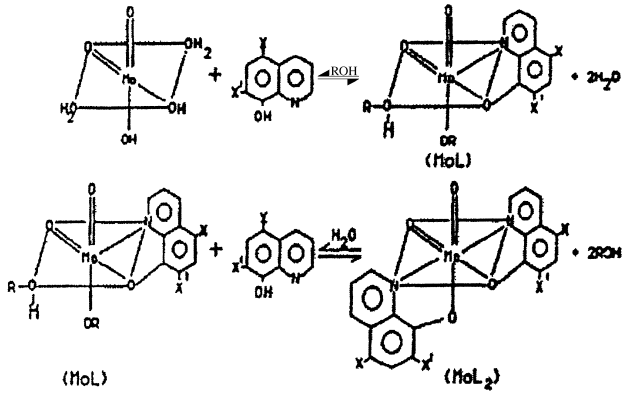
$$A_{MLx} = \left[\frac{A - A_{initial}}{A_{final} - A_{initial}}\right] A_{final} \qquad (3)$$

The slope of $\log[(A\text{-}A_{initial})/(A_{final}\text{-}A)]$ vs $\log[HL]_0$ may be expected to yield the value of $(x–1)$. The value of $(x–1)$ is read from the slope of the straight line and is found to be unity showing that the composition of the higher complex is ML_2. The result is same with both the oxine derivatives (diiodoquin/clioquinol). It may be noted that as per the math-

* To receive any correspondence.

ematical analysis the ligand concentration at the equilibrium was reckoned after accounting for the one required for ML formation.

The following relations probably explain the formation and extraction of 1:1 and 1:2 complex species into *n*-butanol, and are consistent with the usually observed 6 coordination of Mo(VI) in many of its complexes. The aqueous molybdenum(VI) is conveniently represented as $H_2MoO_4.2H_2O$ in Scheme 1.



Scheme 1

The above formulations are based on the tacit assumption, that the complexes are monomeric in molybdenum, that QH(halo derivative of quinolinol) moiety is a bidentate group and that six coordination of Mo(VI) is satisfied in the complexes. Since ROH is the extracting solvent it can also function as a neutral donor. The replacement of H_2O molecules in the molybdenum species by ROH makes it less hydrophilic and facilitates extraction into the organic phase. It is further probable that the free OH groups in the molybdenum species undergo esterification with ROH thereby checking the tendency of the species to form dimeric species through diol condensation.[8] The structure proposed was consistent with similar structures proposed by Amos and Sawyer with the *cis* structure for oxo groups in the MoO^+ unit.[9]

The formation of a 1:1 complex that is extractable into an organic phase has not been so far reported for Mo(VI) and 8-quinolinol or its derivatives, though the sulphonic acid of 5-iodo-8-quinolinol (ferron) is known to give a 1:1 complex in aqueous reactions. Probably the low aqueous solubility of the ligand (8-hydroxyquinoline as well as its derivatives (except sulphonic acid) and the corresponding Mo(VI) complexes, might be the hindering factor for their formation in aqueous solution.

The author is thankful to AICTE New Delhi for financial support, also to Prof. K. Sreeramam for guidance in undertaking this work.

Technique used: Solvent extraction-spectrophotometry

References: 9

Received 10 October 2001; accepted 28 April 2002
Paper 01/1083

References cited in this synopsis

1 A. Burger, *Medicinal Chemistry*, Part 1, 3rd edn, John Wiley & Sons, New York, 635, 540–542.
2 A.G. Gilman, L.S. Goodman and A. Gilman, In: *The Pharmocological Basis of Therapeutics* (Goodman and Gilman's eds.) 6th Ed., Macmillan, New York, 1980, p.1064.
5 K. Sriramam, G.S.N. Sastry and T. Saratchandrababu, *Ind. Drugs* 1988, **25**, 515.
6 K. Sriramam, T. Saratchandrababu, L. Ramadevi and J. Sreelakshmi, *Analusis*, 1990, **18**, 93–95.
8 W.R. Scheidt, *Inorg.Chem.*, 1973, **12**, 1758.
9 L.W. Amos, and Sawyer, *Inorganic Chemistry*, 1974, **13**, 78.