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Περίληψη

Η ενθαλπία ΔΗ των ετερογενών αντιδράσεων σε θερμικές μετατροπές είναι δυνατόν να προσδιοριστεί από τις καμπύλες TG και DTG των παραγωγογραφημάτων και με τη χρήση παραμέτρων όπως η θερμοκρασία T_m όπου παρατηρείται ο μέγιστος ρυθμός μετατροπής, η ταχύτητα θέρμανσης Φ, ο ρυθμός μετατροπής της ουσίας $(-da/dt)_m$ και ο βαθμός μετατροπής της ουσίας $(1-a_m)$, από τη σχέση:

$$\Delta H = R.T^2_m \, . \, (-da/dt)_m . \Phi^{-1} \, . \, (1-a_m)^{-1}.$$

Δυστυχώς όμως, στην αντίστοιχη βιβλιογραφία μέχρι σήμερα, δεν υπάρχουν πληροφορίες περί της ακρίβειας και αξιοπιστίας των λαμβανομένων με τη μέθοδο αυτή αποτελεσμάτων σε σύγκριση με τα αντίστοιχα που παίρνονται με άλλες μεθόδους. Ακριβώς αυτό το κενό έρχεται να συμπληρώσει η παρούσα εργασία.

Μελετήθηκε η θερμική διάσπαση του $CaCO_3$ αφ’ ενός και του $CaHPO_4.2H_2O$ αφ’ ετέρου και υπολογίστηκε η ενθαλπία ΔΗ των αντιδράσεων αυτών τόσο από την παραπάνω σχέση όσο και από τα εμβαδά των καμπυλών DTA.

Από τα αποτελέσματα που ελήφθησαν συνεπάγεται ότι η προτεινόμενη μεθοδολογία οδηγεί σε αρκετά ακριβείς και αξιόπιστες τιμές ΔΗ, ακόμη και σε διαδοχικές διεργασίες τα όρια των οποίων δεν είναι σαφώς καθορισμένα μεταξύ τους.

Πέραν τούτου, η ευρεία χρήση της μεθόδου αυτής επιβάλλεται και από το γεγονός ότι αυτή εμφανίζεται ως η πλέον αποδοτική, αφού, παράλληλα με τον υπολογισμό της ΔΗ επιτρέπει τον προσδιορισμό άλλων θερμοδυναμικών και κινητικών παραμέτρων όπως της ενέργειας ενεργοποίησης Ε, της κινητικής παραμέτρου n και του προεκθετικού παράγοντα της εξίσωσης Arrhenius Z.

Key Words: Derivatographic determination, Enthalpy, Heterogeneous reactions, Thermal transformation.

Κατά τη μελέτη των ετερογενών αντιδράσεων στα συστήματα στερεό/ρευστό, τον τελευταίο καιρό, παρατηρείται μια στροφή προς τις μη ισόθερμες συνθήκες διεξαγωγής των αντιστοίχων πειραμάτων. Οι συνθήκες αυτές επιτυγχάνονται σχετικά εύκολα και με μεγάλη ακρίβεια κυρίως στους παραγωγογράφους, όπου καταγράφοντας τις καμπύλες Τ, DTA, TG και DTG καταγράφεται ουσιαστικά η θερμική συμπεριφορά του υπό μελέτη συστήματος ή της δεδομένης χημικής ένωσης.

Πέραν τούτου, κατάλληλη επεξεργασία των καμπυλών DTA, TG και DTC μπορεί να οδηγήσει στόν υπολογισμό τόσο των θερμοδυναμικών (ενέργεια ενεργοποίησης Ε, ενθαλπία ΔΗ) όσο και των κινητικών (τάξη n, σταθερά ταχύτητας Κ) μιας δεδομένης μετατροπής.

Μια τέτοια μέθοδος προτάθηκε από τους Horovitz-Metzger[1], Allakhverdov-Stepin[2] και Gorbachev-Logvinenko[3] και εφαρμόστηκε με επιτυχία από τους Nirsha and al.[4,5,6,7,8,9,10,11] καθώς και από τους υπογράφοντες[12,13] για τη μελέτη της θερμικής αφυδάτωσης διαφόρων αλάτων.

Η παραπάνω μέθοδος βασίζεται στην υπόθεση ότι, με βάση τα παραγωγογραφικά δεδομένα, η κινητική της μετατροπής περιγράφεται με την εξίσωση:

$$-\frac{da}{dt} = K \cdot a^n \qquad\qquad -1-$$

όπου: a - βαθμός μη μετατροπής της ουσίας

n - κινητική παράμετρος (τάξη της αντίδρασης)

t - χρόνος

Κ - σταθερά ταχύτητα της αντίδρασης

$$K = Z \cdot e^{0 E/RT} \qquad\qquad -2-$$

Ζ - προεκθετικός παράγοντας της εξίσωσης Arrhenius

Ε - ενέργεια ενεργοποίησης

R - παγκόσμια σταθερά αερίων

Τ - Θερμοκρασία

Σύμφωνα με τη μέθοδο αυτή, από τις καμπύλες της μεταβολής μάζας (TG) και του ρυθμού μεταβολής μάζας (DTG) ενός παραγωγογραφήματος και με τη χρήση παραμέτρων, όπως: η θερμοκρασία $T_m(^oK)$, η ταχύτητα θέρμανσης $\Phi = dT/dt$ $(^oK.min^{-1})$, ο ρυθμός μετατροπής της ουσίας $(-da/dt)_m$ (min^{-1}) και ο βαθμός μετατροπής της ουσίας $(1-a_m)$, οι οποίες λαμβάνονται από τα σημεία καμπής των καμπυλών DTG, υπολογίζεται η ενθαλπία της θερμικής μετατροπής από τη σχέση[4,5,6]:

$$\Delta H = \frac{R.T^2_m.(-da/dt)_m}{\Phi.(1-a_m)}, \quad kcal.mole^{-1} \qquad\qquad -3-$$

Ταυτόχρονα μπορούν να υπολογισθούν η κινητική παράμετρος n, η ενέργεια ενεργοποίησης Ε και ο προεκθετικός παράγοντας της εξίσωσης Arrhenius Ζ από τις σχέσεις[1,2,3,4,5,6]:

$$a_m = 1,062.n^{1/(1-n)} \qquad\qquad -4-$$

$$E = \frac{n.R.T^2_m.(-da/dt)_m}{\Phi.a_m}, \quad kcal.mole^{-1} \qquad\qquad -5-$$

$$Z = \frac{E.a_m^{(n-1)}.\Phi}{n.R.T^2_m}.e^{E/RT}, \quad min^{-1} \qquad\qquad -6-$$

Διαπιστώνουμε ότι η μέθοδος είναι αρκετά εύχρηστη και αποδοτική, αφού επι-
τρέπει τον ταυτόχρονο προσδιορισμό των ΔΗ, Ε, n και Κ. Εκείνο που μέχρι σήμε-
ρα δεν είναι γνωστό είναι η ακρίβεια και αξιοπιστία των λαμβανομένων με τη μέθο-
δο αυτή αποτελεσμάτων σε σύγκριση με τα αντίστοιχα που παίρνονται με άλλες με-
θόδους, κυρίως δε αυτών που αφορούν τη μεταβολή της ενθαλπίας ΔΗ.

Η παρούσα εργασία στοχεύει να συμβάλλει προς την κατεύθυνση αυτή και έρ-
χεται να συμπληρώσει αυτό το κενό στην αντίστοιχη βιβλιογραφία.

Για το σκοπό αυτό, εφαρμόζοντας την παραπάνω μέθοδο, μελετήσαμε αφ' ενός
το παραγωγογράφημα της διάσπασης του $CaCO_3$ (σχήμα 1) και αφ' ετέρου συγκρί-

ΣΧΗΜΑ 1. *Καμπύλες DTA, TG και DTG παραγωγογραφήματος $CaCO_3$: Βάρος δείγματος -47,9mg,
ρυθμός θέρμανσης $\Phi=5°K.min^{-1}$, ταχύτητα εγγραφής -50mm. h^{-1}, ευαισθησίες TG-100mg, DTG-
20mg.min^{-1} και DTA-50μV.*
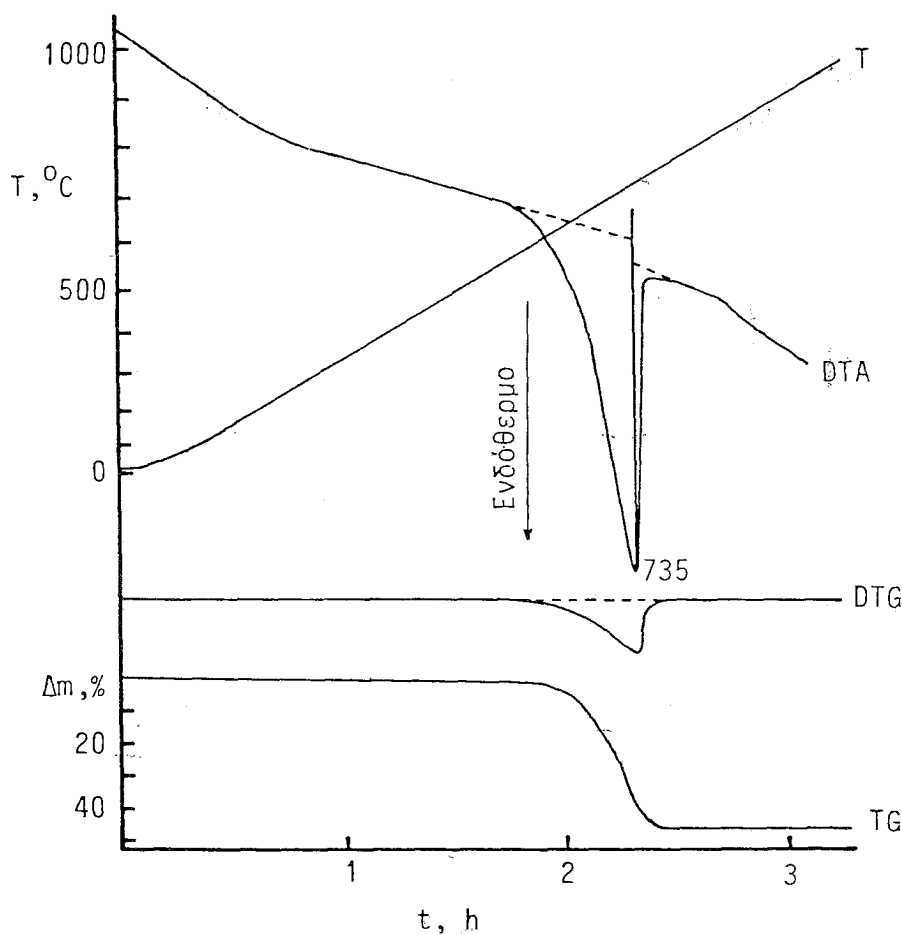
ναμε τα αποτελέσματα της αφυδάτωσης του $CaHPO_4.2H_2O$, που αναφέρονται σε προηγούμενη εργασία μας[12], με τα αποτελέσματα του υπολογισμού της ΔΗ από τα εμβαδά των καμπυλών DTA (διαφορικής θερμικής ανάλυσης) τόσο από το παραγωγογράφημα του τελευταίου με $Φ=5°K.min^{-1}$ (σχήμα 2), όσο και από την κατά βαθ-

ΣΧΗΜΑ 2. *Καμπύλες DTA, TG και DTG παραγωγογραφήματος $CaHPO_4.2H_2O$: βάρος δείγματος 100,5mg, ρυθμός θέρμανσης -$Φ=5°K.min^{-1}$, ταχύτητα εγγραφής -50mm.h^{-1}, ευαισθησίες TG-100mg, DTG-10mg.min^{-1} και DTA-50μV.*
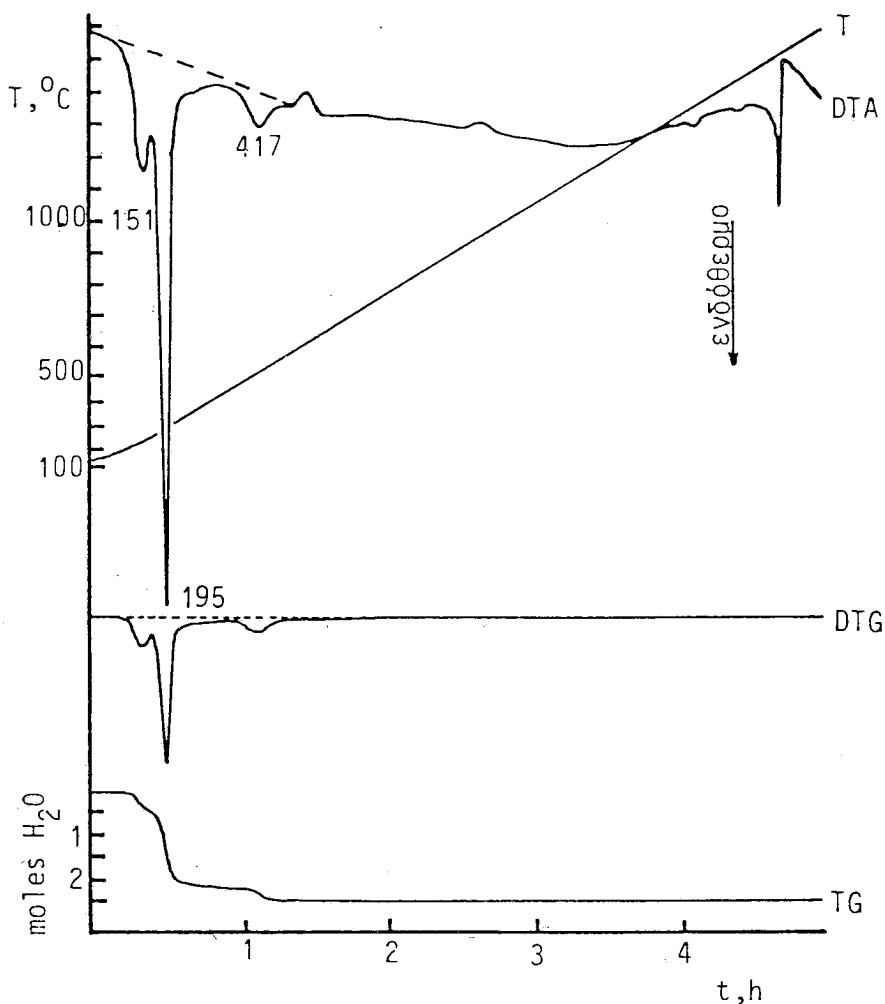
μίϊες απομάκρυνση του κρυσταλλικού νερού αυτού (σχήμα 3).
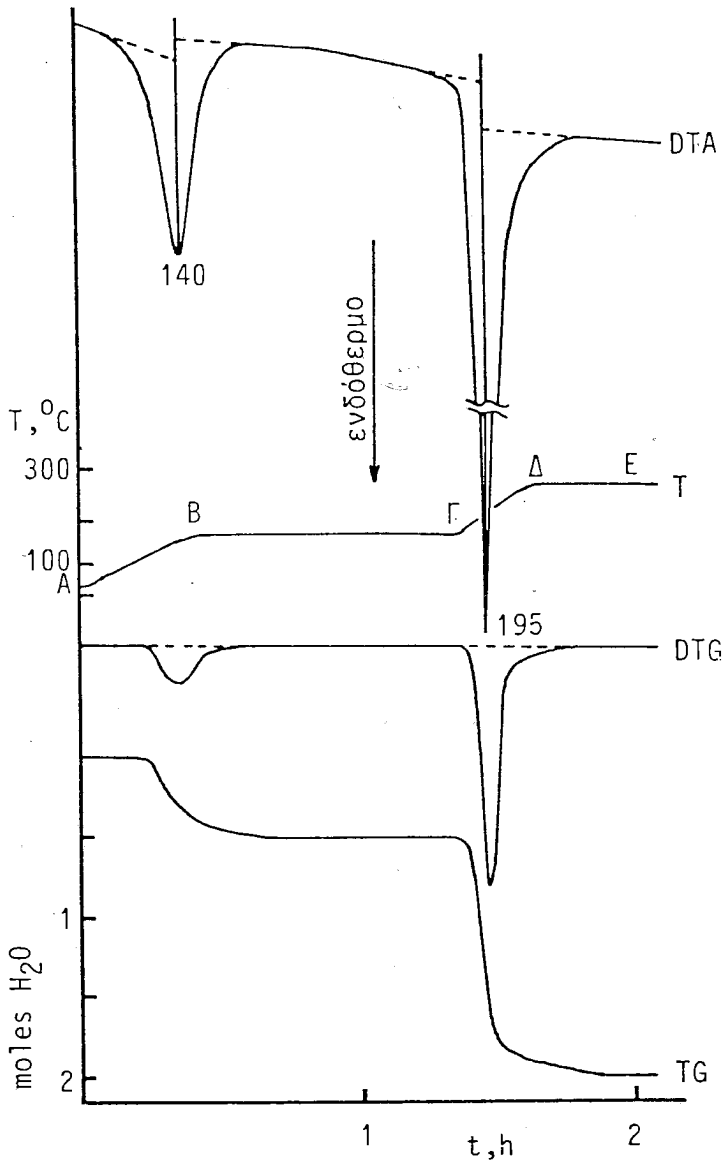
ΣΧΗΜΑ 3. *Καμπύλες DTA, TG και DTG παραγωγογραφήματος του $CaHPO_4.2H_2O$ με πρόγραμμα θέρμανσης ανά βαθμίδες (καμπύλη T): Βάρος δείγματος -99,7mg, ρυθμός θέρμανσης - $\Phi=5°K.min^{-1}$, ταχύτητα εγγραφής -50mm.h^{-1}, ευαισθησίες TG-50mg, DTG-10mg.min^{-1} και DTA-50μV.*

Η εφαρμογή των σχέσεων 3,4,5 και 6 για τη θερμική διάσπαση:

$$CaCO_3 \xrightarrow{T_m=735°C} CaO + CO_2$$

-7-
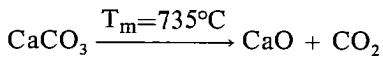
έδωσε τα εξής αποτελέσματα: $\Delta H=39{,}6$kcal.mole^{-1}, n=0,19, E=48,3kcal.mole^{-1} και $Z=6{,}76.10^{10}$min^{-1} [K=6,76.10^{10}.exp(-24.308/T)], ενώ ο υπολογισμός της ΔΗ από την καμπύλη DTA του παραγωγογραφήματος (σχήμα 1) οδηγεί στην τιμή $\Delta H=399$cal.g^{-1} = 39,9 kcal.mole^{-1}. Από την άλλη πλευρά, στη βιβλιογραφία[14] για τους 815°C αναφέρεται η τιμή $\Delta H=40{,}2$.kcal.mole^{-1}. Παρατηρούμε, δηλαδή, ότι η τιμή της ΔΗ που υπολογίσθηκε με την εν λόγω μέθοδο (39,6kcal.mole^{-1}) είναι αρκετά ακριβής και αξιόπιστη.

Ο υπολογισμός της ΔΗ, από τα εμβαδά της καμπύλης DTA (σχήμα 2), για τα τρία στάδια της θερμικής αφυδάτωσης του $CaHPO_4.2H_2O$ είναι δύσκολος αν όχι αδύνατος. Κι αυτό γιατί τα εν λόγω στάδια δεν είναι σαφώς χωρισμένα μεταξύ τους. Έτσι μόνο συνολικά μπορούμε να υπολογίσουμε τη μεταβολή της ενθαλπίας για την αντίδραση:

$$CaHPO_4.2H_2O \rightarrow 0{,}5\ Ca_2P_2O_7 + 2{,}5H_2O \qquad\qquad\text{-8-}$$
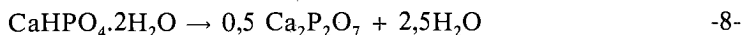
η οποία βρέθηκε: $\Delta H = 300$cal.g^{-1} = 51,6kcal.mole^{-1}.

Οι τιμές των ΔΗ για τις αντιδράσεις:

$$CaHPO_4.2H_2O \xrightarrow{\ T_m=151°C\ } CaHPO_4.1{,}5H_2O+0{,}5H_2O \qquad\text{-9-}$$

$$CaHPO_4.1{,}5H_2O \xrightarrow{\ T_m=195°C\ } CaHPO_4+1{,}5H_2O \qquad\text{-10-}$$

$$\text{και}\qquad CaHPO_4 \xrightarrow{\ T_m=4{,}17°C\ } 0{,}5Ca_2P_2O_7+0{,}5H_2O \qquad\text{-11-}$$
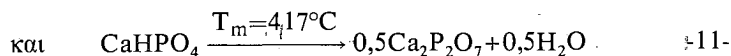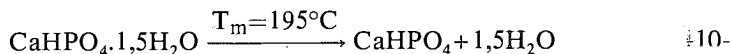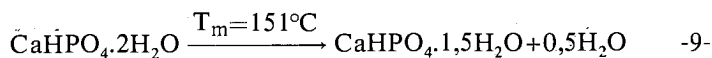
που υπολογίσθηκαν με την εν λόγω μέθοδο σε προηγούμενη εργασία μας[12] είναι αντίστοιχα 11,27, 25,35 και 18,36kcal.mole^{-1}, και οδηγούν σε μια συνολική μεταβολή της ενθαλπίας, για την αντίδραση -8-, $\Delta H_{ολ.} = 54{,}98$kcal.mole^{-1}, τιμή που φαίνεται να επαληθεύεται αρκετά ικανοποιητικά αν συγκριθεί με αυτή που υπολογίσθηκε από το εμβαδό της καμπύλης DTA (51,6kcal.mole^{-1}).

Με στόχο το διαχωρισμό των δύο πρώτων σταδίων της απομάκρυνσης του κρυσταλλικού νερού από το $CaHPO_4.2H_2O$ σε ανεξάρτητα φαινόμενα, ακολουθήθηκε πρόγραμμα θέρμανσης δείγματος αυτού ως εξής (σχήμα 3, καμπύλη Τ): αύξηση της θερμοκρασίας με Φ=5°K.min^{-1} μέχρι τους 140°C (τμήμα Α-Β), θέρμανση στη θερμοκρασία αυτή επί ~55min(τμήμα Β-Γ), αύξηση της θερμοκρασίας εκ νέου με τον ίδιο ρυθμό θέρμανσης μέχρι 280°C (τμήμα Γ-Δ) και θέρμανση επί ~30min στην τελευταία θερμοκρασία (τμήμα Δ-Ε).

Ο υπολογισμός των ΔΗ με βάση τα εμβαδά, από την καμπύλη DTA του σχήματος 3, για τις αντιδράσεις 9 και 10 μας έδωσε τις τιμές 11,28 και 27,96kcal.mole^{-1} αντίστοιχα. Συγκρίνοντας τις τιμές αυτές με εκείνες που υπολογίσθηκαν με την εν λόγω μέθοδο (11,27 και 25,35kcal.mole^{-1} αντίστοιχα) παρατηρούμε ικανοποιητική σύμπτωση.

Από τα παραπάνω πειραματικά δεδομένα συνεπάγεται ότι οι τιμές που υπολογίζονται με τη χρήση της εξίσωσης -3- από τα παραγωγογραφήματα της μεταβολής της ενθαλπίας ΔΗ (και κατ' επέκταση της ενέργειας ενεργοποίησης Ε, της κινητικής παραμέτρου n και του προεκθετικού παράγοντα της εξίσωσης Arrhenius Z) είναι αρκετά ακριβείς και αξιόπιστες. Η μέθοδος αυτή φαίνεται, επίσης, να μας επιτρέπει

με ικανοποιητική ακρίβεια, τον υπολογισμό της ΔΗ σε εκείνες τις διαδοχικές διερ-
γασίες, τα όρια των οποίων δεν είναι σαφώς καθορισμένα μεταξύ τους και όπου ο
υπολογισμός των ΔΗ με τη χρήση των εμβαδών των καμπυλών DTA δε θα ήταν
εφικτός.

Summary

A contribution in the derivatographic determination of the enthalpy of heterogeneous reactions in thermal transformation

T. CH. VAIMAKIS, A.T. SDOUKOS

By means of the equation $\Delta H = R.T^2_m.(-da/dt)_m.\Phi^{-1}.(1-a_m)^{-1}$ and the parameters such as temperature T, rate of heating Φ, rate of transformation of the substance $(-da/dt)_m$ and degree of transformation of the substance $(1-a_m)$, the enthalpy ΔH of heterogeneous reactions of the thermal transformation type is determined from TG and DTG derivatographic curves. However, the reliability of the method, as refered in the relative bibliography, has not tested yet.

From the thermal decomposition of $CaCO_3$ and $CaHPO_4.2H_2O$ the enthalpy of those reactions was determined by using the above noticed equation and the DTA curves.

The results proved that the tehnique (which also may be used to determined the activation energy E, the reaction order n and the Arrhenius pre-exponential factor Z) is accurate and can be applied even in cases of succesive phenomena with uncertain limits.

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1,3-DIPOLAR CYCLOADDITIONS OF MESITONITRILE OXIDE WITH SUBSTITUTED CYCLOBUTENEDIONES

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Summary

The cycloaddition reactions of several substituted cyclobutenediones with mesitonitrile oxide gave mainly mono- and bisspirodioxazoles from reaction of the carbonyl double bonds. Unsymmetrically substituted cyclobutenediones show a remarkable selectivity since only one of the two possible isomeric monospirodioxazoles has been formed. In two cases tris-adducts have been isolated from the reaction of all dipolarophilic centers.

Key words: Cyclobutenediones, Mesitonitrile Oxide, Cycloaddition, Spirodioxazoles.

Introduction

Cyclobutenediones are an interesting class of stable small ring compounds, with formal similarity with quinones, which have been found to possess considerable stability comparing to the corresponding highly unstable cyclobutadienes. The chemistry of cyclobutenediones is the subject of many papers and several reviews have been appeared in the literature.[1-4] However very little is known on their behaviour as dipolarophiles.[5, 6] On the other hand, 1,3-dipolar cycloaddition reactions of quinones have been extensively studied. The first cycloaddition reaction between nitrile oxides and quinones has been studied by Quilico et al.[7] who found that *p*-benzoquinone gives with benzonitrile oxide condensed isoxazoline derivatives. The cycloaddition occurs to the carbonyl double bond only in presence of borium trifluoride (BF_3) with the formation of spiro-1,3,4-dioxazoles.[8] On the other hand, tetrahalo-*p*-benzoquinones[9] as well as tetra-substituted *p*-benzoquinones[10] give with nitrile oxides only spirodioxazole derivatives. In analogous reactions with-*o*-quinones, it has been found[11, 12, 13] that the addition occurs on the ethylene and on the carbonyl double bond with the formation of isoxazoline or 1,3,4-dioxazole derivatives. Of special interest are the reactions of tropone with nitrile oxides[14] which proceeds in a similar way and the reaction of diphenyl cyclopropenone with nitrile oxide where a non-isolated carbonyl addition product is initially formed.[15]

In a preliminary communication[5] we have described the dipolarophilic behaviour of several symmetrically substituted cyclobutenediones with mesitonitrile oxide. In all cases cycloadducts are formed mainly from the carbonyl group despite the usually low reactivity of C=O bond towards cycloaddition reactions with nitrile oxides.[16] As

a further study on cyclobutenedione dipolarophilic reactivity, reactions with several unsymmetrically substituted cyclobutenediones were carried out. It is expected that the two carbonyls should show a different dipolarophilic reactivity. Actually this is the case.

Results and discussion

Cyclobutenediones are in general very weak dipolarophiles. Reactions were completed only after a long heating with excess of mesitonitrile oxide according to the following general reaction scheme.

3a,b,d-h   4b,c,d,h

a: $R^1 = R^2 = Ph$; b: $R^1 = R^2 = - CH_3$; c: $R^1 = R^2 = - Cl$;
d: R^1. $R^2 = - CH = CH - CH = CH -$;
e: $R^1 = Ph$. $R^2 = - OCH_3$;
f: $R^1 = Ph$. $R^2 = p-CH_3O - C_6H_4 -$;
g: $R^1 = Ph$. $R^2 = p-CH_3 - C_6H_4 -$;
h: $R^1 = Cl$. $R^2 = Ph$.

5a,b
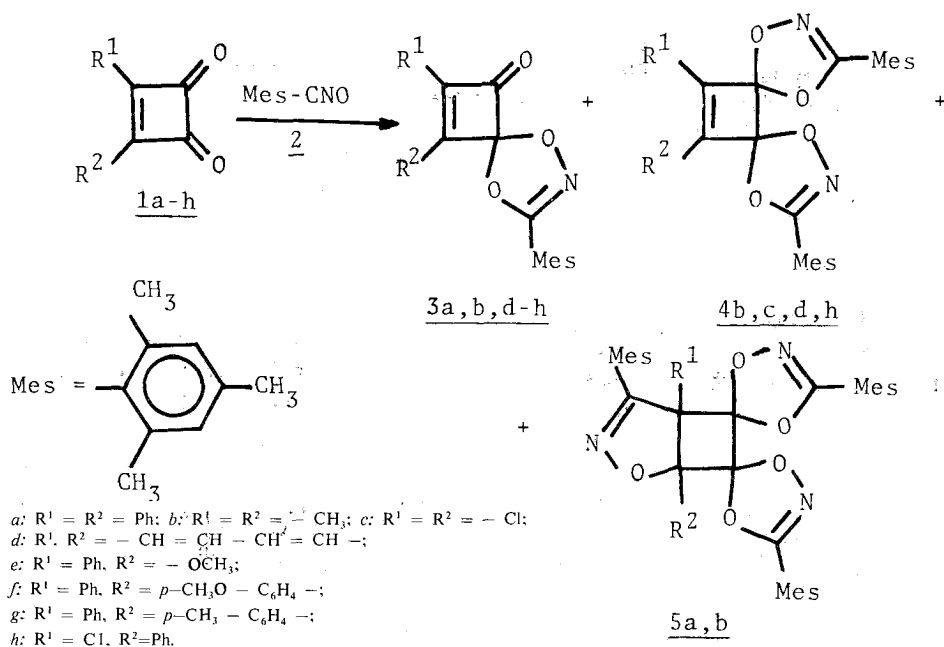
The main reaction product was the mono-adduct 3. However, in the reaction with cyclobutenedione 1c only bis-adducts, in two stereo-forms,[5] have been isolated. Bis adducts were also isolated from the reactions with cyclobutenediones 1b, 1d and 1h, while in two cases tris-adducts 5a, 5b have been isolated. Of special interest is that unsymmetrically substituted cyclobutenediones gave only one mono-adduct, in spite of the fact that two possible isomers could be formed.

All mono-adducts 3 exhibit in ir spectra characteristic carbonyl absorption at 1760-1780 cm^{-1} and absorption at 1630-1640 cm^{-1} for C=N bond. Bis- and tris-adducts 4 and 5 give only C=N absorption at 1630-1640 cm^{-1}.

The ^{1}H-nmr spectra of all cycloadducts formed are in accordance with the proposed structure. An interesting homoallylic long range coupling (J=0.5Hz) is observed in cycloadduct 3b as in the case of analogous substituted butenes.[17] Of special interest are the nmr spectra of compounds 3b and 4b. There is an upfield shift of the adjacent to the dioxazole ring methyl protons in comparison to the parent cyclobutenedione methyl protons (Scheme 1).

2.35(s)   2.35(s)   2.27(d)   1.92(d)   1.87(s)   1.87(s)
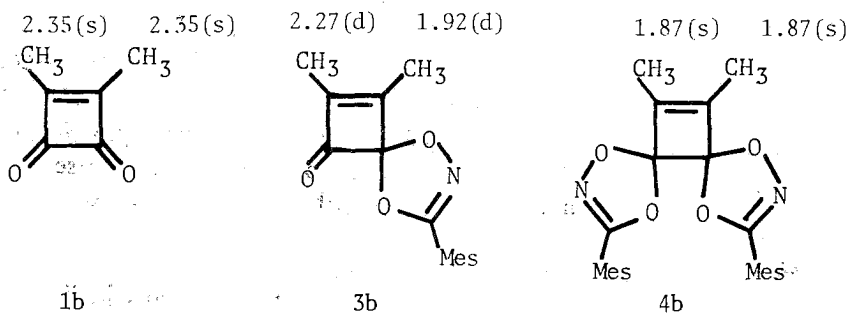
Scheme 1

Thus the adjacent to the dioxazole ring methyl protons show an upfield shift of 0.43 δ while the adjacent to the carbonyl methyl protons an upfield shift of only 0.08 δ. Similarly, methoxy protons adjacent to the dioxazole ring in mono-adduct *3e* were upfield shifted by 0.28 δ. Analogous changes, although smaller than the above mentioned, are observed to *o*-protons of the adjacent to the dioxazole ring aryl group in mono-adducts *3f* and *3h*. (Table I). However, in both cyclobutenedione *1g* and

TABLE I: ¹H Nmr chemical shifts of cyclobutenediones *1e-h* and mono adducts *3e-h*.

CHEMICAL SHIFTS (δ)

	a	Δ	b	Δ	c	Δ	d	Δ
1e	7.83-8.21 m (8.02)	0.18	7.43-7.79 m (7.61)	0.17	4.65 s	0.28	—	—
3e	7.61-8.08 m (7.84)		7.30-7.58 m (7.44)		4.37 s		—	
1f	7.93-8.20 m (8.06)	0.10	7.47-7.76 m (7.61)	0.11	8.20 d	0.24	7.08 d	0.05
3f	7.83-8.10 m (7.96)		7.37-7.63 m (7.50)		7.94 d		7.03 d	
1h	—	—	—	—	8.16-8.45 m (8.31)	0.24	7.50-7.87 m (7.68)	0.09
3h	—		—		7.96-8.18 m (8.07)			
1g	7.87-8.23 m (8.05)	0.15	7.37-7.70 m (7.53)	0.18	—	—	—	—
3g	7.67-8.03 m (7.90)		7.15-7.65 m (7.35)		—		—	

mono-adduct *3g* *o*-tolyl- and *o*-phenyl-protons are superimposed to multiplets, so mono-adduct *3g* is assumed to have an analogous structure to *3f*. These changes in chemical shifts can be taken as an indication that the isolated cycloadducts have the proposed structures.

In the mass spectra, mono- and bis-cycloadducts show almost the same fragmentation pattern as that given in the following scheme for mono-spirodioxazoles *3:*
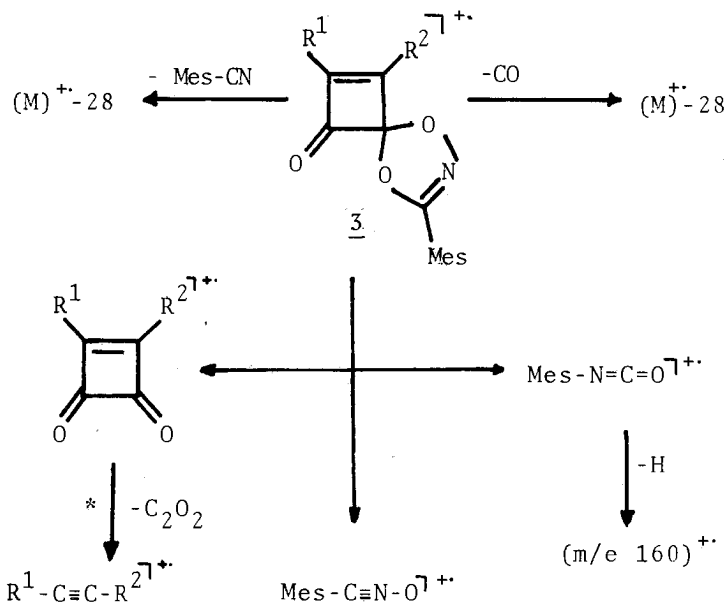
They show peaks of negligible intensity for the molecular ion, except of *4c* where no peak for the molecular ion could be detected. The most characteristic fragmentation is a retro-1,3-dipolar cycloaddition which is also observed in other analogous cases of heterocyclic compounds formed by 1,3-dipolar cycloaddition.[18-21] On the other hand, this fragmentation could be attributed to a thermal ring cleavage of dioxazole residue[16] which leads to the parent carbonyl compounds and aryl isocyanate. This main fragmentation is followed by peaks which correspond to fragments of the parent cyclobutenedione and nitrile oxide or aryl isocyanate.

It is of interest to note that from the cyclobutadienone fragment it is always observed an elimination of C_2O_2 group, leading to a substituted acetylene ion. This transition is followed by a metastable peak. Of special interest is the fragmentation of benzocyclobutenedione fragment of compound *3d*, where it is observed a double CO elimination leading to the fomation of benzyne. An analogous elimination is also observed in the photochemical decomposition of benzocyclobutenedione.[22] Furthermore in all cases it is observed a fragment of m/e 160 corresponding to an elimination of hydrogen radical from mesityl isocyanate (m/e161) which is characteristic for methyl substituted aryl isocyanates.[23]

As regards the tris-adducts *5*, they gave no peaks for the molecular ion, but instead a $M^+ - C_{10}H_{11}NO$, corresponding to an elimination of one mesitonitrile oxide

molecule. Another interesting point, in the mass spectra of these compounds, is the ion $M^+ - 346$ which is attributed to the fragment arising from M^+ by splitting of the cyclobutene ring and loss of two dioxazole rings. In all cases where the mass spectra show no peaks for the molecular ion, the molecular weight was determined osmometrically.

As we have previously mentioned,[5] cycloaddition with *1c* led to the formation of two stereoisomeric bis-spirodioxazoles *3c'* and *3c"*. These compounds have quite similar spectral properties (ir, nmr, ms) and different mp's and chromatographic behaviour.

3c'   3c"
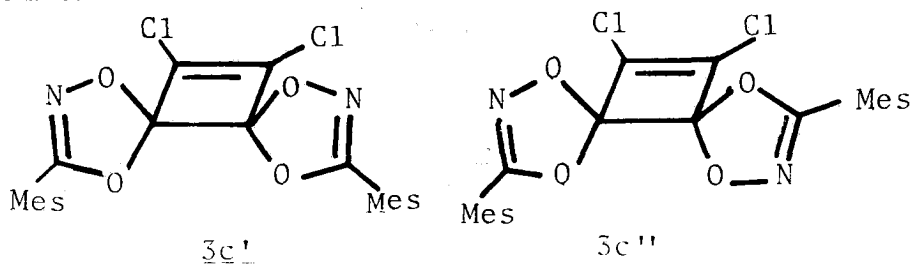
We have assigned,[5] somehow arbitrarily cycloadduct with higher melting point (175-176°C) as "anti" isomer *3c"* and the other one (mp116-117°C) as "syn" isomer *3c'*. In order to distinguish these isomers an X-ray crystallographic analysis was carried out on compound with mp 175-176° by Rentzeperis, Kokkou and Bozopoulos.[24] In contrary to our previous assignment, this cycloadduct has the "syn" structure *3c'*.

This compound *(3c')* crystallizes in space group $P2_1/c$ (monoclinic) with $Z=4$ and cell constants $a=16.661$, $b=9.011$, $c=24.231$, $\beta=139.01$. The structure was refined to a final $R=0.056$ value. Its clinographic projection is given in Fig. 1.
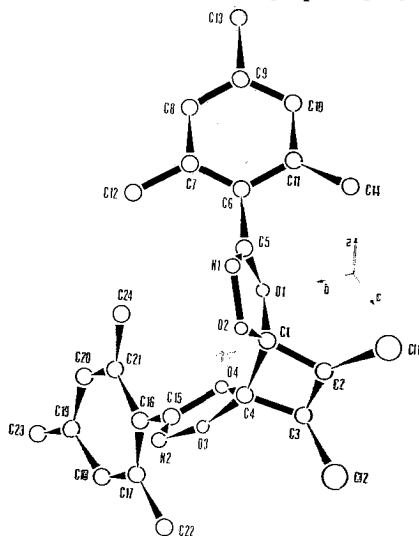
FIG. 1: *Clinographic projection of cycloadduct 3c' (mp 174-176°).*

The low reactivity of ethylene bond of cyclobutenediones can be explained by the fact of a relatively long C=C bond (~1.41 Å) in some cyclobutenedione derivatives,[25,26] as a result of cross conjugation.[27] Lo Vecchio[28] has firstly given a correlation between dipolarophilic reactivity and length of ethylene double bond of dipolarophile.

On the other hand, cross conjugation seems to be a simple model to explain the observed difference in reactivity of the two carbonyl double bonds in unsymmetrically substituted cyclobutenediones. Cross conjugation of the carbonyl group with methoxy, p-anysil and p-tolyl group should be stronger than with phenyl group. Thus the carbonyl group in cross conjugation with phenyl group has more double bond character and reacts preferentially according to the proposed structures of mono-adducts 3e, 3f and 3g.

The above explanation is consistent with the comparison of the two C=O bands of cyclobutenediones 1e-h and the corresponding C=O bands of mono adducts 3e-h, in their ir spectra. In all cases the C=O band of the mono-adduct is close related to the lower frequency C=O band of cyclobutenediones; this means less double bond character for the remaining carbonyl group, a fact which also supports the proposed structures.

Furthermore, in an X ray crystal structure of 1-phenyl cyclobutenedione,[29] the carbonyl group which is in cross conjugation with phenyl group has longer bond length (1.22 Å) than the other one (1.19 Å).

As regards the proposed structure of cycloadduct 3h, this can be explained if we assume a stronger cross conjugation from phenyl group than from chlorine.

Attempts to correlate the difference in chemical reactivity of carbonyls in unsymmetrically substituted cyclobutenediones, based on FMO interaction according to Houk's method,[30, 31] gave no definite results.

The energy levels and coefficients of frontier molecular orbitals of 1-phenyl cyclobutenedione are summarized in Table II and they have been resulted by

TABLE II: Orbital energies and coefficients of 1-phenyl cyclobutenedione.

Coefficients
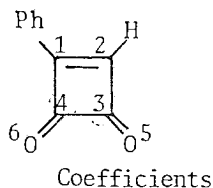
Orbital	Energy (eV)	C_1	C_2	C_3	C_4	O_5	O_6
NHOMO	−15.5	−0.421	−0.300	0.185	0.192	0.322	0.352
HOMO	−11.6	0.276	0.457	−0.066	−0.020	−0.345	−0.174
LUMO	0.8	−0.411	0.429	0.231	−0.053	−0.285	0.070
NLUMO	3.3	0.098	−0.396	0.308	0.576	−0.287	−0.549

CNDO/2 calculations with coordinates given from X-ray data.[29] This model compound is assumed to have the same behaviour with the used cyclobutenediones. On the other hand, orbital energies and coefficients of benzonitrile oxide are already known[30] (Table III).

TABLE III: Orbital energies and coefficients for benzonitrile oxide.

Orbital	Energy (eV)	C_C	C_N	C_O
HOMO	−10	−0.438	−0.308	0.602
LUMO	−1	0.326	−0.477	0.235

From these values it is concluded that the observed site-selectivity can be explained if we consider that for HOMO-dipole controlled reactions a NLUMO dipolarophile interaction should predominate and for LUMO-dipole controlled reaction a NHOMO of dipolarophile.

The above mentioned data are not completely reliable because of the semiempirical nature of calculations, so a cross over in the order of orbitals cannot be excluded as in the case of several substituted fulvenes.[31] However, accurate experimental values of frontier orbital energies are needed in order to have an explanation based on FMO-theory.

Experimental

Melting points determined with a Kofler hot stage apparatus are given without correction. Ir spectra were obtained with a Perkin-Elmer Model 297 spectrophotometer whereas nmr spectra, reported in δ units (TMS) were recorded on a Varian A60A spectrometer. Mass spectra were measured with a Hittachi-Perkin-Elmer RMU-6l spectrometer with an ionization energy of 70 eV. Molecular weights were measured with a Hewllet Packard 301A osmometer and elemental analyses were obtained with a Perkin-Elmer 240 analyzer.

Preparation of starting materials

Although many of the cyclobutenediones used in this work are known compounds, their preparation has been given without experimental details. In these cases, more experimental details are given.

1,2-Dichloro-cyclobutenedione was prepared from the commercially available 1,2-dihydroxy cyclobutenedione (squaric acid), according to the following procedure.[32]

Squaric acid (7.2 mmoles) and thionyl chloride (10 mmoles) with a catalytic amount of N,N-dimethyl formamide (0.1 ml) were heated under reflux for 5 hours. To the cooled reaction mixture anhydrous diethyl ether was added and the unreacted squaric acid (0.44mmoles) was removed by filtration. The filtrate was evaporated *in vacuo* and the residue was sublimated at 50°C (16 mm Hg). Yield 74%, mp 51-52°C (lit.[33] 52°C).

1,2-Diphenyl cyclobutenedione was prepared by the following modification of the procedure reported earlier.[34]

To an ice cooled and mechanically stirred solution of 1,2-dichloro cyclobutenedione (0.026 moles) in 20 ml dry benzene, aluminum chloride (0.034 moles) was added in small portions under dry nitrogen. Stirring was continued for two hours and then an additional amount of dry benzene (20 ml) was added. After heating at 50°C for 40 min. the reaction mixture was poured on crashed ice-dilute hydrochloric acid mixture. The aqueous solution was extracted twice with ether (2×50 ml) and the crude product was recrystallized from an ether- hexane mixture. Yield 86%, mp 95-97°C (lit. [34]97-97.5°C).

1-Chloro-2-phenyl cyclobutenedione $1h$ is a known compound,[35] but its preparation under Friedel-Crafts condition from 1,2-dichloro cyclobutenedione has not been described yet. This compound has been prepared according to the following procedure:

Aluminum chloride (0.024moles) was added in small portions to an equimolar amount of 1,2-dichloro cyclobutenedione and benzene in 1,2-dichloroethane solution (20 ml), under the same conditions as described in the preparation of 1,2-diphenyl cyclobutenedione. After the addition was completed, the reaction mixture was stirred at room temperature for 5 hours and then it was poured on a crashed ice-water-hydrochloric acid mixture. The mixture was extracted with ether (2×50 ml) and the crude reaction product was finally recrystallized from ether-hexane. Yield 67%, mp 112-114°C (lit. [35]113.8-114.8°C).

1-Methoxy-2-phenyl cyclobutenedione $1e$ was prepared from 1-chloro-2-phenyl cyclobutenedione and methanol.[35]

1-(p-Methoxy-phenyl)-2-phenyl cyclobutenedione $1f$ and 1-(p-methyl-phenyl) -2-phenyl cyclobutenedione $1g$ were prepared under Friedel-Crfts conditions from anisole or toluene and 1-chloro-2-phenyl cyclobutenedione instead of 1-bromo-2-phenyl cyclobutene dione.[36]

Benzocyclobutenedione $1d$ was prepared from 1,1,2,2-tetrabromobenzocyclobutene and silver trifluoroacetate,[37] whereas dimethyl cyclobutenedione $1b$ from 1,2-dimethyl tetrafluorocyclobutene and sulfuric acid.[38]

Mesitonitrile oxide 2 was prepared according to a known procedure from mesitylaldoxime and N-bromo-succinimide in the presence of triethylamine.[39]

Reaction of 1,2-diphenyl cyclobutenedione 1a with mesitonitrile oxide

Diphenyl cyclobutenedione (0.7 g, 3 mmoles) and mesitonitrile oxide (1.3 g, 9 mmoles) in dichloromethane solution (~15 ml) were heated under reflux for 70 hours. After evaporation of the solvent the residue was chromatographed on Alumina and eluted with benzene. The first elution gave a small amount of unchanged cyclobutenedione (0.06 g) and then the cycloadduct $2a$ (0.3g, 25% yield, m.p. 132-133°C; ir (nujol) 1770 (C=O), 1630 1615 (C=N, C=C) cm^{-1}; ^{1}H nmr (CDCl$_3$, δ) 2.28 (s, 6H), 2.35 (s, 3H), 6.85 (s, 2H), 7.16-7.45 (m, 6H), 7.58-7.97 (m, 4H); ms: m/e (relative intensity) 77(13), 89(20), 91(13), 119(13), 130(28), 133(34), 145(98), 160(30), 161(100), 178(100), 234(55), 367(<1) 395 (<1) M$^+$.

Anal. Calcd. for $C_{26}H_{21}NO_3$ (MW 395) C, 78.96; H, 5.35; N, 3.54. Found: C, 78.97; H, 5.35; N, 3.48.

Then it was eluted compound *5a* (0.03g, 3% yield, mp 233-235°C, from benzene-hexane); ir (nujol): 1635 (C=N) cm^{-1}; nmr (CDCl$_3$, δ): 1.75 (s, 6H), 2.02 (s, 6H), 2.22 (unresolved singlets, 12H), 2.35 (s, 3H), 6.67 (s, 2H), 6.83 (s, 2H), 6.97 (s, 2H), 7.05 − 7.87 (m, 10H); ms m/e (relative intensity): 91(18), 119(8), 130(100), 133(16), 145(88), 146(46), 161(76), 178(18), 234(11), 339(40), 395(1); no peak for the molecular ion; osmometric determination of molecular weight gave values between 710 and 730.

Anal. Calcd. for C$_{46}$H$_{43}$N$_3$O$_5$ (M.W. 717.83): C, 76.96; H, 6.05; N, 5.85. Found: C, 76.78; H, 6.07; N, 5.52.

Reaction of 1,2-dimethyl cyclobutenedione 1b with mesitonitrile oxide

An ether-hexane solution of 1,2-dimethyl cyclobutenedione *1b* (0.3 g, 2.7 mmoles) and mesitonitrile oxide (0.9 g, 6mmoles) was heated under reflux for 40 hours. Reaction was monitored by TLC. The crude reaction product was chromatographed on Silica and eluted with hexane-chloroform 1:1 (250ml) and 1:3 (250ml) mixtures. Mesitonitrile oxide together with mesityl isocyanate came out first. Then it was eluted a mixture of *3b* and *4b* and finally pure *5b*. Mixture of *3b* and *4b* was rechromatographed under the same conditions affording pure *3b* and *4b*.

Compound *3b:* (0.05 g, 8%, mp 69-71°C, hexane): ir (nujol): 1780 (C=O), 1635 (C=N) cm^{-1}; nmr (CDCl$_3$, δ): 1.92 (d, 3H, J = 0.5 Hz), 2.27 (d, 3H, J=0.5 Hz), 2.32 (s, 6H), 2.35 (s, 3H), 6.98 (s, 2H); ms m/e (relative intensity): 91(12), 110(25), 119(9), 133(21), 145(25), 160(14), 161(100), 243(1), 271 (<1) M$^+$.

Anal. Calcd. for. C$_{16}$H$_{17}$NO$_3$ (MW 271.3): C, 70.83; H, 6.32; N, 5.16. Found: C, 71.04; H, 6.40; N, 5.16.

Compound *4b* (0.08 g, 7%, mp 174-176°C, hexane): ir (nujol): 1630 (C=N), 1610 (C=C) cm^{-1}; nmr (CDCl$_3$, δ): 1.87 (s, 6H), 2.3 (s, 6H), 2.4 (s, 12H), 6.93 (s, 4H); ms m/e (relative intensity): 91(38), 110(34), 119(28), 130(65), 132(49), 145(65), 146(95), 160(48), 161(100), 432 (<1) M$^+$.

Anal. Calcd. for C$_{26}$H$_{28}$N$_2$O$_4$ (MW 432.50); C, 72.20; H, 6.53; N, 6.48. Found: C, 72.46; H, 6.58; N, 6.55.

Compound *5b* (0.13 g, 8%, mp 194-196°C, hexane): ir (nujol): 1630 (C=N), 1610 (C=C) cm^{-1}; nmr (CDCl$_3$, δ): 1.37 (s, 3H), 1.6 (s, 3H), 2.06 − 2.41 (unresolved singlets, 27H), 6.77 − 7.0 (unresolved singlets, 6H); ms m/e (relative intensity): 91(16), 110(7), 119(14), 130(28), 133(24), 145(26), 146(16), 160(16), 161(100), 215(20), 432 (<1); no peak for the molecular ion at m/e 585; osmometric determination of molecular weight gave values around 585.

Anal. Calcd. for C$_{36}$H$_{39}$N$_3$O$_5$ (MW 593.70): C, 72.82; H, 6.62; N, 7.08. Found: C, 72.85; H, 6.68; N, 6.91.

Reaction of 1,2-dichloro cyclobutenedione 1c with mesitonitrile oxide

Mesitonitrile oxide (1.7 g, 10.5 mmoles) and 1,2-dichlorocyclobutenedione *1c* (0.75 g, 5 mmoles) in anhydrous ethyl ether (~20 ml) were refluxed for 60 hours. The crude reaction product was chromatographed on Silica with hexane-chloroform (3:1) affording a small amount of unchanged mesitonitrile oxide and cycloadducts *3c″* and *3c′.*

·Compound *3c''* (0.2 g, 8%, mp 116-117°C, hexane): ir (nujol): 1630 (C=N) cm^{-1}; nmr (CDCl$_3$, δ) 2.27 (s, 6H), 2.35 (s, 12H), 6.93 (s, 4H); ms m/e (relative intensity): 86(21), 91(14), 94(10), 119(8), 130(85), 132(16), 145(74), 146(58), 150(7), 152(5), 160(14), 161(100), no peak for the molecular ion at m/e 472; osmometric determination of molecular weight gave values around 475.

Anal. Calcd. for C$_{24}$H$_{22}$Cl$_2$N$_2$O$_4$ (MW 473.35), C, 60.89; H, 4.68; N, 5.92. Found: C, 60.73; H, 4.63; N, 6.01.

Cycloadduct *3c'* (0.52 g, 21%, mp 174-176°C, hexane): ir (nujol): 1640 (C=N) cm^{-1}; nmr (CDCl$_3$, δ): 2.28 (s, 6H), 2.33 (s, 3H), 6.90 (s, 4H); ms is the same as cycloadduct *3c''*; osmometric determination of molecular weight gave values around 470. A clinographic projection of this cycloadduct is given in Fig. 1.

Anal. Calcd. for C$_{24}$H$_{22}$Cl$_2$N$_2$O$_4$ (MW 473.35), C, 60.89; H, 4.68; N, 5.92. Found: C, 61.01; H, 4.69; N, 5.92.

Reaction of benzocyclobutenedione 1d with mesitonitrile oxide

Mesitonitrile oxide (0.45 g, 2.8 mmoles) and benzocyclobutenedione (0.37 g, 2.8 mmoles) in dichloromethane solution (∼15 ml) were refluxed for 30 hours. The crude reaction product was chromatographed on Silica affording cycloadduct *3d* and cycloadduct *4d*.

Cycloadduct *3d* (0.13 g, 18%, mp 84-86°C, hexane); ir (nujol): 1780 (C=O), 1640, 1630 (C=N, C=C) cm^{-1}; nmr (CDCl$_3$, δ): 2.32 (s, 3H), 2.45 (s, 6H), 6.83 (s, 2H), 7.67-8.08 (m, 4H); ms m/e (relative intensity): 76(27), 104(100), 119(18), 130(100), 132(26), 145(100), 146(100), 160(21), 161(100), 265(1), 293 (<1) M$^+$.

Anal. Calcd. for C$_{18}$H$_{15}$NO$_3$ (MW 293.31): C, 73.70; H, 5.15; N, 4.78. Found: C, 73.63; H, 5.15; N, 4.61.

Cycloadduct *4d* (0.1g, 6%, mp 144-145°C, hexane); ir (nujol): 1640, 1630, 1610 (C=N, C=C) cm^{-1}; nmr (CDCl$_3$, δ): 2.27 (s, 6H), 2.37 (s, 12H), 6.92 (s, 4H), 7.63 (s, 4H); ms m/e (relative intensity): 76(40), 104(44), 119(15), 130(100), 132(16), 145(94), 146(100), 161(100), 454(1) M$^+$.

Anal. Calcd. for C$_{28}$H$_{26}$N$_2$O$_4$ (MW 454.50) C, 73.99; H, 5.77; N, 6.16. Found: C, 73.62; H, 5.81; N, 6.06.

Reaction of 1-methoxy-2-phenyl cyclobutenedione 1e with mesitonitrile oxide

1-Methoxy-2-phenyl cyclobutenedione (0.56 g, 3 mmoles) and mesitonitrile oxide (1 g, 6 mmoles) in dichloromethane solution (∼ 15 ml) were refluxed for 150 hours. The crude reaction product was chromatographed on silica with benzene affording cycloadduct *3e* (0.13g, 13%, mp 128-129°C, benzene-hexane); ir (nujol): 1755 (C=O), 1630, 1610 (C=N, C=C) cm^{-1}; nmr (CDCl$_3$, δ): 2.33 (s, 3H), 2.47 (s, 6H), 4.37 (s, 3H), 6.95 (s, 2H), 7.30-7.58 (m, 3H), 7.58-8.13 (m, 2H); ms m/e (relative intensity): 89(75), 91(33), 119(23), 130(78), 132(75), 133(60), 145(96), 146(90), 160(55), 161(100), 188(50), 204(27), 349 (<1) M$^+$.

Anal. Calcd. for C$_{21}$H$_{19}$NO$_4$ (MW 349.37): C, 72.19; H, 5.48; N, 4.01. Found: C, 71.93; H, 5.48; N, 4.15.

Reaction of 1-(p-methoxy-phenyl)-2-phenyl cyclobutenedione 1f with mesitonitrile oxide

1-(*p*-Methoxy-phenyl)-2-phenyl cyclobutenedione (0.528 g, 2 mmoles) and mesitonitrile oxide (0.644 g, 4 mmoles) in dichloromethane solution (~15 ml) were refluxed for 100 hours. The crude reaction product was chromtographed on Silica with benzene, affording cycloadduct *3f* (0.17 g, 14%, mp 149-152°C, dichloromethane-hexane); ir (nujol): 1760 (C=O), 1630 (C=N, C=C) cm^{-1}; nmr (CDCl$_3$, δ): 2.37 (s, 3H), 2.43 (s, 6H), 4.92 (s, 3H), 6.95 (s, 2H), 7.03 (d, 2H, J=8Hz), 7.94 (d, 2H, J=8 Hz) 7.36 - 7.63 (m, 3H), 7.83 - 8.10 (m, 2H); ms m/e (relative intensity) 91(13), 119(10), 130(12), 132(14), 145(8), 146(46), 160(15), 161(100), 208(61), 264(28), 280(15), 425 (<1) M$^+$.

Anal. Calcd. for C$_{27}$H$_{23}$NO$_4$ (MW 425.46): C, 76.22; H, 5.45; N, 3.29. Found: C, 75.90; H, 5.23; N, 3.67.

Reaction of 1-(p-methyl-phenyl)-2-phenyl cyclobutenedione 1g with mesitonitrile oxide

The cyclobutedione *1g* (0.49g, 2 mmoles) and nitrile oxide (0.97 g. 6 mmoles) in dichloromethane solution were refluxed for 150 hours. The crude reaction product was chromatographed on silica with chloroform-hexane 4:1 affording the cycloadduct *3g* (0.08 g, 10%, mp 144-147°C, benzene-hexane); ir (nujol): 1770 (C=O), 1630 (C=N), 1610 (C=C) cm^{-1}: nmr (CDCl$_3$, δ): 2.28 (s, 3H), 2.38 (s, 6H), 2.42 (s, 3H), 6.9 (s, 2H), 7.15-7.65 (m, 5H), 7.67-8.03 (m, 4H); ms m/e (relative intensity): 91(16), 119(11), 130(20), 133(28), 146(62), 160(16), 161(100), 191(22), 248(33), 381 (<1) 409 (<1) M$^+$.

Anal. Calcd. for C$_{27}$H$_{23}$NO$_3$ (MW 409.16): C, 79.19; H, 5.66 N, 3.42. Found: C, 79.14; H, 5.73; N, 3.41.

Reaction of 1-chloro-2-phenyl cyclobutenedione 1h with mesitonitrile oxide

1-Chloro-2-phenyl cyclobutenedione *1h* (0.96 g, 4.9 mmoles) and mesitonitrile oxide (1.8 g, 11.2 mmoles) in dichloromethane (~15 ml) were refluxed for 100 hours. The crude reaction product was chromatographed on Silica affording cycloadducts *3h* and *4h*.

Cycloadduct *3h* (0.11 g, 7%, mp 144-145°C, benzene-hexane); ir (nujol): 1785 (C=O), 1625 (C=N), 1610 (C=C); nmr (CDCl$_3$, δ): 2.32 (s, 3H), 2.43 (s, 6H), 6.97 (s, 2H), 7.5 - 7.95 (m, 3H), 7.96 - 8.18 (m, 2H); ms m/e (relative intensity): 91(20), 101(18), 119(13), 130(75), 132(22), 136(85), 145(75), 146(80), 160(21), 161(100), 192(34), 208(13), 353 (<1) M$^+$.

Anal. Calcd. for C$_{20}$H$_{16}$ClNO$_3$ (MW 353.79), C, 67.89; H, 4.56 N, 3.96. Found: C, 68.21; H, 4.62; N, 3.90.

Cycloadduct *4h* (0.08 g 4%, mp 179-180°C dichloromethane-hexane); ir (nujol): 1625 (C=N), 1610 (C=C) cm^{-1}; nmr (CDCl$_3$, δ): 2.27 - 2.37 (unresolved singlets, 12H), 2.4 (s, 6H), 6.97 (broad singlet, 4H), 7.37 - 7.75 (m, 3H), 7.75 - 8.17 (m, 2H); ms m/e (relative intensity): 91(15) 101(10), 119(10), 130(84), 145(59), 146(50), 160(15), 161(100), 192(10), 208(8), 353 (<1), 514 (<1) M$^+$.

Anal. Calcd. for C$_{30}$H$_{27}$ClN$_2$O$_4$ (M.W. 515): C, 69.96; H, 5.29; N, 5.44. Found: C, 69.80; H, 5.25; N, 5.35.

Περίληψη

*Αντιδράσεις 1,3-Διπολικής Κυκλοπροσθήκης Μεσιτονιτριλοξειδίου με ὑποκατεστη-
μένες Κυκλοβουτενοδιόνες*

Οι αντιδράσεις 1,3-διπολικής κυκλοπροσθήκης μεσιτονιτριλοξειδίου με ὑπο-
κατεστημένες κυκλοβουτενοδιόνες οδηγούν κυρίως στο σχηματισμό μονο- και δις-
σπειροβιοζαζολίων ἀπό αντίδραση των καρβονυλικών διπλών δεσμών των κυκλο-
βουτενοδιόνων με το νιτριλοξείδιο, παράρδα που ο καρβονυλικός διπλός δεσμός
ύστερα σε ὁμολόφυλη δραστικότητα από τον αιθυλενικό διπλό δεσμό. Μόνο σε δύο
περιπτώσεις απομονώθηκαν σε πολύ μικρή απόδοση προϊόντα όπου έχει αντιδράσει
και ο αιθυλενικός διπλός δεσμός.

Σε αντίθεση με ὀρθικετο ὑποκατεστημένες κυκλοβουτενοδιόνες παρατηρείται
μια ἀξιοσημείωτη εκλεκτικότητα σχηματισμο μονο-σπειροβιοζαζόλιων. Ετσι από
τα δύο δυνατά ισομερή μόνο το ένα απομονώνεται. Η εκλεκτικότητα αυτή ερμη-
νεύεται σαν αποτέλεσμα διαφορετικών ανξυγιακών παραδόχειων επιβράσεων των ηλεκτα-
στατών στο κυκλοβουτενοδιονικό σύστημα.

Μελέτονται ακόμη οι φασματοσκοπικές ιδιότητες των προϊόντων που αρή-
φωνούν με τις προτεινόμενες δομές.

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FLOTATION TECHNIQUES FOR THE SEPARATION OF TRACE POLLUTANTS

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Summary

In this paper, examples are given for the separation by flotation techniques of arsenic, germanium, or chromium ions from a solution, at a laboratory stage. Different technological variables that affect the process were investigated, such as the type of flotation (dispersed-air or dissolved-air flotation), concentration level, pretreatment required, pH effect, separation succeeded, etc.

Introduction

There are many inorganic constituents in waste solutions that their entry into sewage plants is usually undesirable, as they will impair the biological operations of sewage treatment. Also, there is the need to ensure that the industrial effluents do not contain deleterious contents, which may destroy fish and ecological life in streams, or even the sea into which the effluent eventually will be discharged.

Flotation is a separation process that selectively separates surface-active compounds from a solution, collecting them at the gas-liquid interface and thereby concentrating them towards the surface. In effluent treatment, it is effective for the separation of materials at low concentrations. In the case of the presence of a surface-inactive pollutant in solution (waste), this can be removed if an appropriate surfactant is added, and sometimes with the addition of a collector.

One of the useful characteristics of flotation is its ability to concentrate from extremely dilute solutions (in the range up to fractions, of ppm), possibly too dilute to handle economically by other means. And this is the reason why the process is also used as an analytical technique for preconcentration of substances. Foam flotation offers a method of treating wastewater for noxious traces of materials and in the meantime, a means of reclaiming values from wastes, in today's world of limited mineral resources. These are two aspects of the same problem, the second giving a promise of profitability in effluent treatment.

All is needed is some bubbling equipment to generate gas bubbles. The method has been established in mineral processing. Two techniques are often distinguished: the dispersing of air through a sintered glass, porous metal or ceramic diffuser, known as dispersed-air flotation; and secondly, the recycling part of the treated effluent stream, usually, from a continuous flotation process with air dissolution at high pressure followed by throttling and precipitation of fine bubbles, which is known as dissolved-air flotation[1,2]. In the first category, belongs also the so called electrolytic flotation.[3]

Generally, in effluent treatment a separation process is effective if it works as well with trace pollutants. Foam (or bubble) separation processes remove surface-active compounds from a solution, collecting them at the gas-liquid interface of the bubbles and thereby concentrating them towards the surface. In the case of presence of a surface-inactive pollutant ion in solution (waste), this can be separated if an appropriate surfactant is added and sometimes with the addition of a collector (adsorbing or complexing agent); this method was termed ion flotation.[4]

From an economic point of view, according to Sebba[4] the amount of collector needed in ion flotation is related directly to the amount of the colligend (e.g. surface-inactive metal ion to be removed) and its state, but is not influenced by the amount of solution, So to float from a very dilute solution could be just as economic as from a concentrated one, and in many cases (as will see) it works better.

Chromium compounds are applied in aluminium anodizing and other metal plating and electroplating operations, usually as a decorative finish. They are also added to cooling water to inhibit corrosion. One of the large producers of chromium-plated metal parts are the automobile parts manufactures. Also, other sources of chromium wastes are from the manufacture of paint pigments and chrome tanning.[5] Hexavalent chromium treatment frequently involves its reduction to the trivalent form.

Most of the arsenic production today is from the processing of flue dust associated with copper, lead, zinc, gold or cobalt smelting. These are possible sources of pollution with their wastes. With increased environmental control devices on all types of processes and the advent of new processing technologies, an expanded supply of arsenical residues is anticipated in the future.[6]

The average occurence of arsenic in sea water is 0.003 ppm, while the mean concentration in fresh water of U.S. is 0.064 ppm. However, near mineral wells concentrations in excess of 4 ppm are common. Elevated levels of arsenic in a river system also, was attributed to geothermal source waters. Generally, the major impact that the element may have on the environment will be related to water quality.

Germanium rarely forms minerals of its own. It occurs mainly in traces in other ores, and among them coal. Methods are available for germanium recovery from fly ash.[7] Germanium, therefore, is a scattered element and the problem of concentrating it is of special significance. Processes investigated are precipitation, solvent extraction, ion exchange, distillation, flotation, etc.

Where all the three elements can be met in trace quantities is, for instance, the pulverised fuel ash produced in vast quantities from coal fired power plants. During the combustion, concentration of trace metals occurs and when fly ash is removed from the stack with a scrubber or an electrofilter, it becomes a solid waste. Proper

disposal requires knowledge of the leachability, so that ash can be landfilled in an environmentally acceptable manner.[8] Meanwhile, fly ash could be utilised; there are countries that cover all their industrial production necessities in germanium using as raw material the fly ash.

In this paper examples are given with chromium, arsenic or germanium ions. Laboratory experimental work was carried out for the removal of each of the above ions from a dilute aqueous solution of it.

It is noted here that germanium ions is not considered as a pollutant, but rather as a potentially worth recovering value.

Experimental part

The dispersed-air flotation system had the usual arrangments[1,4]. It was consisted of a nitrogen cylinder connected to the cell through a gas humidifier, a filter, an open mercury U-tube manometer, a rotameter and a low flowrate controller. Provision was also included for constant temperature experiments. The flotation cell had an approximate volume of 120 cc and was made from a Schott fritted glass funnel glass blowed to a piece of tubing (the funnel was D4 unless stated). The latter had a ground glass joint at the other end, so that an extension was used in cases of high foaming.

For comparison dissolved-air flotation experiments were carried out in a portable jar tester for laboratory use pioneered by Water Research Centre (UK). The system, although was primarily designed for sedimentation tests, could readily be adapted with a special 1,500 cc calibrated jar and a mini saturator for dissolved-air flotation evaluations. The jar, having a conical bottom with a drain and two side sampling points, was equipped with a stirrer motor giving stable speeds, fast for initial mixing and slow to assist flocculation. Water saturated with air, from a compressor, under pressure of around 75 psi (in the saturator) was introduced to the base of the unit via a nozzle.

Colorimetric chemical analysis has been applied: for arsenic content the molybdenum blue method was followed[9], for chromium the reaction with diphenylcarbazide,[10] and for germanium the phenylfluorone method in acidic solutions.[11]

Results and discussion

Flotation of Chromium Ions

Chromium (VI) is extensively hydrolyzed in water, giving only neutral or anionic species. Those well established are $HCrO_4^-$, CrO_4^{2-} and $Cr_2O_7^{2-}$; there is some evidence for the formation of H_2CrO_4 in relatively concentrated acid. These species exhibit very intense charge transfer spectra, which are the basis for most of the equilibrium studies. All the equilibria occur rapidly with $Cr_2O_7^{2-}$ dominating in acidic solutions and CrO_4^{2-} in basic.[12]

Our work on chromium (VI) had the aim of getting some preliminary insight in ion flotation, and was also based on previous experience found in bibliography[13,14]. Grieves, among others, investigated the separation by flotation of dichromate with ethyl hexadecyldimethylammonium bromide (EHDA) as cationic surfactant.

Some of our results are shown in Figure 1, using laurylamine as surfactant in an 1% ethyl alcohol solution. Addition of ethanol as a frother had the further advantage that the sizes of bubbles are smaller, because of the lower surface tension of the solution. Removals Re% were expressed as $[1-C/C_0)] \times 100$, having at time $= 0$, $C = C_0$.

Initial cell concentrations were 10 ppm in chromium. Optimum pH range was found as 7 to 8.5, when using a laurylamine concentration of 8×10^{-4}M. Chromium removals over ·75% were obtained at pH 7, with retention time 10 min. Nitrogen flowrate in the range 100-300 cc/min did not have any effect on removal. Initial mixing before flotation have neither any appreciable effect, so a mixing time of 10 min was used.
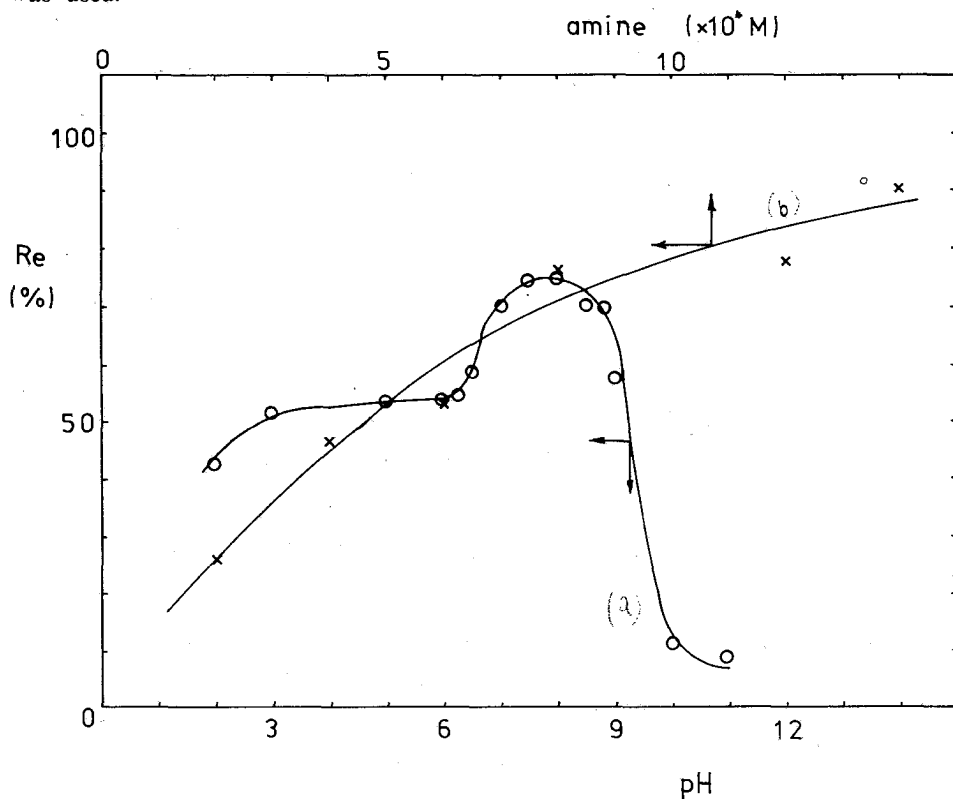
FIG. 1. *The effect of laurylamine concentration at a pH = 7 (curve b) or pH of solution with surfactant concentration 8.10^{-4} M (curve a) on chromium ion flotation removals, Re.*

Changes in pH have marked effects on the nature and charge of both the collector and colligend, so ion flotation is particularly susceptible to variations of this parameter.[4] Almost all investigators refer to some aspect of this dependence. Also, the colligend may be precipitated (for example, as hydroxide) and then removed; therefore, variation of the pH can lead even to a change in the nature of the process, having precipitate flotation instead of ion flotation.

Another investigation was the pulsed addition of collector. Instead of one dose at the commencement of flotation, a number of small additions at various intervals thereafter were made. But there was no difference in the recoveries achieved by the two techniques.

Figure 2 shows the influence of ionic strength. Interference, when using a cationic collector, was more marked in the presence of PO_4^{3-} ions than SO_4^{2-} ions than Cl^- ions. It is generally agreed that the presence of neutral salts decreases the efficiency of ion flotation. According to Pinfold[1], this arises because of the competition for collector between the colligend and the added ions.
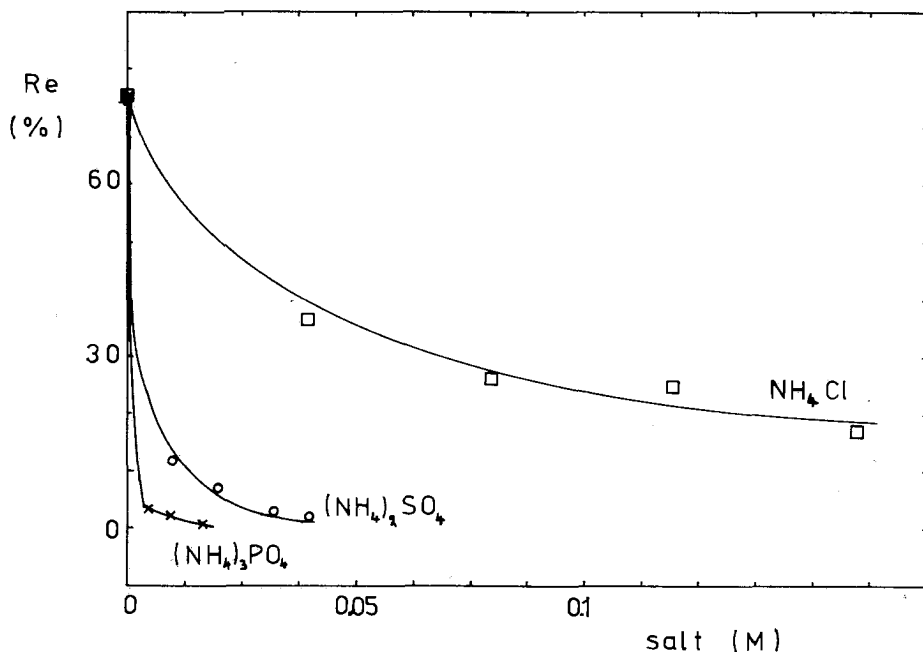
FIG. 2. *Effect of various salt concentrations in the solution versus chromium removals*; 8.10^{-4} *M sur-factant, pH of solution 7.*

The dissolved-air flotation experiments in same conditions, shown as Figure 3, gave lower recoveries for chromium. The recycle ratio was 1:6 with initial cell volume of 300 cc. The process gave around 50% recoveries with higher initial concentrations of chromium. The reason propably was that it was noticed an apparent difficulty to have formed a stable froth layer, which could support the rising sublate. An addition of a polyelectrolyte could possibly help, as used elsewhere[15], but not tested in the present.

It is concluded from the dispersed-air flotation tests that separation of chromium from dilute solutions could be succeeded having a ratio of {Cr}: [laurylamine] of 1:4. However, this is four times greater of the stoichiometric theoretical concentration. In higher concentrations (around 90 ppm Cr^{6+}), it was found out a removal over 90%
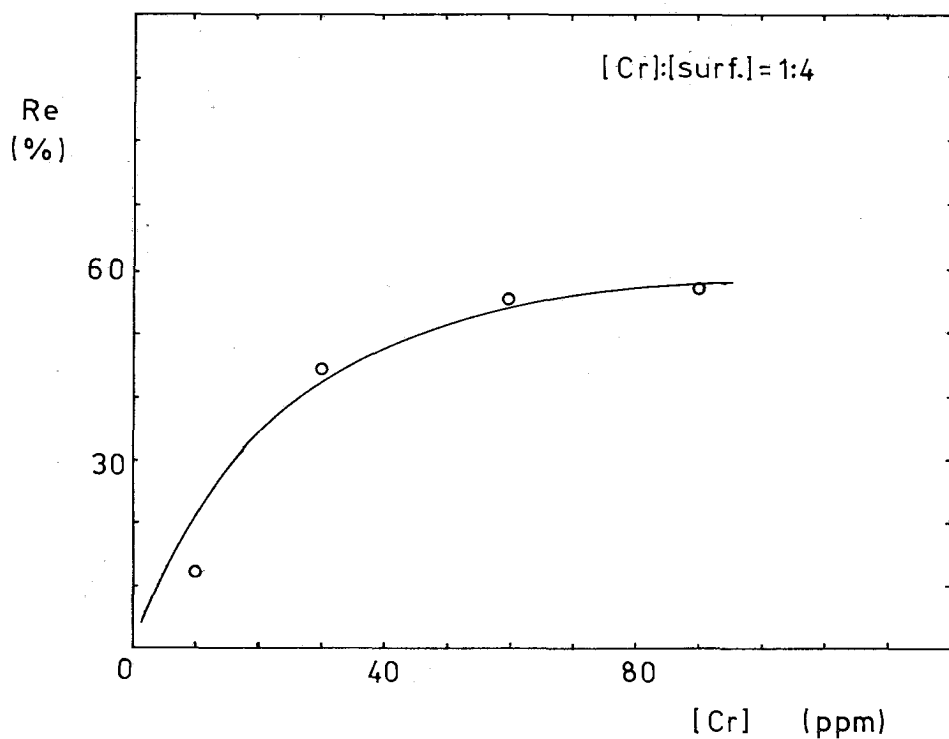
FIG. 3. *Effect of pollutant·concentration·(Cr) versus chromium removals, under constant ratio of Cr: (laurylamine) in dissolved-air flotation (Air-water recycle: 16.7%, saturated at 5 atm).*

with a ratio of 1:2, showing a reduced need for surfactant at high cell concentrations. The effect also of the ionic strength of solution could be considered a disadvantage of ion flotation, in the case investigated.

Flotation of Arsenic Ions

The only reported works on flotation of arsenic ions, to our knowledge, are those which used the method for analytical reasons, i.e. concentration of sub-microgram amounts of it. Applications were known for seawater[16], and natural waters.[17]

Many other methods of treatment have been studied, as coagulation, precipitation, bed filtration, lime softening, etc. In one of them[18], the importance of adsorption onto amorphous ferrous and aluminum hydroxides was determined; but the findings cast doubt on this importance as a removal mechanism in water treatment precipitation processes. The most likely mode of removal was thought to be occlusion.

It is noted that occlusion has been restricted to include only phenomena such as ion entrapment, lattice substitution and solid solution formation. Even so, occlusion is vague, hard to measure and difficult to distinguish from adsorption in rapid precipitations.

Examining the chemical forms of arsenic in aqueous solutions[19], it is noticed that arsenious anhydride (or arsenic trioxide) solubility is influenced by the pH, in solutions free from complexing substances. As_2O_3 is an amphoteric oxide which dissolves in water and in dilute solutions of pH between 1 and 8, with the formation of undissociated arsenious acid $HAsO_2$. At pH's above 8 solubility increases with the formation of arsenite ions AsO_2^-.

The process studied here was the so-called adsorbing colloid flotation developed mainly at the Vanderbilt University, Tennessee.[20] It involves generally the removal of a solute by adsorption on (or perhaps coprecipitation with) a carrier floc, which is then floated. As collectors (adsorbents) for arsenic, ferric sulphate and alum were also tested in this paper. Preliminary experiments investigated the efficiency of «adsorption» and the parameters that affect it. So, filtration and analysis followed the tests.

With ferric sulphate, initial conditioning was not found to affect the process and an average time of 10 min was selected for mixing. Changing the iron concentration, for 10 ppm of arsenic, a ratio [Fe]:[As] of 6:1 (and over) was found to give removals near 100% (Fig. 4). The pH of solution was a crucial parameter giving low removals at acidic or basic solutions, while for intermediate values (pH = 5-9) complete removal of arsenic was achieved. Due to the colloid state of the precipitate, problems were observed with filtration.
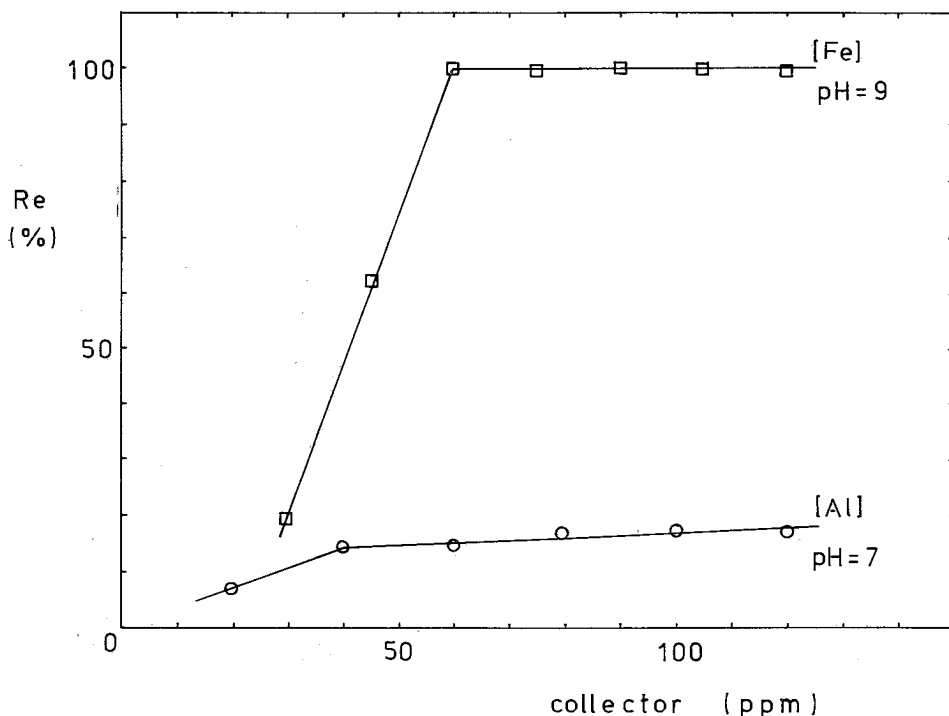

FIG. 4. *Removal of arsenic anions (10 ppm) by adsorption after the addition of ferric {Fe} or aluminium {Al} sulphates versus the concentration of the collector (sodium oleate).*

With alum the obtained results were less promising. At pH = 9.5-10.0, initial concentration of 50 ppm As and ratio [As]:[Al] 1:7, the removals were around 63%. Some of the preliminary results are shown in Figure 4.

Dispersed-air flotation experiments followed after the coprecipitation with ferric hydroxide. A retention time of 30 sec and nitrogen flowrate of 100 cc/min were found to give 90% separation. A small quantity (of around 0.2 cc) of ethanol was added for foaming, whille sodium oleate was the surfactant. It is known that ferric hydroxo complexes are positively charged, so an anionic surfactant was used. Optimum surfactant's concentration was found to be 15 ppm. Without ferric sulphate, flotation results were as low as 5%.

Other variables studied was the influence of arsenic concentration, keeping constant the ratio {As} : {Fe} : {oleate} at optimum value. Process efficiency was decreasing with increased arsenic concentrations. Ageing of the ferric sulphate solution had some reducing effect on its activity. For example, after 100 h arsenic removals dropped under 90%. The pH of the solution played an important role in flotation, as shown in Figure 5. An adjustment of pH, after the flocs were formed, was necessary.
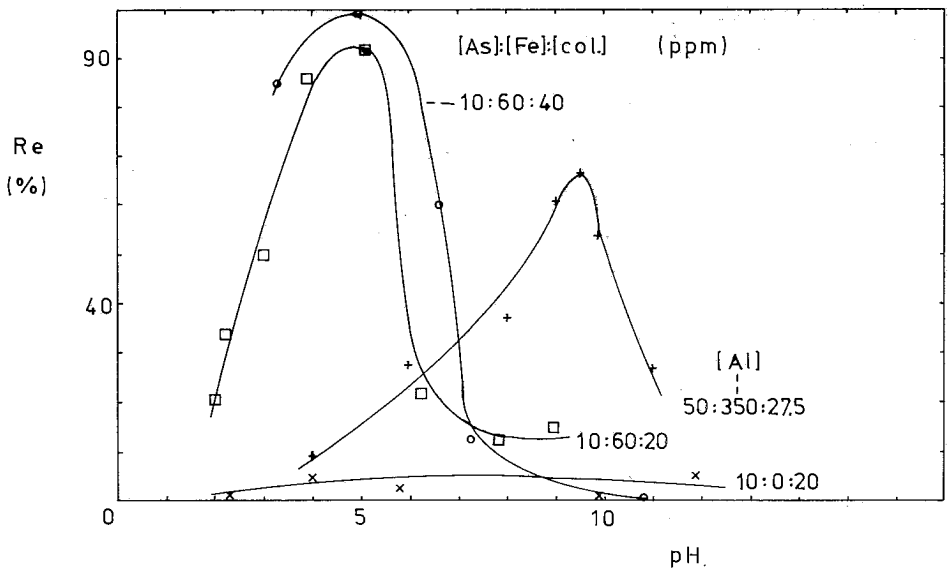
FIG. 5. *The effect of pH of solution in adsorbing colloid flotation of arsenic ions, on adsorbates formed from ferric or aluminium sulphate. Collector used: sodium oleate.*

Disssolved-air flotation tests were also carried out. Parameters investigated were the stirrer revolutions, flotation time, and recycle ratio. Figure 6 shows some of these results. In conclusion, we can say that process is effective for the separation of arsenic from waste waters.

Generally, one of the problems of foam fractionation and ion flotation is said to be the relatively large quantity of surfactant required to remove a given amount of
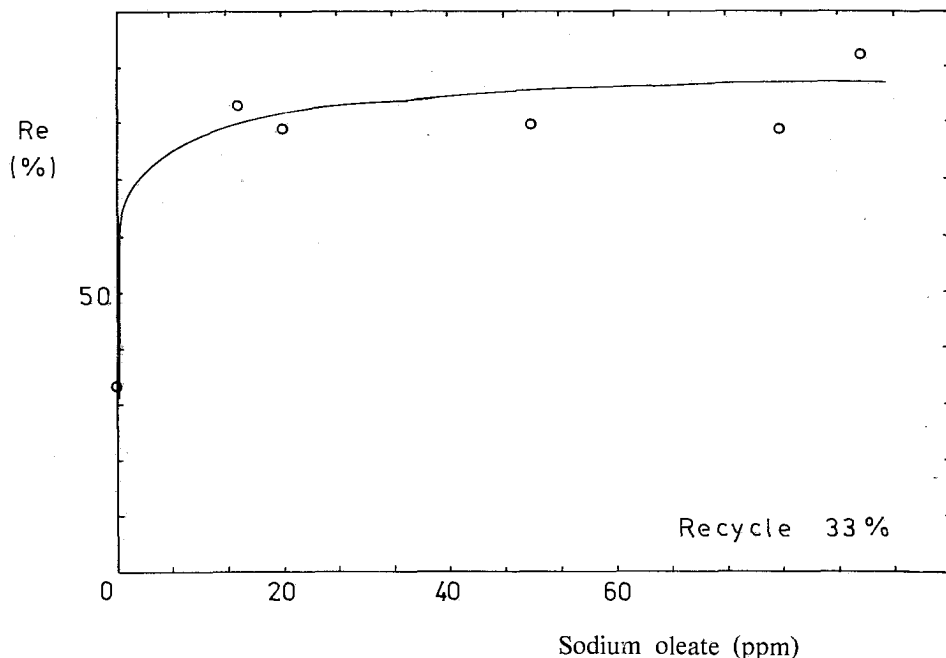
FIG. 6. *Effect of variation of the surfactant (sodium oleate) concentration, on the removal of arsenic ions after preliminary treatment with ferric sulphate and dissolved air flotation.*

the solution component to be separated. The relative high cost of surfactant perhaps precluded the use of these methods for large scale operations in effluent treatment. Precipitate and adsorbing colloid flotation, on the contrary, do not involve a stoichiometric reaction of surfactant with the substance being removed. For this reason attention was focused on them.[20]

However, with these techniques the process can not be selective. For instance, adsorbing coloid flotation was described for the simultaneous separation of trace levels of germanium, antimony, arsenic and selenium from an acidic aqueous solution.[21] It is believed that this could be a disadvantage from the technological aspect of selective recovery, if necessary, of a valuable by-product.

Flotation of Germanium

Published work involves the flotation of tannate and gallate complexes, of citrato- and tartrato-germanic acid and also of trihydroxofluoronate complexes with rosin aimine acetate, done by Seifullina and coworkers[22], among others. Processes of complex formation as the forementioned has been widely used for concentrating germanium.

The reason is that nearly all the germanium present in solution, at low concentrations (below 10^{-2}M) and at pH from 2 up to 7, exists in the form of undissociated metagermanic acid H_2GeO_3 and cannot be floated. At pH lower than 2 appear univalent $Ge(OH)_3^+$ cations, while in alkaline solutions anionic forms appear owing to

the dissociation of H_2GeO_3, according to Nazarenko.[23] With both, due to competition by ions of the same charge, absence of flotation is apparent.

The problem of removing germanium from dilute aqueous solutions with the aid of collectors (or surfactants), which act by electrostatic interaction, is usually solved by the selection of effective flotation activators. Pyrogallol is known to form strong complex acids of composition GeL_3 (where L is the ligand) with germanium in dilute solutions, and so could be tested as activator. Other substances are generally the polyhydroxy-compounds. Noteworthy complexes are also formed by germanium and humic acids and in the geochemistry of germanium, the accumulation of the element in coals was attributed to humic acids.

Figure 7 shows some of the experimental results with pyrogallol and laurylamine as surfactant. As tested variable was germanium cell concentration, and temperature against removals, which were near 90%. An optimum value of 1:2:3 for {Ge} : {laurylamine}: {pyrogallol} was found. A decrease in recovery was noticed with temperature. A possible reason is that adsorption is an exothermic process and an increase in temperature leads to a decrease in the amount of surfactant on gas bubbles, with a parallel reduction in recovery.
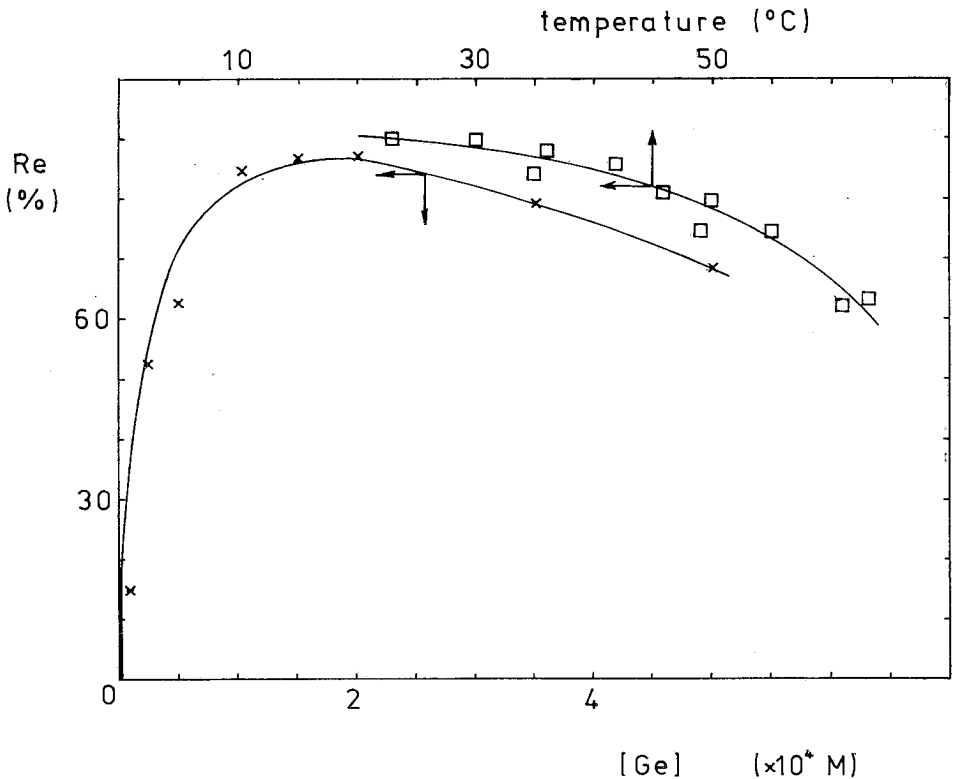

FIG. 7. *Effect of initial concentration and temperature on recovery of germanium ions by flotation,* {Ge}:{laurylamine}:{Pyrogallol} *ratio is* 1:2:3.

Keeping the same system the effect of ionic strength of solution has been also studied on germanium without any pH adjustment, as shown in Figure 8. The effect of this parameter appeared again to be substantial. The recoveries were reduced down to 10% in high concentrations of phosphoric salt.
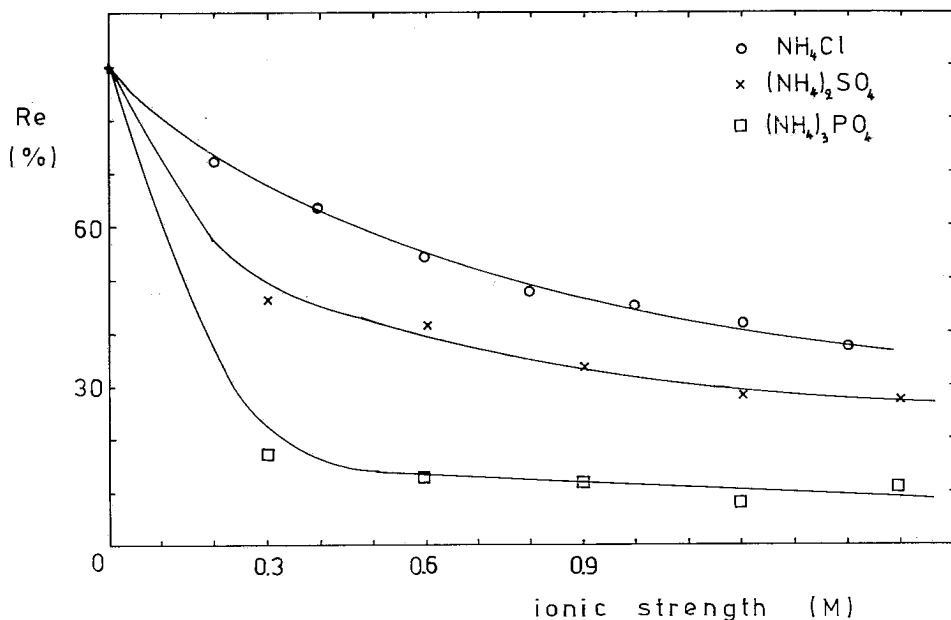
FIG. 8. *The effect of ionic strength on germanium ions flotation.*

More results obtained under the same flotation conditions, are shown in Figures 9 and 10. In the first, the effect of gas flowrate was studied at optimum conditions and in the second, different fritted glasses in the flotation cell were used, having a reported porosity change from 10-16 μm up to 100-160 μm. An increase in the porosity gave better results, as the bubbles size is expected to decrease, giving greater surface areas.

It was seen that the complex acids H_2GeL_3, which dissociate forming $(GeL_3)^{2-}$ anions, can be floated by cationic collectors (amine-type substances). The latter give a product-precipitate of the possible composition C_2 {GeL_3}, where C is the collector.

Our work is continuing in this area. It will be interesting for technological reasons to see whether this technique could separate selectively the different ions; for example, arsenic from germanium.

In conclusion, flotation is a promising method for trace pollutants separation and further attention with closer investigation is warranted.

Conclusions

Different flotation techniques, according to the studied system, have been investigated for the separation and treatment of chromium, arsenic, or germanium ions
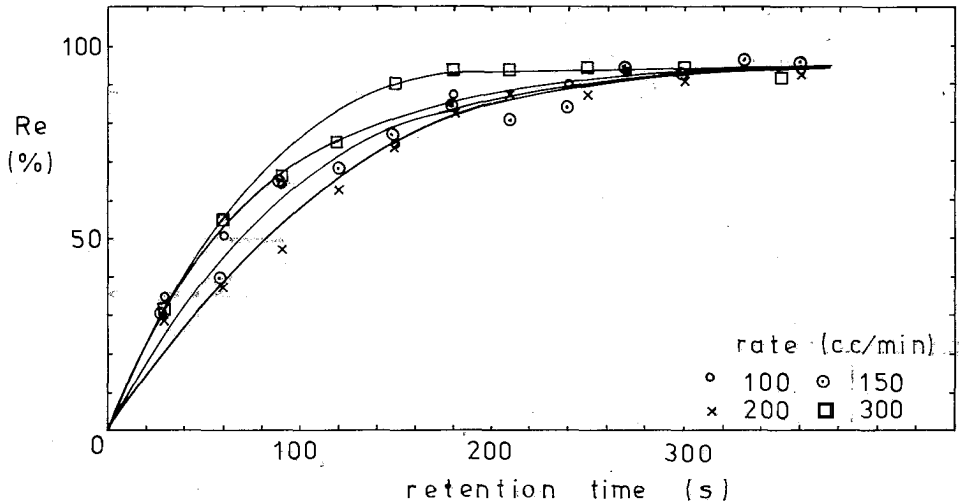
FIG. 9. *Flotation recovery of germanium ions versus time under various gas flowrates.*
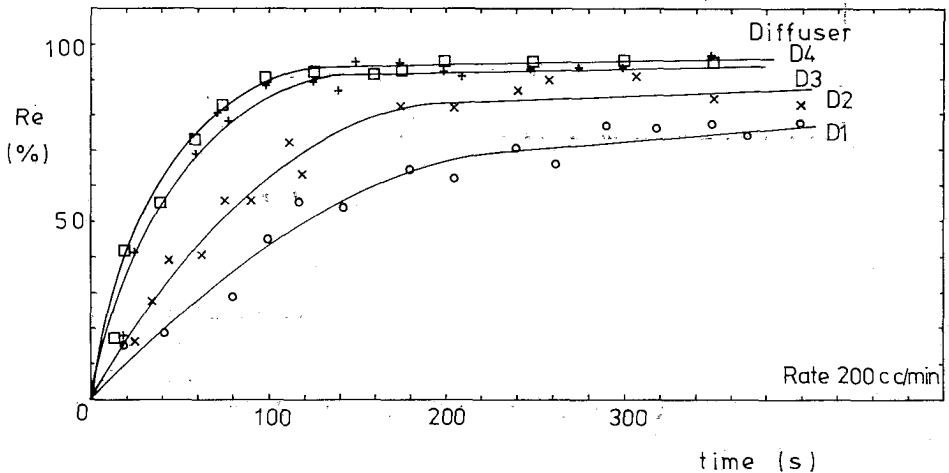
FIG. 10. *Germanium ions removal versus time under various porosities of the diffuser, with constant gas flowrate (200 cc/min).*

from dilute aqueous solutions, containing each time one only of the above element ions. The ways developed for the generation of gas bubbles were the dispersed-air and dissolved-air flotation. Methods studied involved ion flotation and adsorbing colloid flotation and the following optimum conditions were found.

Chromium ions were floated with laurylamine giving removals over 75%. Gas flowrate in the range 100-300 cc/min had not any appreciable effect. The pH of solution was a crucial parameter and the optimum range should be found. Ionic strength, with the addition of ammonium salts, was affecting considerably the removals in the sequence $PO_4^{3-} > SO_4^{2-} > Cl^-$, due to competition for the collector of similarly charged ions.

Flotation generally requires the formation of a stable froth layer to be effective. Also, higher collector concentrations than the stoichiometric were needed in ion flotation of chromium, and particularly in the lower range of Cr^{6+} concentration (around 10 ppm).

Adsorbing coloid flotation was found to be especially effective for the treatment of waste or surface waters containing traces of arsenic. The pollutant was coprecipitated with ferric hydroxide and the floc was floated by sodium oleate. An optimum ratio of {As} : {Fe} : {oleate} = 10:60:40 ppm was found giving removal near 100% at pH 5. However, it was not noticed any economy in the quantity of chemicals required, as mentioned in the bibliography.

Finally, germanium ions was effectively separated after treatment with pyrogallol and flotation by laurylamine. The process gives promises for being selective-the selective separation of germanium from arsenic is a known technological problem. The recovery of germanium from dilute aqueous solutions by ion flotation is a potential method of reclaiming metal values and also recycle materials of waste streams. Possible application of this work is the processing of fly ash and recovery of valuable metals.

Περίληψη

Τεχνικές επίπλευσης για το διαχωρισμό ιχνών ρυπαντών

Η επίπλευση είναι μία φυσική διεργασία που εκλεκτικά διαχωρίζει επιφανειακά ενεργές ενώσεις από ένα διάλυμα, συγκεντρώνοντας αυτές στην Α/Υ διεπιφάνεια και απ' εκεί τις επιπλέει με τις φυσαλίδες στην επιφάνεια της δεξαμενής. Στην τεχνολογία αντιρρύπανσης είναι αποτελεσματική για το διαχωρισμό βιομηχανικών ρυπαντών που βρίσκονται σε μικρές συγκεντρώσεις. Στην περίπτωση ύπαρξης επιφανειακά ανενεργής ουσίας, όπως το παράδειγμα του γερμανίου που δίνεται, αυτή μπορεί να απομακρυνθεί αν προστεθεί η κατάλληλη επιφανειακά ενεργή ουσία και μερικές φορές μία επιπλέον ουσία προσροφητική ή συμπλοκοποιητική (συλλέκτης). Στην πειραματική εργασία εξετάστηκαν διάφοροι τεχνολογικές παράμετροι επίπλευσης, που επιδρούν στην απομάκρυνση ιόντων χρωμίου, αρσενικού ή γερμανίου από αραιό υδατικό διάλυμα κάθε στοιχείου, όπως ο τρόπος παραγωγής των αέριων φυσαλίδων (επίπλευση διασπαρμένου ή διαλυμένου αέρα), το επίπεδο συγκεντρώσεων, η απαιτούμενη προκατεργασία, η επίδραση του pH του διαλύματος, η επιτυγχανόμενη ανάκτηση, κλπ. Οι μέθοδοι επίπλευσης που μελετήθηκαν ήταν η ιονική επίπλευση, με παράδειγμα την απομάκρυνση χρωμίου με λαυρική αμίνη και η επίπλευση προσροφημένου κολλοειδούς, με εφαρμογή στην απομάκρυνση αρσενικού από αραιά διαλύματα. Το τελευταίο έγινε ύστερα από συγκαταβύθιση με υδροξείδιο του τρισθενούς σιδήρου και χρησιμοποίηση του ελαϊκού νατρίου σαν επιφανειακά ενεργή ουσία. Τα εργαστηριακά αποτελέσματα ήταν ιδιαίτερα ενθαρρυντικά. Η επίπλευση αποτελεί μία τεχνολογικά πιθανή μέθοδο ανάκτησης του γερμανίου από υγρά απόβλητα.

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ETUDE POTENTIOMETRIQUE DES EQUILIBRES DE DISSOCIATION DES ACIDES TARTRIQUE ET SUCCINIQUE EN MILIEUX EAU-METHANOL ET EAU-DIOXANNE

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Sommaire

Les constantes d'ionisation des acides tartrique et succinique ont été déterminées à 25°C dans des mélanges eau-méthanol et eau-dioxanne de pourcentage volumique allant de 10 à 50% en cosolvant organique. Les calculs ont été effectués à l'aide d'une nouvelle méthode d'itération autocohérante permettant la détermination des pK thermodynamiques et de å (distance minimum d'approche des ions). Les valeurs obtenues sont discutées en relation avec la nature du solvant et la structure de l'acide.

Key words: Tartaric acid, Succinic acid, dissociation constants, ionisation constants, medium effect, methanol-water mixtures, dioxane-water mixtures.

Introduction

La dissociation des divers acides faibles dans des mélanges hydroorganiques et les influences du milieu solvant sur les équilibres de dissociation ont été largement étudiées dans notre laboratoire.[1-7] Dans le cadre général de ces recherches, nous avons entrepris l'étude systématique des équilibres de dissociation des acides tartrique (H_2T) et succinique (H_2S) dans des mélanges hydro-organiques où l'adjonction du cosolvant organique en quantités croissantes permet de faire varier de façon notable les caractéristiques du milieu.

Nous présentons ainsi dans ce mémoire les résultats concernant les constantes de dissociation des acides ci-dessus dans des mélanges eau-méthanol (H_2O - MeOH) et eau-dioxanne (H_2O - diox.) de pourcentage volumique allant de 10 à 50% en composant organique, à 25°C.

Notons qu' à partir de cette étude comparative nous nous proposons d'élucider dans quelle mesure l'introduction dans la molécule de l'acide succinique de deux groupements - OH impliquerait des variations remarquables sur les équilibres de dissociation de cet acide.

Mais à part l'aspect théorique, du point de vue pratique, l'étude de la dissociation de l'acide tartrique présente en particulier un intérêt certain. En effet, aujourd'hui on sait bien que ce produit organique est un adjuvant des plus actifs susceptible d'inhiber les excroissances dendritiques formées au cours de l'électrodéposition des divers

métaux.[8] D'après des études antérieures on a pu démontrer que l'effet inhibiteur de cet adjuvant dépend très sensiblement du degré de dissociation de l'acide considéré.[9,10] D'autre part, en tenant compte que les propriétés physico-chimiques des divers bains électrolytiques sont souvent réglées par l'adjonction des solvants organiques, il s'en suit donc que, connaissant les constantes de dissociation de H_2T, on détermine d'une certaine manière l'activité inhibitrice de cet acide.

La détermination des constantes de dissociation des acides examinés, dans des solutions aqueuses, a fait l'objet de nombreuses recherches.[11-16] Par contre des mesures systématiques dans des solvants mixtes sont rares et ils concernent, pour la plupart, l'acide succinique en milieux hydroalcooliques riches en alcool.[7,17-19] Certains des résultats concernant les pK de l'acide succinique dans des solvants mixtes sont aussi donnés par d'autres auteurs.[17,18] Cependant nous avons répété ces déterminations parce que les données de la littérature proviennent, soit de mesures faites par titrage au pH-mètre préalablement étalonné à l'aide des tampons aqueux, soit de calculs effectués à partir de méthodes sensiblement différentes de celles que nous avons suivies dans cette étude.

En outre, il nous semble qu'une étude comparative est plus stricte dans le cas où les valeurs comparées ont été déterminées par la même méthode de calcul et sous les mêmes conditions expérimentales.

Partie Experimentale

1. Réactifs

Le méthanol utilisé est un produit Fluka de pureté "puriss. p.a." distillé avant usage. Eb = 64,7°C/760 mmHg.

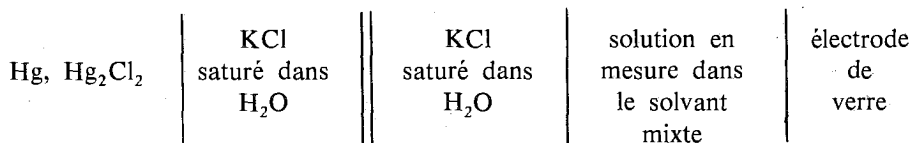Le p-dioxanne utilisé est un produit Carlo Erba de pureté > 99%, Eb = 101°C/760 mmHg est purifié peu avant l'emploi selon la procédure recommandée par Kraus et Vingee.[20]

Les solutions ont été préparées à l'aide de l'eau bi-distillée d'une conductivité de l'ordre de 10^{-6} Ω^{-1} cm^{-1}.

Les acides succinique (Merck, Zur. anal., p.a.) et d-tartrique (Carlo Erba RP-ACS) sont produits commerciaux, leur pureté ayant été vérifiée par titrage. Si celle-ci n'était pas jugée satisfaisante, l'acide était purifié, suivant des méthodes déjà décrites dans la littérature[20] et jusqu'à un titrage indiquant une pureté au moins de 99,5%.

2. Mesures

Les pK des acides étudiés dans cet article ont été déterminés par la méthode de titrage potentiométrique. La mesure du pH est effectuée à l'aide de la pile:

Hg, Hg$_2$Cl$_2$	KCl saturé dans H$_2$O	KCl saturé dans H$_2$O	solution en mesure dans le solvant mixte	électrode de verre

Cette cellule galvanique est du type de celle utilisée par Bonhomme et Juillard[19] dans les mélanges eau-éthanol et par Roletto et Zelano[21] en eau-dioxanne.

Le couple d'électrodes est branché à un pH-mètre "Beckman research pH-meter" dont la précision de lecture et la reproductibilité est de 0,002 unité pH.

La température est maintenue constante à 25,00 $\pm$ 0,01°C grâce à un thermostat "Haake Ultra-Thermostat NBS".

Les mesures sont effectuées sous atmosphère d'azote; celui-ci barbote successivement dans une solution aqueuse basique de pyrogallol, dans de l'acide sulfurique dilué et dans une solution de composition analogue à la solution mesurée et régulée à la même température.

L'agent titrant est une solution de potasse dans le milieu mixte considéré. On l'ajoute à la solution acide à l'aide d'une burette à piston (Metrohm dosimat) dont la précision de lecture est de 0,005 cm³.

Pour les mesures dans les mélanges eau-méthanol, l'étalonnage du couple électrode de verre-électrode au calomel est effectué à l'aide des tampons de Bates, Paabo et Robinson.[22] Les valeurs du $p\alpha_H^*$ [$= -\log \alpha_H^*$] de ces tampons, étant interpolées pour des concentrations exactes en méthanol, sont groupées dans le tableau I. Rappelons que dans le cas où l'activité de H$^+$ dans un milieu quelconque est rapportée à un état de référence défini dans le milieu considéré, cette activité est notée par habitude α_H^*.[22]

Dans les mélanges eau-dioxanne, puisqu'on ne trouve pas des solutions tampons de $p\alpha_H^*$ connu, préparées dans le milieu considéré, le tarage de l'appareil est réalisé à l'aide des tampons aqueux recommandés par N.B.S.[23]

TABLEAU I. Valeurs de divers paramètres physicochimiques (densité d, concentration en H$_2$O C$_{H_2O}$, fraction molaire en MeOH X$_{MeOH}$, constante diélectrique D) de quelques mélanges hydrométhanoliques et de $p\alpha_H^*$ des tampons: acide succinique (m=0,01999) succinate acide de sodium (m=0,009995) et chlorure de potassium (=0,009995). t=25°C.

% MeOH		d (g/ml)	C$_{H_2O}$ (mol/l)	X$_{MeOH}$	D	$p\alpha_H^*$
en volume	en poids					
10	8,01	0,9827	50,2	0,0467	75,13	3,962
20	16,2	0,9694	45,1	0,0983	71,72	4,107
30	24,7	0,9570	40,0	0,1555	67,79	4,261
40	32,4	0,9425	34,9	0,2199	63,40	4,428
50	42,5	0,9257	29,6	0,2936	60,05	4,611

En particulier on a employé la solution tampon de phthalate acide de potassium 0,05 m de pH = 4,01. Cependant, on sait bien aujourd'hui que la mesure du pH dans des mélanges hydroorganiques à l'aide d'un appareil ainsi étalonné ne conduit qu'aux grandeurs apparentes pH$_{ap}$.[22, 24, 26] Déduire alors de ces grandeurs les valeurs correspondantes du $p\alpha_H^*$ implique la connaissance d'un paramètre δ introduit par Bates[22, 24]

$$\delta = pH_{ap} - p\alpha_H^* = \overline{E}_j - \log (_m\gamma_H) \qquad (1)$$

où $\overline{E}_j$ est le potentiel de jonction liquide exprimé en unité de pH et $_m\gamma_H$, l'effet du milieu.[25, 26] En effet, en nous servant d'une méthode analogue dans son principe de celles proposées dans la littérature,[22, 27, 28] nous avons pu déterminer ce paramètre δ, leurs valeurs sont groupées dans le tableau II. Mais les détails de cette méthode ainsi que des résultats concernant des divers systèmes hydro-organiques (binaires ou ternaires) font l'objet d'un prochain article.

TABLEAU II. Valeurs de divers paramètres physicochimiques (densité d, concentration en H_2O C_{H_2O}, fraction molaire en dioxanne X_{DIOX}, constante diélectrique D) et du paramètre δ (=pH_{ap} − $p\alpha_H^*$) de quelques mélanges eau-dioxanne à 25°C.

% dioxanne		d (g/ml)	C_{H_2O} (mol/l)	X_{DIOX}	D	δ
en volume	en poids					
10	10,21	1,0060	50,14	0,0227	70,25	−0,011
20	20,24	1,0145	44,91	0,0493	61,73	−0,019
30	30,15	1,0217	39,61	0,0811	53,18	−0,029
40	39,93	1,0286	34,30	0,1197	44,71	−0,060
50	49,68	1,0335	28,87	0,1680	36,22	−0,123

3. Procédé de calcul pour la détermination de pK

Les constantes K_1 et K_2 ont été calculées à partir des courbes de titrage des acides par une solution de potasse. Les calculs de ces deux constantes ont été effectués par la méthode de Speakman.[29] Nous avons utilisé la forme la plus générale de cette équation:

$$\frac{\overline{h}}{2-\overline{h}}\,(\alpha_{H^+})^2\,\frac{\gamma_{A^{2-}}}{\gamma_0} = \left[\frac{1-\overline{h}}{2-\overline{h}}\,\frac{\gamma_{A^{2-}}}{\gamma_{HA^-}}\,\alpha_{H^+}\right]K_1 + K_1K_2 \qquad (2)$$

avec

$$\overline{h} = \frac{b+[H^+]}{C} \qquad (3)$$

où γ_0 est le coefficient d'activité de la molécule neutre H_2A que nous considérons égal à 1, γ_{HA^-} et $\gamma_{A^{2-}}$ les coefficients d'activité des anions HA^- et A^{2-}, C la concentration analytique de l'acide, b la concentration de la base forte ajoutée. Les coefficients d'activité des anions s'expriment par la loi de Debye-Hückel:

$$\log \gamma_i = -\frac{Az_i^2\,\sqrt{I}}{1+B\,\mathring{a}\,\sqrt{I}} \qquad (4)$$

où les paramètres A et B peuvent être calculés pour chacun des mélanges étudiés par les formules appropriées.[30] L'utilisation de la loi de Debye-Hückel semble ici conduire à une bonne approximation des coefficients d'activité des ions du fait du caractère dilué des solutions étudiées (1,5 10^{-2}m). D'après un calcul relativement simple on constate que la force ionique I est égale à

$$I = b + [H^+] + [A^{2-}] \tag{5}$$

avec

$$[A^{2-}] = \frac{K_{m_1}K_{m_2}}{\alpha^2_{H^+}} \cdot \frac{C}{1 + \dfrac{K_{m_1}}{\alpha_{H^+}} + \dfrac{K_{m_1}K_{m_2}}{\alpha^2_{H^+}}} \tag{6}$$

où K_{m_1} et K_{m_2} sont les deux constantes apparentes définies par les relations

$$K_{m_1} = \frac{\alpha_{H^+} \cdot [HA^-]}{[H_2A]} , \quad K_{m_2} = \frac{\alpha_{H^+} \cdot [A^{2-}]}{[HA^-]} \tag{7}$$

Or, le calcul des coefficients d'activité des anions, à l'aide de la relation (4), exige de connaître, d'une part, les constantes apparentes et, d'autre part, la distance minimum d'approche des ions å. Ce dernier paramètre pourrait être déterminé à partir des mesures conductimétriques, mais la valeur de å, ainsi déterminée, dépend sensiblement de l'équation conductimétrique choisie. En outre, la méthode conductimétrique impose de longues et délicates mesures. Ces problèmes ont poussé de nombreux auteurs à proposer une valeur moyenne pour å égale à 5 Å.[31-34] Mais si le choix de cette valeur permet d'éviter dans bon nombre de cas des erreurs grossières, il ne constitue en général qu'une approximation plus ou moins satisfaisante.

Nous avons essayé de nous affranchir de cette contrainte en nous servant d'une méthode d'itération qui nous permet à la fois la détermination de å et des pK thermodynamiques.

Le point de départ de cette méthode est la relation (2) qui se transforme an

$$y = K_1K_2 + K_1 x \tag{8}$$

Dans une première étape, à l'aide des données expérimentales tirées de la courbe de titrage considérée, on calcule les variable y et x, en mettant $\gamma_{A^{2-}} = 1$ et $\gamma_{HA^-} = 1$. Dans le calcul de $\overline{h}$ nous avons confondu l'activité de H^+ avec sa concentration, ce qui n'entraîne pas une erreur importante car $[H^+]$ est généralement faible devant b, mais pas toujours négligeable. Par ailleurs, la relation (8) montre une dépendance linéaire entre y et x. Il est donc possible de la résoudre statistiquement en utilisant la méthode des moindres carrés. Evidemment dans le cas où les coefficients d'activité des anions sont considérés égaux à 1, la relation (8) conduit aux constantes apparentes K_{m_1} et $\acute{K}_{m_2}$.

A partir des graphiques représentant la variation $y = f(x)$ on obtient les valeurs de K_{m_1} et K_{m_2} pour tous les mélanges eau-méthanol et eau-dioxanne.

Il est intéressant de souligner que si on se limite aux solvants mixtes pauvres en composant organique ($D > 40$), on observe en général une dépendance linéaire entre pK et l'inverse de la constante diélectrique ($1/D$) du solvant.[26, 30, 35, 36] La pente de cette droite est exprimée par une relation donnée par Bjerrum et Larson et basée sur le modèle électrostatique de Born. Cette relation appliquée dans le cas des acides dicarboxyliques prend la forme[26]

$$\frac{dpK_n}{d(1/D)} = \frac{Ne^2}{2RT\ln 10}\,\Phi_n \qquad (9)$$

avec n est égal à 1 ou 2 respectivement pour le premier ou deuxième équilibre de dissociation de l'acide considéré. En désignant par $r_\pm$ le rayon moyen des ions positifs et négatifs, on a

$$\Phi_1 = \frac{1}{r_{H^+}} + \frac{1}{r_{HA^-}} = \frac{2}{r_\pm}\,, \quad \Phi_2 = \frac{1}{r_{H^+}} + \frac{4}{r_{A^{2-}}} - \frac{1}{r_{HA^-}} = \frac{4}{r_\pm'} \qquad (10)$$

En partant donc des diagrammes $pK_{m_1} = f(1/D)$ et $pK_{m_2} = f(1/D)$ correspondant aux mélanges eau-méthanol ou eau-dioxanne, on obtient respectivement, compte tenu de la relation $å = 2r_\pm$, les valeurs initiales $å_1$ et $å_2$. La valeur moyenne entre $å_1$ et $å_2$ est la première estimation sur $å$, soit $\bar{a}_1$.

Dans une deuxième étape, en partant de cette valeur de $å$, on peut avoir de la même façon que précédemment, une première estimation sur les valeurs de K_1 et K_2 thermodynamiques pour tous les mélanges respectifs. Ensuite, on aboutit à une deuxième approximation sur la valeur de $å$, soit $\bar{a}_2$, etc.

L'ensemble des opérations est répété n fois jusqu'à ce que la valeur a_n obtenue pour la $n^{ième}$ approximation reste invariable entre deux approximations successives. Evidemment, les constantes de dissociation définitives correspondent à cette dernière valeur.

Globalement on estime que la précision et la reproductibilité de cette méthode sur les valeurs de pK à $\pm 0{,}01$.

4. Résultats et discussion

Les valeurs de pK_1 et pK_2 des acides dicarboxiliques succinique (noté par la suite H_2S) et tartrique (noté par la suite H_2T) dans les mélanges hydroorganiques étudiés sont groupées dans le tableau III. Dans ce même tableau on porte les valeurs correspondantes de $å$ calculées à l'aide de la méthode itérative utilisée dans ce mémoire.
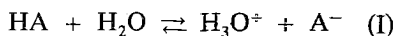
Notons que les pK de H_2S dans les mélanges hydrométhanoliques utilisés ont été déterminés par titrage au pH-mètre, utilisant un étalonnage dans le milieu solvant considéré (à l'aide des tampons du tableau I) d'une part, et un étalonnage dans l'eau d'autre part. Dans ce dernier cas, les mesures de pH ont été corrigées compte tenu de la variation du potentiel de jonction liquide.[22, 24] Par ailleurs, dans une étude anté-

TABLEAU III. Valeurs de pK_1 et pK_2 des acides dicarboxyliques succinique et tartrique dans différents mélanges eau-méthanol et eau-dioxanne à t=25°C.

% volume	Acide Succinique		Acide Tartrique	
	pK_1	pK_2	pK_1	pK_2
H₂O - MeOH				
	å = 4,3 ± 0,1 Å		å = 5,26 ± 0,09	
10	4,35	5,79	3,18	4,58
20	4,47	5,97	3,32	4,71
30	4,63	6,19	3,47	4,88
40	4,83	6,45	3,66	5,08
50	4,99	6,70	3,85	5,29
H₂O - dioxanne				
	å = 5,9 ± 0,2 Å		å = 6,34 ± 0,07 Å	
10	4,46	5,94	3,26	4,60
20	4,68	6,23	3,52	4,92
30	5,03	6,66	3,82	5,28
40	5,46	7,21	4,25	5,76
50	5,89	7,78	4,75	6,27

rieure on avait aussi déterminé les pK̃ de cet acide dans des mélanges hydrométhanoliques, par la même methode expérimentale, utilisant cependant un étalonnage réalisé à l'aide des tampons de De Ligny et Luiks.[37] Les trois modes d'étalonnage conduisent pratiquement aux résultats identiques vérifiant ainsi la validité du procédé d'étalonnage suivi dans la présente étude.

A partir de ces résultats on a étudié l'effet du milieu solvant sur les équilibres de dissociation des acides examinés. Dans ce traitement, on a considéré la réaction générale de transfert protonique

$$HA + H_2O \rightleftarrows H_3O^+ + A^- \quad (I)$$

en admetant que le proton, selon toute probabilité, est sous la forme H_3O^+ dans les mélanges hdroorganiques riches en eau. Il est évident que la constante de l'équilibre (I) est liée au pK correspondant par la relation

$$pK' = pK + \log \alpha_{H_2O} \quad (11)$$

Notons qu'une valeur approchée de l'activité de l'eau α_{H_2O} dans les solvants hydroorganiques est fournie par sa concentration.[21]

Les valeurs des paramètres physicochimiques, figurant dans les tableaux I et II, indispensables à la réalisation de cette étude, ont été puisées dans des travaux antérieurs.[38-40]

Dans une première étape on a tracé les courbes représentant la variation des pK_n' ($pK_n + \log C_{H_2O}$) en fonction de $1/D$, n étant successivement égal à 1 ou 2. Le support théorique de ces graphiques dérivant du modèle électrostatique de Born impliquerait une variation linéaire de pK_n' en fonction de l'inverse de la constante diélectrique $1/D$, si la théorie s'appliquait rigoureusement. En effet, à partir des résultats rassemblés dans le tableau III, on a pu constater que les dépendances $pK_n' = f(1/D)$ peuvent être assimilées à des droits jusqu'à des teneurs de 40% en volume de dioxanne, dans les mélanges eau-dioxanne et pour toutes les teneurs en méthanol dans les mélanges hydrométhanoliques. Nous en donnons quelques exemples dans la figure 1.
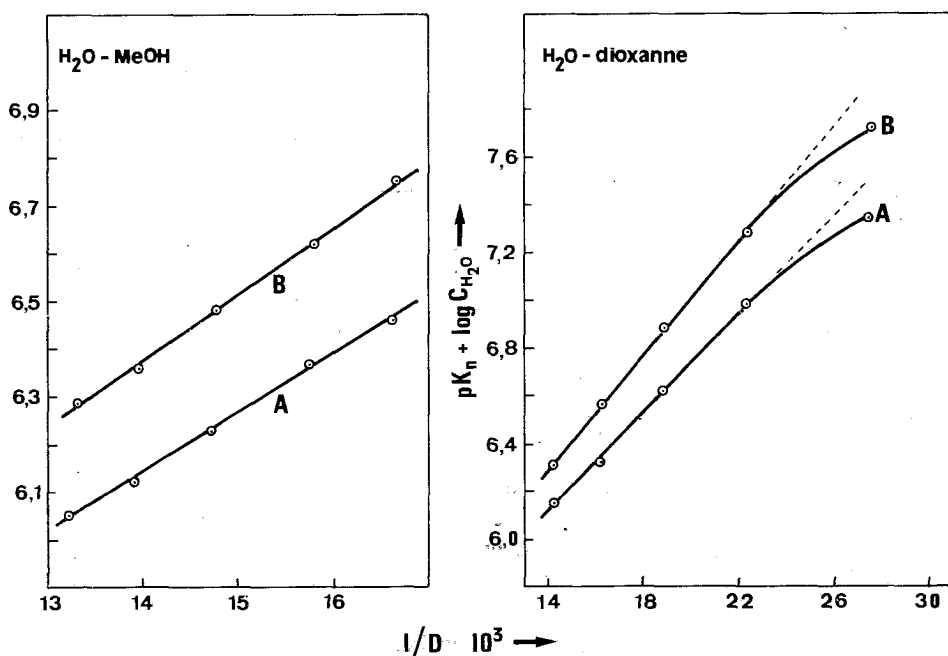
FIG. 1. *Variation de $pK_n + \log C_{H_2O}$ en fonction de l'inverse de la constante diélectrique à 25°C. A: acide Succinique (n=1). B: acide Tartrique (n=2).*

L'insuffisance de la théorie de Born de s'appliquer aux mélanges eau-dioxanne riches en composant organique pourrait être attribuée en lignes générales à l'intervention des diverses interactions spécifiques, de nature non coulobienne, entre la soluté et le solvant.[36] En effet, selon les données de la littérature[36] ces interactions deviennent importantes à partir d'une constante diélectrique de 40 environ, ce que l'on a observé dans la présente étude.

A part les diagrammes $pK_n = f(1/D)$, l'effet du milieu solvant sur la dissociation des acides peut être illustré par des graphiques représentant la variation de pK_n'

avec la teneur en composant organique, cette teneur étant exprimée par habitude en pourcentage en poids, en pourcentage volumique ou en franction molaire X. Ce dernier mode de représentation se révèle très commode étant donné que les graphiques correspondants conduisent, le plus souvent, à des droites.[7, 41-43]

Nous avons tracé, pour chacun des acides étudiés, la courbe $pK_n' = f(X)$ correspondant aux mélanges eau-méthanol et eau-dioxanne. Nous avons constaté que ces courbes peuvent être assimilées à de bonnes droites, de la forme générale,

$$pK_n' = a_n + b_n \, X, \tag{12}$$

jusqu'à des teneurs de 40% en dioxanne, dans les mélanges eau-dioxanne et pour toutes les compositions utilisées des mélanges hydrométhanoliques. Les valeurs des paramètres a_n et b_n de l'équation (12), calculées à l'aide de la méthode des moindres carrés, sont rassemblées dans le tableau IV. Dans ce même tableau IV, on porte les valeurs correspondantes de r^2 (coeffient de détermination linéaire) indiquant que les portions des courbes $pK_n' = f(X)$, correspondant à des teneurs relativement faibles en cosolvant organique, peuvent effectivement s'exprimer par des relations linéaires.

TABLEAU IV. Valeurs des paramètres a_n et b_n de l'équation (12) correspondant à l'acide succinique et tartrique dans des mélanges eau-méthanol et eau-dioxanne. $t = 25°C$.

Acide	n	H₂O - MeOH (0-50%)			H₂O - dioxanne (0-40%)		
		a_n	b_n	R^2	a_n	b_n	R^2
Succinique	1	5,97±0,02	1,74±0,09	0,9913	5,93±0,04	8,73±0,47	0,9943
	2	7,36±0,01	2,79±0,07	0,9983	7,35±0,04	11,49±0,53	0,9957
Tartrique	1	4,79±0,01	1,80±0,03	0,9990	4,76±0,02	8,48±0,23	0,9985
	2	6,18±0,01	1,98±0,05	0,9983	6,07±0,01	10,21±0,18	0,9994

Dans un articles récent[7] concernant la dissociation de quelques acides dicarboxyliques aliphatiques dans des mélanges hydrométhanoliques, on a pu démontrer que la pente b_n (= dpK_n'/dX) est largement influencée par l'existence dans sa molécule d'un substituant chargé comme $-COO^-$.

Les résultats acquis dans cet article précedent nous ont incité, dans la présente étude, à entreprendre d'élucider dans quelle mesure la pente b_n d'un acide dicarboxylique serait aussi influencée par l'existence dans sa molécule d'un ou plusieurs substituants polaires comme $-OH$. Il nous semble que toutes ces influences pourraient être mises en évidence en comparant, dans chacun des systèmes de solvants mixtes, la valeur de b_n d'un acide correspondant substitué - comme l'acide tartirique (acide dihydroxysuccinique). Evidemment tous ces effets peuvent être estimés quantitativement par le paramètre

$$u_n = b_{ns} - b_{nt} \tag{13}$$

où b_{ns} et b_{nt} expriment les valeurs de b_n de l'acide succinique et tartrique respectivement.

Tout d'abord à l'aide des valeurs figurant dans le tableau IV on a calculé, dans le cas des mélanges hydrométhanoliques, la valeur du paramètre u_1 (= b_{1s} − b_{1t}), trouvées égale à

$$u_1 = -0,06$$

On estime que cette valeur est négligeable, étant donné que les paramètres correspondants b_{1s} et b_{1t} ont été déterminés avec une précision moyenne (écart-type) du même ordre de grandeur (v. tableau IV).

On pourrait peut-être interpréter ce résultat en partant de considérations théoriques. Evidemment, le paramètre b_n peut s'écrire

$$b_n = \frac{dpK_n}{dX} = \frac{dpK_n}{d(1/D)} \frac{d(1/D)}{dX} \tag{14}$$

Avec ce traitement le paramètre b_n a été exprimé par le produit de deux facteurs. Le premier facteur, d'origine électrostatique, se décrit par la relation (9). Il est très possible de considérer que dans le cas où l'état de solvatation des ions reste constant, ce terme doit rester invariable lorsqu'on passe d'un milieu à un autre. Par contre le second terme doit être largement influencé par la nature chimique des composants du milieu solvant. Si cela est vrai on s'attendrait à une variation remarquable de ce dernier terme (d $(1/D)/dX$) lorsqu'on passe des mélanges hydrométhanoliques aux mélanges eau-dioxanne. En effet, c'est justement ce que l'on a observé. A l'aide des valeurs rapportées dans les tableaux I et II on a pu constater que la variation de 1/D en fonction de X peut être ajustée à une bonne droite, pour toutes les compositions des mélanges hydrométhanoliques, et jusqu'à 40% en dioxanne dans le cas des solvants mixtes d'eau-dioxanne. En nous servant de la méthode des moindres carrés, on a aboutit aux relations suivantes:

Mélange H_2O − MeOH
$$1/D = 0,0126 + (0,0138 \pm 0,0004) \, X_{MeOH} \quad R^2 = 0,9978$$

Mélange H_2O − dioxanne
$$1/D = 0,0122 + (0,084 \pm 0,003) \, X_{DIOX} \quad R^2 = 0,9976$$

D'après les relations ci-cessus, on constate effectivement que la valeur de β = d $(1/D)/dX$, égale à 0,0138 dans les mélanges hydrométhanoliques, est multipliée par 6 lors du passage de ces solvants en milieu eau-dioxanne où β = 0,084.

D'après tout cela, en tenant compte des relations (9) et (10), l'équation (14) devient:

$$b_n = \frac{\beta \, Ne^2 \, \Phi_n}{2RT \cdot \ln 10} \tag{15}$$

d'où

$$b_1 = \frac{\beta N e^2}{2RT\ln 10} \left(\frac{1}{r_{H^+}} + \frac{1}{r_{HA^-}} \right) \tag{16}$$

et

$$b_2 = \frac{\beta N e^2}{2RT\ln 10} \left(\frac{4}{r_{A^{2-}}} + \frac{1}{r_{H^+}} - \frac{1}{r_{HA^-}} \right) \tag{17}$$

en désignant r_{H^+} le rayon des protons trouvés dans la solution. En ce qui concerne r_{HA^-} et $r_{A^{2-}}$, d'après divers auteurs[35], ces grandeurs expriment en réalité le rayon du groupe portant la charge de l'anion correspondant.

De la confrontation des relations (13) et (15) on aboutit à

$$u_1 = b_{1s} - b_{1t} = \frac{\beta N e^2}{2RT\ln 10} \left(\frac{1}{r_{HS^-}} - \frac{1}{r_{HT^-}} \right) \tag{18}$$

où les grandeurs r_{HS^-} et r_{HT^-} correspondent respectivement aux monanions de l'acide succinique et tartrique.

Etant donné que le paramètre u_1, dans le cas des mélanges eau-méthanol, pratiquement s'annule, il en resulte que dans ces milieux $r_{HS^-} = r_{HT^-}$. Or l'introduction dans la moléule de l'acide succinique de deux dipôles $-OH$ n'a aucune influence sur le rayon du groupe portant la charge ($-COO^-$) formé juste après la première dissociation.

En ce qui concerne le paramètre $u_2 = b_{2s} - b_{2t}$, compte tenu de l'égalité $r_{HS^-} = r_{HT^-}$, en procédant de la même façon que précédemment on aboutit à

$$u_2 = b_{2s} - b_{2t} = \frac{2\beta N e^2}{RT\ln 10} \left(\frac{1}{r_{S^{2-}}} - \frac{1}{r_{T^{2-}}} \right) \tag{19}$$

Dans le cas des mélanges hydrométhanoliques on constate facilement que la paramètre u_2, contrairement à u_1, atteint une valeur positive trouvée égale à 0,81. Evidemmment cette valeur ne peut pas être considérée négligeable étant donné que les erreurs commises sur la détermination des b_2, rapportées dans le tableau IV, sont bien inférieures à elle.

D'abord, en partant de la relation (19), on pourrait interpréter la valeur $u_2 = 0,81$ en considérant que $r_{S^{2-}} < r_{T^{2-}}$. On admet ainsi que le rayon du second groupe carboxylate de l'acide tartrique (H_2T) est plus grand que celui de l'acide succinique.

Cependant, la relation (19) est basée sur le modèle électrostatique de Born. Ce modèle repose sur l'hypothèse de la sphéricité des ions dont la charge est localisée au centre de la sphère. Nous pensons donc qu'il n'est pas légitime d'étendre cette hypothèse dans le cas des dianions de ces diacides, deux fois ionisés, où les charges se trouvent à la fois assez loin du centre de l'ion, et l'une de l'autre. D'autre part, selon Bjerrum,[44] la deuxième ionisation d'un diacide est gênée par la présence de la charge

apparue sur le premier groupe —COO⁻ déjà ionisé. Or, le proton encore fixé à l'acide doit vaincre un potentiel supplémentaire V crée par la premier groupe —COO⁻:

$$V = - \frac{e}{DR'} \tag{20}$$

où R′ désigne la distance séparant le proton ionisable et le premier groupement car-boxylate.

D'après tout cela on peut déduire que les rayons $r_{s^{2-}}$, $r_{T^{2-}}$ calculés de la con-frontation des résultats exprérimentaux avec la relation (19) expriment très probable-ment des grandeurs apparentes, liées à la molécule d'un acide hypothétique possédant des ions avec une configuration de charge sphérique et dont le comportement ionique en solution est semblable à celui de l'acide réel. Il est évident que le rayon de cet aci-de hypothétique résultant de la relation (19) est d'autant plus petit que la distance R′ est plus courte.

Or, ayant observé que $r_{s^{2-}} < r_{T^{2-}}$, il s'ensuit que la distance R′ est plus courte dans l'acide succinique que dans l'acide tartrique. Notons encore qu'il ne serait pas légitime d'attribuer la variation observée sur les valeurs des grandeurs $r_{s^{2-}}$ et $r_{T^{2-}}$ à n'importe quelle influence des hydroxyles. Rappelons que la valeur $u_1 = 0$ ne nous a pas permis précédemment de formuler une telle hypothèse.

Pour confirmer cette très intéressante conclusion d'après laquelle deux acides di-carboxyliques symétriques de la même longueur de la chaîne carbonée présentent des distances R′ sensiblement différentes entre elles, on a appliqué la théorie électrosta-tique de Kirkwood-Westheiner.[45] D'après cette théorie, la constante diélectrique in-troduite dans la relation (20) est remplacée par un paramètre ajustable D_E appelé "constante diélectrique effective". Kirkwood et Westheimer calculent D_E à partir des données structurales. Ils considèrent que le travail électrostatique dépend non seule-ment des charges et de la distance entre elles, mais aussi de la forme des molécules. Ils supposent que les diverses particules participant aux équilibres de dissociation sont contenues dans des cavités de forme et de taille identique de constante diélec-trique $D_i = 2{,}0$. Pour les molécules courtes, ils adoptent une forme sphérique, les longues sont représentées par des ellipsoïdes prolates. Cette théorie permet de cal-culer D_E et une grandeur R étant proportionnelle à la distance R′ de Bjerrum. Il en résulte que cette grandeur R exprime la distance séparant les protons dans le diacide considéré (H_2A). Nous avons constaté que cette grandeur restait pratiquement con-stante dans tous les mélanges hydrométhanoliques. Ainsi la valeur moyenne pour l'a-cide succinique $\bar{R}_s = 6{,}15$ Å est sensiblement inférieure à celle correspondant à l'aci-de tartrique $\bar{R}_t = 6{,}65$ Å.

On pourrait interpréter ces résultats en partant des considérations structurales. Ainsi, dans le cas des diverses particules de l'acide tartrique, il est sans doute raison-nable, en accord avec la littérature,[12] d'admettre des liaisons H internes:

Il est vite apparu que la distance $\bar{R}_t$ dans la structure (II) atteint effectivement une valeur maximale.

En revanche, dans le cas de l'acide succinique il n'y a pas de possibilité de for-mation de liaisons H internes. La distance $\bar{R}_s$ alors exprime en réalité la valeur
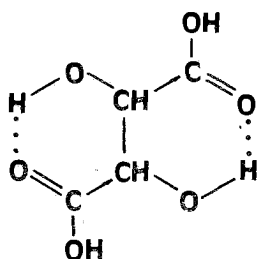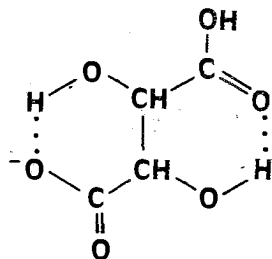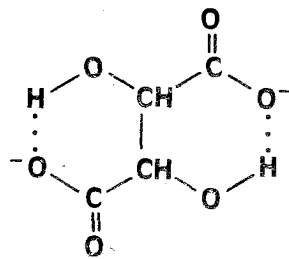
$$I\left(H_2T\right) \qquad II\left(HT^-\right) \qquad III\left(T^{2-}\right)$$

moyenne des diverses distances résultant de la libre rotation des carboxyles autour des liaisons C-C.

D'après tout cela on peut conclure que dans le cas de l'acide tartrique la formation des liaisons H internes (en proportion considérable parmi ses particules trouvées en solution) gène ici la libre rotation impliquant ainsi $\overline{R}_t > \overline{R}_s$.

Enfin, il ne faut pas omettre de souligner que dans le cas des mélanges eau-dioxanne un traitement analogue conduit généralement aux conclusions identiques.

Summary

Potentiometric study of the dissociation equilibria of tartaric and succinic acids in water-methanol and water-dioxan systems

The dissociation constants of Tartaric and Succinic acids were determined at 25°C in water-methanol and water-dioxan mixtures of a 10, 20, 30, 40 and 50% organic cosolvent content. The calculations were performed with the aid of a new method of successive approximations which allows for the simultaneous calculation of the thermodynamic pK's and of the minimum distance of approach of the ions (å).

The results obtained are examined in relation to the nature of the solvent and the structure of the acid molecule.

Περίληψη

Ποτενσιομετρική μελέτη των ισορροπιών διαστάσεως του τρυγικού και ηλεκτρικού οξέος σε υδατομεθανολικά και υδατοδιοξανικά συστήματα

Οι σταθερές διαστάσεως του Τρυγικού και του Ηλεκτρικού οξέος προσδιορίσθηκαν στους 25°C μέσα σε υδατομεθανολικά και υδατοδιοξανικά μείγματα περιεκτικότητας 10, 20, 30, 40 και 50% σε οργανικό συνδιαλύτη. Οι υπολογισμοί πραγματοποιήθηκαν με τη βοήθεια μιας καινούργιας μεθόδου διαδοχικών προσεγγίσεων, η οποία επιτρέπει τον ταυτόχρονο υπολογισμό των θερμοδυναμικών pK και της ελάχιστης αποστάσεως προσεγγίσεως των ιόντων (å).

Τα αποτελέσματα που προέκυψαν εξετάζονται σε σχέση με τη φύση του διαλύτη και τη δομή του μορίου του οξέος.

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NOTE

## BIS[4,5-b]PYRIDINO-1,1',3,3'-TETRATHIAFULVALENE: SYNTHESIS AND CHARGE TRANSFER COMPLEXES

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Introduction

The interest in solid state properties of the simple salts of organic sulfur or selenium containing π-donors was increased last years because of the observation of ambient presure superconductivity in the salts $(TMTSF)_2ClO_4$ and $(BEDTTTF)_2I_3$ [where TMTSF=tetramethyltetraselenafulvalene and BEDTTTF = bis (ethylenedithio) tetrathiafulvalene][1-3]. In this paper the preparation of bis [4,5-b] pyridino--1,1',3,3'-tetrathiafulvalene (abbriviated as B[4,5-b] PTTF), of a number of its charge transfer complexes and preliminary results of their electrical and optical properties are described. The new π-donor was prepared according to the scheme 1.
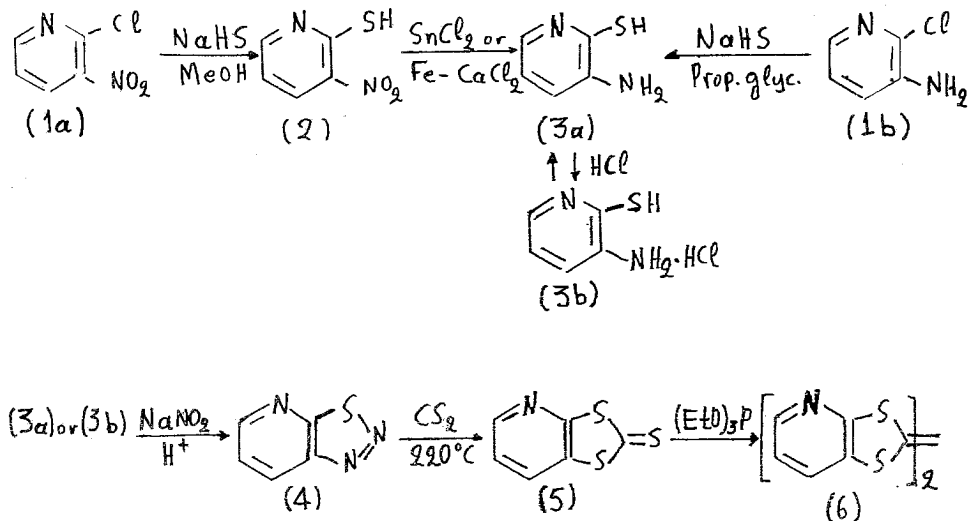
Scheme 1

2-Chloro-3-nitropyridine (1a) was transformed to 2-mercapto-3-nitropyridine (2)[4]. 2-Chloro-3-aminopyridine (1b)[5,6] or compound (2)[4,7] was transformed to 2-mecrapto-

3-aminopyridine (3a)*. Compound (3a) or its hydrochloric salt (3b)[5] was transformed to 1,2,3-pyrido-[4,5-b] thiadiazole (4)[7,8]. Reaction of thiadiazole (4) in carbon disulfide at 220°C in an autoclave afforded 1,3-pyrido [4,5-b] dithiol--2-thione(5)[7]. Refluxion of a solution of (5) in triethylphosphite afforded B[4,5-b] PTTF (6). By electrooxidation of a CH_2Cl_2-solution of (6) in presence of $Bu_4N^+X^-$ (where X^- = BF_4^-, ClO_4^-, PF_6^-, Br^-, I_3^- etc) a number of charge transfer complexes was obtained.

Experimental

Materials and instrumentation

Commerical 2-chloro-3-nitropyridine and 2-chloro-3-aminopyridine were used as starting materials without further purification. Also, commercial triethylphosphite was used after double distilation. Elemental analysis was performed by ILSE BEETZ mikroan. Lab., 8640 Kronach (W. Germany). Conductivity measurements were made by the four probe-method using a Keithley-225 current source, a Keithley-614 electrometer (µA), and a Keithley-602 electrometer (mV). The reflectance and absorption spectra were recorded on a Varian -2390 spectophotometer. ^1H NMR spectra were recorded on a Varian FT 80A NMR spectrophotometer.

Preparation of bis[4,5-b]pyridino-1,1´3,3´-tetrathiafulvalene.

2g of 1,3-pyrido[4,5-b]dithiol-2-thione (5) were dissolved in 8ml of warm triethylphosphite and the resulting solution was heated at reflux temperature for 10min. The solution was cooled and the resulting «first» precipitate was filtered, washed with ethanol and dried (yield: 18-25%). The compound was found to be soluble in CH_2Cl_2, $CHCl_3$, CH_3CN etc. Recrystallization from $CHCl_3$ gave a golden yellow solid (mp=278°C). M.Calc. 306.5, found (mass spectroscopy) 306.
Analysis (%):

for $C_{12}H_6N_2S_4(306.5)$; Calcd:C, 47.03;H, 1.97;N,9.15;S,41.85; Found: C, 47.16; H,2.13;N.9.17;S,41.92; UV(CH_3CN); λ/nm(e)358: (2290), 302(3420), 280(3420), 211(8700); ^1H NMR ($CDCl_3$): δ 8.23, 8.17, 7.44, 7.42, 7.30, 7.23, 7.09, 7.02. A very small amount of a «second» precipitate was obtained after cooling the filtrate at -15° C. UV (CH_3CN); λ/nm(ε)** :330(2400), 302(3310), 278(3200), 212(8700). It was suggested that the «first» precipitate is the thermodynamically more stable transform of (6) (t-B[4,5-b] PTTF) and the «second» precipitate the cis-form c-B[4,5-b]PTTF).

Preparation of the charge transfer complexes

Charge transfer complexes of the type (B[4,5-b]PTTF)$_n$X were prepared by the electrocrystallization of t-B[4,5-b] PTTF (1.55×10^{-3}M) and $Bu_4N^+X^-$ (5×10^{-3}M, where X=BF_4, ClO_4, PF_6, Br, I_3 etc) in CH_2Cl_2 using platinum electrode at

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* Also Se-analogs of (3)-(5) were prepared by similar methods using NaHSe and CSe_2 instead of NaHS and CS_2, respectively.[8]

** ε-value of 212nm of the «second» precipitate was considered to be equal to that of 211nm of the «first» precipitate.

$1\mu A/cm^2$ at 22°C. The length of the anodic oxidation was varied allowing for 35% and 10% oxidation of the neutral B[4,5-b] PTTF. The 35% oxidation required 2-3 days while the 10% oxidation was completed in 2 days. This short term oxidation was carried out so that the earliest formed crystals could be used. The crystals were washed with CH_2Cl_2 and air dried. $(B[4,5-b]PTTF)_2BF_4$ which was the extensively studied compound is crystallized in copper-black needles with lustrus appearence. Analysis:

for $C_{24}H_{12}N_4S_8BF_4$ (699.77);Cald: C, 41.19; H, 1.72: N, 8.02; S,36.66; Found: C, 41.15,H,2.14;N,8.00, S, 36.33. Also the compounds with X=ClO_4, PF_6, Br_3, I_3 etc were obtained in crystalline forms.

Electrical and Optical Properties and Discussion

The dc-conductivity of compressed pellets of $(B[4,5-b]\ PTTF)_nX$ measured at room temperature (σ_{RT}) was found to be of the order of $10^{-1}\Omega^{-1}cm^{-1}$, namely higher than that of $(BPTTF)_nX$ [where BPTTF is bis (pyrazino) tetrathiafulvalene][9-12] and of the same order of magnitude as that of $(DBTTF)_nX$ and Se analogs (where DBTTF=dibenzo-tetrathiafulvalene)[13,14]. Also were found similarities in the reflectance and absorption spectra. The reflectance spectrum of a compressed pellet of (B[4,5-b] PTTF)$_2$ BF$_4$ for example, is similar to that of $(BPTTF)_2BF_4$[11]; it shows bands at 235,300 (sh), 380-430, 490 (sh), 630,900 (sh) and an upward slope from 1500 nm to longer wavelengths. The value of the reflectivity at 2500 nm was found to be 0.16, while that of $(BPTTF)_2$ BF$_4$ $(\sigma_{RT}=10^{-2}\Omega^{-1}\ cm^{-1})$[11] and $(DBTTF)_8$ $(SnCl_6)_3$ $(\sigma_{RT}=100$ $\Omega^{-1}cm^{-1})$[15] was 0.14 and 0.76, respectively.

The absorption spectrum of (B[4,5-b] PTTF)$_2$BF$_4$ rubbed on a quartz plate shows the same bands as those of the reflectance spectrum. The electrical and optical data obtained from (B[4,5-b] PTTF)$_2$BF$_4$ indicate that the new donor and selenium analogs could be used for preparation materials with conductivity higher than that of $(BPTTF)_nX$. Detail studies on a large number complexes of B[4,5-b]PTTF and selenium analogs will be subject of a future paper.

Acknowledgements

Summary

Bis [4,5-b] pyridino-1,1',3,3'-tetrathiafulvalene was prepared as a golden-yelow solid after refluxing of a solution of 1,3-dithiole [4,5-b] pyridine-2-thione [RN:69212-30-2] in neat triethylphosphite and cooling. Electrooxidation of its CH_2Cl_2-solutions in presence of $Bu_4N^+X^-$ (where X^- = BF_4^-, ClO_4^-,PF_6^-, Br^-, I_3^- etc) gave conducting and highly reflecting crystalline solids.

Key words: Tetrathiafulvalenes, π-donors, charge transfer complexes, synthetic metals.

Περίληψη

Δι[4,5-b] πυριδίνο-1,1',3,3'-τετραθειαφουλβαλένιο: Σύνθεση και σύμπλοκα μεταφοράς φορτίου.

Το δι[4,5-b] πυριδίνο-1,1´,3,3´-τετραθειαφουλβαλένιο παρασκευάστηκε σαν χρυσοκίτρινο στερεό μετά από βράσιμο σε φυάλη με κατακόρυφο ψυκτήρα διαλύματος 1,3-διθειολο-[4,5-b] πυριδίνο-2-θειόνης [RN:69212-30-2] σε φωσφορώδη τριαιθυλεστέρα. Ηλεκτροοξείδωση διαλυμάτων αυτού σε CH_2Cl_2 παρουσία $Bu_4N^+X^-$ (όπου $X^-=BF_4^-$, ClO_4^-, PF_6^-, Br^-, I_3^- etc) έδωσε αγώγιμα κρυσταλλικά υλικά μέ λάμπουσα επιφάνεια.

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