

THE SCAVENGING OF THE PRECURSORS OF THE SOLVATED ELECTRON FROM THE
POSITRON LIFETIME SPECTROSCOPY AND THE DOPPLER BROADENING OF ANNIHILATION
LINE SHAPE TECHNIQUE

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The electron scavenging properties in water of two series of solutes are investigated, using the positron as a probe. For a better interpretation of the data, both the lifetime spectroscopy and the Doppler broadening of annihilation line shape technique are used. All solutes inhibit the positronium (Ps) formation, by the scavenging of electrons. The first series consists of the halate ions, that should follow the Hunt linear relation between the rate constant for reaction with the solvated electrons, $k_{(e_{aq}^- + S)}$, and that for its precursor(s), $1/C_{37}$. The Ps inhibition constants, k , are 0.14, 1.44 and 3.45 M^{-1} for ClO_3^- , BrO_3^- and IO_3^- respectively. This sequence is quantitatively consistent with that of the respective $k_{(e_{aq}^- + S)}$. The second series includes the SeO_4^{2-} , Te(OH)_6 and BrO_4^- species, and the Ps inhibition constants are 5.62, 10.5 and 14.3 respectively. These values are much higher than expected from the $k_{(e_{aq}^- + S)}$ constants, on basis of the Hunt relation, in agreement with previous results from pulse radiolysis experiments.

It is not less than ten years ago that Hamill proposed a model for the radiolysis of water (1) in which the role of the very primary species H_2O^+ and e^- , the "dry" electron, was particularly emphasized. Since that time, the attention has been gradually diverted from the rather well known behaviour and properties of the solvated electron, e_{aq}^- , to that of its precursor(s), as the time resolution of the pulse radiolysis (PR) equipments was being improved. The reactivities of some solutes towards the dry electron have now become available, most generally expressed in terms of $1/C_{37}$, on basis of a relation proposed by Hunt and co-workers (2-4) to account for the variations, with the solute concentration, of the e_{aq}^- yield in PR experiments, which is reduced to $1/e$ of its initial value at concentration C_{37} of the solute.

A comparison of the reactivities of a variety of solutes towards the solvated electron, $k(e_{\text{aq}}^- + S)$, and the respective C_{37} was shown to lead to a rather well defined linear relation between these two parameters, either in water (4) or in ethanol (5). However, some solutes studied recently by Jonah et al. (6) do not fit in with this trend, which would cast some doubt on the validity of the Hunt relation on general grounds, although these "abnormal" solutes have been admittedly chosen on purpose.

On another hand, after the spur model for positronium (Ps) formation in liquids was first proposed by Mogensen (7), in which Ps should be formed by the reaction of a positron with one of the electrons released in its terminal spur, several experiments have been aimed to find some correlation between the electron scavenging properties of solutes and their inhibiting power, as regards the Ps formation (v.e.g. 8, 9).

In previous articles, we developed the assumption that Ps might be formed via two pathways, either by the reaction of quasi-free positrons and electrons, or through the localized, not yet fully solvated, particles, the amount of Ps formed by the latter process corresponding to a fraction "f" of the total Ps yield (10-12). In this frame, a semi-empirical expression was derived to account for the

variations of I_3 , the ortho-positronium intensity, as a function of concentration C of solute :

$$I_3 = I_3^0 \frac{1}{1 + kC} \left(\frac{1}{1 + KC} + 1 - f \right) \frac{1}{1 - \frac{k'C}{\lambda - \lambda_3^0}} \quad (I)$$

Where I_3^0 is the o.Ps intensity in the neat solvent, k and K are the inhibition constants related to quasi-free and localized electron scavenging, respectively. The last multiplying term is required in the case of a quencher, viz a solute that reacts with the thermalized Ps atoms (13) : k' is the quenching rate constant, $1/\lambda_3^0$ is the lifetime of o.Ps in the neat solvent, while $1/\lambda$ is that of the positron-containing product of the reaction. In the case of oxidation, for instance :



the latter species is the free positron, and $\lambda = \lambda_2^0$, the rate constant for free annihilation. The k' parameter can be deduced independently, from the variations of τ_3 , the lifetime of the longest-lived species, according to :

$$1/\tau_3 = \lambda_3^0 + k'C \quad (II)$$

On basis of this model, it seemed interesting to investigate some of those "abnormal" solutes, for which no parallel is found, in PR experiments, between the rate constant for e_{aq}^- scavenging and $1/C_{37}$, using the positron as a probe.

Among the candidate solutes, the selenate ion (6,16), already shown not to participate in the general trend for k to parallel $k_{(e_{aq}^- + S)}$ (8) is re-investigated, using DBARL for a better accuracy in the interpretation of the inhibition process. Telluric acid (6) and the perbromate ion are the further compounds of this study. The C_{37} of the latter does not seem to have been determined, but the fact that the akin IO_4^- ion lies at the limit of validity of Hunt's law (6) and, similarly, to that of the k vs $k_{(e_{aq}^- + S)}$ relation (8) directed our choice.

Finally, this paper also reports results on the halate ions : only the C_{37} , related to BrO_3^- has been reported (3), this ion obeying the Hunt relation ; but it may be expected that the ClO_3^- and BrO_3^- ions should also behave normally, to this respect. A comparison of the behaviour of these ions regarding the positrons, to that of the halides, which were found to form positron bound states (11, 15), might also prove instructive.

Besides the usual lifetime spectroscopy (LS), the Doppler broadening of annihilation radiation line shape technique (DBARL) has also been used, in order to ascertain whether only the scavenging of electrons would be involved in the inhibition processes. It may be reminded that the latter method is very sensitive to the presence of p.Ps and of any positron bound state such as (e^+S) (14, 15).

EXPERIMENTAL

The experimental LS device has been described previously (13). Treatment of the LS data leads to three components in the lifetime spectrum, corresponding to p.Ps, e_{aq}^+ and o.Ps annihilation ; the related parameters, the intensity I and the lifetime, are to be denoted with subscripts 1, 2 and 3 respectively. Values referring to water are indicated by the superscript 0. The o.Ps yield in water is $I_3^0 = 28.0 \%$.

The DBARL measurements have been performed using a 70 cm^3 ORTEC Ge/Li detector, with a resolution of 1.45 keV at the 514 keV ^{85}Sr photopeak. The data are expressed in terms of the crude experimental full width at half maximum (fwhm) of the annihilation peaks, with an average experimental error about ± 0.01 keV. However, in order to check the presence or absence of any component due to the annihilation from a positron bound state in the Doppler broadened peaks, these have been deconvoluted after the Dannefaer and Kerr method (17), and the deconvoluted spectra were analyzed as a sum of gaussians. Besides the individual deconvoluted fwhm's of the usual p.Ps, e_{aq}^+ and o.Ps components (Γ_1 , Γ_2 and Γ_3 respectively), the presence of any further positron bound state should give rise to a fourth (gaussian) component, with the corresponding Γ_4 and I_4 parameters. Details of the method are to be found in (15).

All chemicals were A.G. reagents used without further purification, except the KBrO_4 which was prepared following Appelman's method (18). The salts used were NaClO_3 , NaBrO_3 , NaIO_3 , K_2SeO_4 and KBrO_4 . The same ampoules, degassed by the usual freeze-thaw technique and vacuum sealed, were used for both LS and DBARL experiments. They contained about 2.6×10^5 Bq carrier-free ^{22}Na .

RESULTS AND DISCUSSION

a. The halates

The LS results for the halates are displayed in fig.1, as I/I_3 vs C. Since none of the halates show significant Ps quenching properties ($k' \approx 0$), it may be inferred from the good linearity of the curves that the main process for these ions is the inhibition of Ps formation through the capture of quasi-free electrons or positrons (see relation I). In this case, relation I simplifies to :

$$I_3 = I_3^0 \frac{1}{1 + kC} \frac{1}{1 - \frac{k'C}{\lambda_2^0 - \lambda_3^0}} \quad (\text{III})$$

It is not excluded that the ions react, in part of their action, with the presolvated particles, but the data indicate this process would be confined to a tiny contribution. Relation III has been successfully fitted to the data in fig.1 : the derived parameters are given in table 1, together with the rate constants for solvated electron scavenging, and the respective calculated curves are drawn as solid lines in fig.1.

Table 1 : Inhibition and quenching parameters from relation III and rate constants for solvated electron scavenging.

Solute	k (M ⁻¹)	k' (M ⁻¹ ns ⁻¹)	k _{(e_{aq}⁻ + S) × 10⁻⁹ (M⁻¹ s⁻¹) (19,20)}
ClO ₃ ⁻	0.14	0.009	3.35
BrO ₃ ⁻	1.44	0.036	3.4
IO ₃ ⁻	3.45	0.075	8.5
SeO ₄ ⁼	5.62	0.041	1.1
Te(OH) ₆	10.5	0.00	16
BrO ₄ ⁻	14.3	5.66	7

It must be noted the data for ClO₃⁻ seem to show a slight deviation from the linearity of 1/I₃ vs C : there is a tendency for the decrease in I₃ to be delayed up to about 0.2 M. This might indicate the presence of an other process (hole capture ?) but the variations of I₃ are very smooth and the analysis of the 1/I₃ vs C curve on basis of relation III remains quite satisfactory.

The halates are known, in PR experiments, as efficient to weak electron scavengers, passing from IO₃⁻ to ClO₃⁻. Although several values have been reported for the k_(e_{aq}⁻ + S) rate constants (19), the values in table 1 are quite representative. The ratios

$k_{(e_{aq}^- + IO_3^-)} / k_{(e_{aq}^- + BrO_3^-)}$ and $k_{(e_{aq}^- + BrO_3^-)} / k_{(e_{aq}^- + ClO_3^-)}$ are 2.5 and 10, respectively. These are in very good agreement with the ratios of the inhibition constants from table 1, $k_{(IO_3^-)} / k_{(BrO_3^-)} = 2.4$ and

$k_{(BrO_3^-)} / k_{(ClO_3^-)} = 10$. Thus, the striking parallel between the k_(e_{aq}⁻ + S) and k inhibition constants series strongly suggests that the halates inhibit the Ps formation by scavenging the electrons released in the

positron terminal spur. Since the k constants are related to the scavenging of quasi-free electrons, it may also be inferred that the halates obey the Hunt relation (20).

Further information on the inhibition mechanism has been sought by using the DBARL technique. The fwhm in pure water is 2.78 keV, and that in concentrated quenching and inhibiting solutions ($\text{Na}_2\text{Cr}_2\text{O}_7$, KMnO_4), which should be representative of the sole e_{aq}^+ (15), is : fwhm = 3.09 keV. These values are higher than those previously reported (2.67 and 3.04 keV respectively) (15) due to the difference in the energy resolution of the detection systems.

The experimental results for the halates are shown in fig.2. The fwhm increases with concentration for the three ions, with efficiencies in the order $\text{IO}_3^- > \text{BrO}_3^- > \text{ClO}_3^-$. Since in pure water the total fwhm includes the contributions from p.Ps, e_{aq}^+ and o.Ps, its increase in the presence of an additive should reflect the disappearing of the narrowest components, o.Ps and, more significantly, p.Ps (15, 21). The fwhm curves thus confirm that the halates inhibit the Ps formation, and the order of the efficiencies is the same as deduced from the LS results.

As discussed above, the inhibition of Ps formation might be due to the reaction of the halates either with the positron or with the electrons in the positron spur. In the latter case, the fwhm should gradually increase, with concentration, to fwhm 2, when the inhibition is almost complete, while it should tend to some characteristic value, related to the (e^+S) complex, in the case of positron capture. The highest fwhm value, for the most effective ion, the iodate, is still significantly below the possible asymptotic value, fwhm 2. Solubility set the limit of the concentrations used, but fwhm above 3 keV may be anticipated from the shape of the curve in fig.2, for molar IO_3^- concentrations. Thus, the possibility of complete inhibition of Ps formation by quasi-free electron scavenging by the IO_3^- and, very likely too, by the BrO_3^- ions is quite consistent with qualitative examination of the curves. The curve for ClO_3^- is too smooth to allow such a conclusion.

Quantitative treatment of the DBARL results was made by deconvoluting the annihilation peaks and analyzing the deconvoluted spectra as sums of gaussians. The intensity I_3 was fixed to the experimental LS value, and I_1 was set to 1/3 of I_3 (15). In such conditions, the fitting program rejected the presence of a fourth component ($I_4 = 0$) that might have arisen if a complex such as (e^+S) was being formed in the solutions. For the three remaining components, the individual line widths found were quite satisfactorily close to those for pure water : $\Gamma_1 = 1.04 \pm 0.06$ keV ; $\Gamma_2 = 2.64 \pm 0.01$ keV ; $\Gamma_3 = 2.45 \pm 0.05$ keV. These values also agree with those previously reported (15). As suggested in (15), the fwhm curves were calculated, using the $\Gamma_{1,2,3}$ values deduced from pure water and relation III together with the parameters in table 1, derived from the LS measurements. The calculated curves are drawn as solid lines in fig.2. The agreement with the experimental data is remarkable, thus unequivocally confirming the inhibiting action of the halates on Ps formation by the capture of quasi-free electrons.

b. $SeO_4^{=}$, $Te(OH)_6$ and BrO_4^-

The $1/I_3$ variations for these species are shown in fig.3. Similarly to the halates, $SeO_4^{=}$ and $Te(OH)_6$ do not show significant quenching properties, while the BrO_4^- ion reacts rather effectively with the thermalized Ps atoms. Thus, for the sake of comparison with the other species, the experimental I_3 values for BrO_4^- have been corrected for the quenching effect, and the $1/I_3$ variations in fig.3 relate to the corrected values, as (see relation I) :

$$I_3^{corr} = I_3^{exp} \left(1 - \frac{k'C}{\lambda_2^0 - \lambda_3^0} \right) \quad (IV)$$

Since relation IV includes λ_2^0 , it is thus supposed that the perbromate acts on Ps as an oxidizer.

As for the halates, the curves are quite satisfactorily linear, so that it may be concluded these species inhibit the Ps formation by reacting with a quasi-free particle. The $SeO_4^{=}$ and $Te(OH)_6$

are known as efficient dry electron scavengers (6), and BrO_4^- should also behave in that way, like the IO_4^- ion (6). Thus, the inhibition very probably arises from quasi-free electron scavenging. Further, the linearity of the corrected $1/L_3$ vs C curve for BrO_4^- would confirm the supposition that this ion oxidizes the Ps.

Relation III has been fitted to the data. The derived parameters are recorded in table 1, and the respective calculated curves are drawn as solid lines in fig.3. As may be inferred from the slopes in fig.3, the inhibition constants are in the order $\text{BrO}_4^- > \text{Te(OH)}_6 > \text{SeO}_4^-$.

The rate constants for e_{aq}^- scavenging are lower for SeO_4^- and BrO_4^- than for IO_3^- (see table 1), but their k 's are higher. Since the IO_3^- ion belongs to the group of solutes that follow the Hunt relation, the SeO_4^- and BrO_4^- ions necessarily lie outside of this relation, by having a too high (reactivity for e^-)/(reactivity for e_{aq}^-) ratio. The situation is less dramatic for Te(OH)_6 , but the discrepancy between the ratios $k_{(e_{\text{aq}}^- + \text{Te(OH)}_6)} / k_{(e_{\text{aq}}^- + \text{IO}_3^-)} = 1.9$ and $k_{\text{Te(OH)}_6} / k_{(\text{IC}_3^-)} = 3$ clearly points to Te(OH)_6 also belonging to the "abnormal" solutes series. These conclusions are in very good agreement with those from PR experiments (6).

The DBARL results are displayed in fig.4. The crude fwhm increases rapidly with concentration, but, due to the higher inhibition constants, the highest fwhm values are well above 3 keV, and the shapes of the curves are quite consistent with the possible asymptotic value $\text{fwhm}_2 = 3.09$ keV. More significantly than for the halates, this qualitative result would indicate that the inhibition of Ps formation arises from e^- scavenging, not from the capture of positrons to form a complex (unless all three hypothetic complexes would have the same Doppler characteristics as e_{aq}^+ , a quite unlikely possibility). Further, in the case of BrO_4^- , it would seem that this ion effectively reacts with Ps as an oxidizer, not to form some (other) kind of complex, such as (PsBrO_4^-) .

The quantitative treatment of the DBARL data also lead to exclude the presence of a fourth component. The DBARL curves were

thus calculated in the same way as for the halates*, and the resulting fwhm variations are drawn as solid lines in fig.4. The agreement with the experimental data is noteworthy and fully confirms that inhibition of Ps formation by e^- scavenging is the most likely possibility for the three species.

c. Reaction rate constants and the solvation of the electron

It is not in the scope of this paper to propose any clearcut explanation concerning the observed changes of reactivity of solutes towards the electrons when these pass from quasi-free to localized to solvated. In particular, kinetic factors may be important in these still poorly known processes. However, some considerations may be made, on basis of the strong parallel which is found between the LS and PR results, as illustrated in this paper.

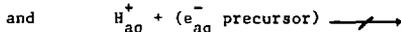
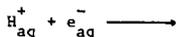
When considering the various electron scavengers that have been studied in PR experiments (v.e.g. 2, 6), it appears these may be classified into three main groups : i) those for which the reactivity decreases abruptly when the electron gradually becomes solvated. The SeO_4^{2-} , $Te(OH)_6$ and BrO_4^- species would belong to this class ; ii) those for which the reactivity decreases in a much smoother way, so that the reactivities for e_{aq}^- and that for its precursors may be correlated; these obey the Hunt relation; iii) the third class includes those solutes which hardly react with the "dry" electrons, but are efficient e_{aq}^- scavengers; the H_{aq}^+ ion would seem quite representative of this group.

Examples for the two first groups as studied by the LS technique are given in this paper, and representatives of the third class are being investigated at the laboratory. However, differences may be found in some instances between the conclusions drawn from PR and LS experiments. It must be reminded that whereas the C_{37} parameter relates to the precursors of the fully solvated electrons, these may be distinguished, following our model, as quasi-free (through the

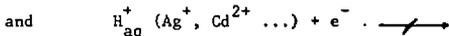
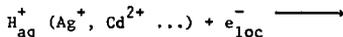
*In LS experiments, I_3 corresponds to the intensity of the longest-lived species, and thus includes the contribution from e_{aq}^+ produced from o.Ps in the case of Ps oxidation, while it should represent the true o.Ps intensity in the DBARL curves. Deduced from the kinetics of reaction 1 plus the decay reactions of Ps and e_{aq}^+ , the following relation was thus used for the BrO_4^- calculated fwhm curves, instead of relation III : $I_3 = I_3^0 / (1 + \frac{k_1 C}{\lambda_3})$. The same expression held for I_1 with I_1^0 and λ_1 in place of I_3^0 and λ_3 , respectively.

k inhibition constant) and localized (through the K parameter in relation I) particles. Thus, whereas the Ag^+ and Cd^{2+} ions would belong to class ii) in PR experiments, we would rather include them in the third group (23, 24) : for these ions, the K constants are well correlated to the $k_{(e_{\text{aq}}^- + S)}$, but not the k's, which have very low values.

On thermodynamical grounds, the third group would appear the most singular : if the reaction of a solute with e_{aq}^- is allowed, it is not clear why the reactivity would turn so weak with e^- , when the solvation energy of the electron (1.7 eV) (25) is gained (at least, of course, when no further complication is involved, such as an increased repulsive field when the scavenger is an anion). This is however found to be the case in PR experiments as :



Or in LS experiments, with :



Further, a quite similar situation is found as regards the positron scavenging : the halides and the SCN^- and S^- ions would react quite effectively with the localized positrons, to form a bound state, not with the quasi-free particles (15).

It was suggested (15) that in such cases as with the Ag^+ or Cd^{2+} ions, the energy gained when passing from e_{aq}^- (e_{loc}^-) to e^- might allow the formation of antibonding states, or of excited states that would swiftly dissociate on collision with the solvent molecules.

The H_{aq}^+ appears as one of the very scarce, to us the unique, solutes for which the parallel between the LS and PR results does not hold. On the latter hypothesis, we may propose that an excited state would be formed by the reaction of H_{aq}^+ with e_{loc}^- that would have a long enough lifetime to appear as an unsolvated electron scavenger

in LS experiments, but too short to appear so in PR experiments. Following our model, the Ps would be formed via the ($e^+ + e^-$) and ($e_{loc}^+ + e_{loc}^-$) reactions but not, or to a negligible extent, by that of the fully solvated particles: this would set the lifetime of the hypothetical H state to a few - at most a few tens - picoseconds to account for the discrepancy. However, the 10.2 eV needed for the formation of the first H excited state (26) would seem too much so as to be provided by dry electrons produced by ionization of the water molecules. Thus, the preceding hypothesis must be considered with great caution, and only represents a provisional proposal to account for the abnormal behaviour of H_{aq}^+ for electron scavenging as concerns both the PR and LS fields.

The two first groups, for which evidence has been widely accumulated regarding the LS/PR results parallel, do not seem peculiar as regards the thermodynamics: in the second group, the energy available would be sufficient, although decreasing from e^- to e_{aq}^- , whatever the solvation state of the electron for the scavenging to occur; while in the first group, the loss of the 1.7 eV electron solvation energy would hamper the ($S + e_{aq}^-$) reaction to be very efficient.

As suggested in (27) for the various solvation states of the NO_3^- ion, it is not excluded that the reactivities would also be affected by the changes in the repulsive coulombic field, as may be the case for SeO_4^{2-} compared to $Te(OH)_6$.

CONCLUSION

The present results definitely show that the conjugated use of the LS and DBARL techniques can lead to detailed information regarding the processes of Ps formation and the inhibition of Ps formation by solutes.

There exists a very strong parallel between the inhibition constants deduced from LS experiments and the reaction rate constants for electron scavenging derived from radiolysis and PR experiments. Thus, the halates are shown to behave normally as regards the Hunt linear $1/C_{37}$ versus $k_{(e^- + S)}$ relation, by having k inhibition constants proportionate to $k_{(e^- + S)}$ the $k_{(e^- + S)}$ rate constants. Conversely, the SeO_4^{2-} , $Te(OH)_6$ and BrO_4^- species are shown to react much more effectively with the quasi-free electrons than would be expected from their rate constant with e_{aq}^- on basis of the Hunt relation, in agreement with PR results.

The number of solutes for which the parallel between the Ps formation inhibiting power and electron scavenging efficiencies is not verified becomes more and more reduced as experimental evidence is accumulated. The formation of transient, very short lived, excited states on reaction with the electron may tentatively be proposed to explain such discrepancies.

ACKNOWLEDGMENTS

The authors wish to thank J.J. Schleiffer for the preparation of $KBrO_4$.

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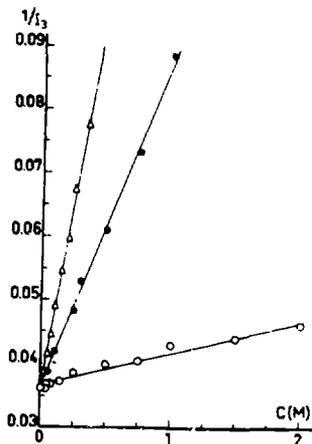


Fig.1 : Variations of $1/I_3$ with concentration C of : O , ClO_3^- ;
 \bullet , BrO_3^- ; Δ , IO_3^- .

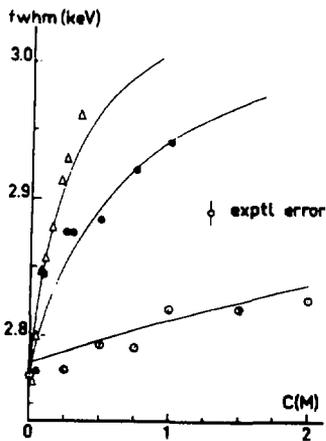


Fig.2 : Variations of fwhm with concentration C of : O , ClO_3^- ;
 \bullet , BrO_3^- ; Δ , IO_3^- .

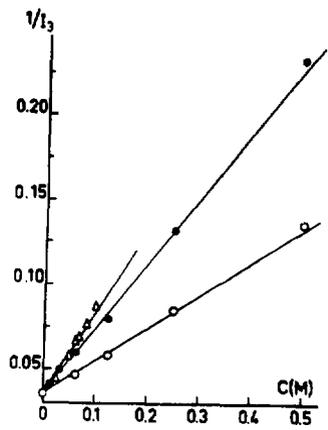


Fig.3 : Variations of $1/I_3$ with concentration C of : \circ , SeO_4^{2-} ; \bullet , Te(OH)_6 ; Δ , BrO_4^- . The curve for BrO_4^- is corrected for the quenching effects.

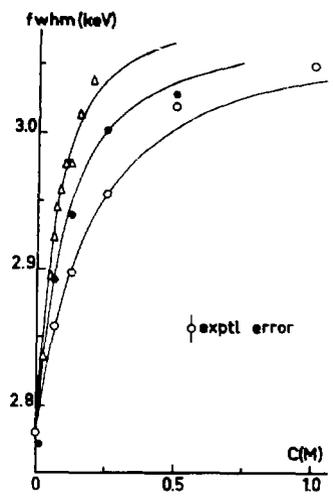


Fig.4 : Variations of fwhm with concentration C of : \circ , SeO_4^{2-} ; \bullet , Te(OH)_6 ; Δ , BrO_4^- .

