

GROUND STATE ASSOCIATION AND FLUORESCENCE QUENCHING OF AROMATIC MOLECULES BY URANYL ION IN ALCOHOLS

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Summary

The apparent rates of the fluorescence quenching of aromatic molecules by the uranyl ion in ethanol solutions are considerably higher than the rate of diffusion. At low uranyl ion concentrations this is attributed to the existence of ground state 1:1 (UO_2^{2+} ·aromatic) complexes which obtain their stability almost entirely from highly positive entropy changes; such associations are very sensitive to the solvent polarity and are not observed in less polar media. The existence of these entropically favourable complexes in ethanol could be confirmed neither by absorption spectroscopy nor by nuclear magnetic resonance spectroscopy, but it is supported by measurements of the viscosity of the solutions and by the effect of temperature on the quenching processes. Negative curvatures of the Stern-Volmer plots at high uranyl ion concentrations in ethanol solutions are attributed to the presence of ion pairs and/or polynuclear uranyl complexes.

1. Introduction

It is known that aromatic molecules form complexes with metal ions and with several other types of acceptor molecules [1 - 3]. Although it is expected that the uranyl ion (UO_2^{2+}) should form complexes with aromatic molecules, because of its good electron-accepting properties, Matushima and Sakuraba [4, 5] found no evidence for such interactions in the quenching of (UO_2^{2+})^{*} luminescence by several aromatic compounds. In this paper we report studies of the fluorescence quenching of aromatic molecules by uranyl salts in alcoholic solvents. Strong static quenching has been found and this is attributed to the ground state association of UO_2^{2+} with the aromatic substrates. However, these associations are much weaker in less polar solvents. We have also investigated the thermodynamic stability of such complexes, and we discuss the nature of their molecular interactions.

2. Experimental details

Steady state fluorescence studies were carried out using a Perkin–Elmer MPF-3 spectrofluorometer. The exciting wavelengths were chosen to minimize uranyl nitrate absorption at the exciting and the emission wavelengths and a correction for such an effect was introduced when necessary. The dynamic studies were carried out using single-photon counting apparatus with a time resolution of 1.5 ns. Under our experimental conditions the fluorescence spectra of the aromatic hydrocarbons are not affected by UO_2^{2+} and there is no significant sensitization of uranyl emission.

Viscosity measurements at 25 ± 0.1 °C were accomplished by using a suspended level Ubbelohde-type viscosimeter (FICA). The precision of the flow-time measurements is better than 0.01 s. Densities were measured using a digital densimeter (Paar DMA 60) with a precision better than 2×10^{-6} g cm^{-3} .

Uranyl nitrate of the highest purity commercially available was used. The aromatic compounds (Aldrich, K & K) were purified by zone refining and the solvents were purified by current techniques.

3. Results and discussion

3.1. Fluorescence studies at low UO_2^{2+} concentrations

Competition between static and dynamic fluorescence quenching can be analysed in terms of the Stern–Volmer equation [6]

$$\frac{I_0}{I} = (1 + k_q\tau[Q])(1 + K[Q]) \quad (1)$$

where I_0 and I are the fluorescence intensities in the absence and in the presence of the quencher, k_q is the dynamic quenching rate constant, τ is the lifetime of the excited state and K is the equilibrium constant of the non-luminescent 1:1 ground state complex responsible for the static quenching. For low quencher concentrations, eqn. (1) reduces to

$$\frac{I_0}{I} = 1 + (k_q\tau + K)[Q]$$

or

$$\frac{I_0}{I} = 1 + K_{sv}[Q] \quad (2)$$

where K_{sv} is the Stern–Volmer slope. For steady state irradiation, the apparent quenching rate constant $k_q(\text{app}) = K_{sv}/\tau$ can be significantly higher than the rate k_d of diffusion when $K > k_d\tau$.

The quenching of the fluorescence of several aromatic compounds by uranyl nitrate was studied in ethanol solutions. At low UO_2^{2+} concentrations (less than 0.005 mol dm^{-3}) good Stern–Volmer plots were observed in

TABLE 1

Stern–Volmer parameters for the fluorescence quenching of aromatic molecules by UO_2^{2+}

Hydrocarbon	K_{sv} ($\text{mol}^{-1} \text{dm}^3$)		τ (ns)	$k_q(\text{app})$ ($\times 10^{10}$ $\text{mol}^{-1} \text{dm}^3 \text{s}^{-1}$)		K (ethanol) ($\text{mol}^{-1} \text{dm}^3$)	k_q^a ($\times 10^{10}$ mol^{-1} $\text{dm}^3 \text{s}^{-1}$)
	Ethanol	95vol.%- cyclo- hexane- 5vol.%- ethanol		Ethanol	95vol.%- cyclo- hexane- 5vol.%- ethanol		
Benzene	2170		31	7.0		1900	2.5
Toluene	1885		34	6.0		1670	
Xylene	1746		30	5.8		1400	
Azulene	560	31	1.4	40	2.2	545	
Anthracene	520	66	5.5	9.5	1.3	460	2.1
Tetracene	375		7.2	5.2		300	
Perylene	163	58	6.0	2.7	1.0	95	< 2.3
Naphthalene	1900		105	1.9		800	
Phenanthrene	1625	160	59	1.0		—	
Fluoranthene	350		56	0.7	0.3	—	
Pyrene	3500		450	0.8		—	1.8
Coronene	522		307	0.2		—	

^aFrom dynamic studies.

all cases. The values of the Stern–Volmer slopes and the apparent quenching rate constants are presented in Table 1. These results are attributed to UO_2^{2+} quenching since NO_3^- was found to have no significant effect on the fluorescence intensity ($[\text{NO}_3^-] \leq 2 \times 10^{-2} \text{mol dm}^{-3}$). The rate constants found with some aromatic compounds, namely with benzene, methylbenzenes, azulene, anthracene, tetracene, perylene and naphthalene, are higher than the rate of diffusion ($k_d \approx 1 \times 10^{10} \text{mol}^{-1} \text{dm}^3 \text{s}^{-1}$). Dynamic studies were carried out with anthracene, perylene, benzene and pyrene, and the quenching rate determined at high UO_2^{2+} concentrations was found to be almost diffusion controlled: $2 \times 10^{10} \text{mol}^{-1} \text{dm}^3 \text{s}^{-1}$. This value is slightly higher than the value currently accepted for the diffusion rate, for reasons which will be discussed in Section 3.2.

In contrast with the results in ethanol, the quenching rate constants in the much less polar medium 95vol.%cyclohexane–5vol.%ethanol are much lower and are comparable with the rate of diffusion (Table 1). Studies in pure cyclohexane were not carried out owing to the low solubility of the uranyl salts. These results imply that in ethanol there is considerable static quenching by UO_2^{2+} and, consequently, significant ground state association of UO_2^{2+} with several of the aromatic compounds. However, such association is not significant in less polar media. From the Stern–Volmer plots and the reported values of k_d and τ , the equilibrium constants of the ground state complexes, assuming 1:1 stoichiometry for (UO_2^{2+} ·aromatic), were

estimated. The values reported in Table 1 refer to cases where the contribution from the static quenching is dominant (greater than 50%).

The effect of temperature on the Stern–Volmer constants was also investigated. Figure 1 illustrates the results of such a study for azulene in ethanol and in 95vol.%cyclohexane–5vol.%ethanol solutions. In cyclohexane solutions the observed activation energy of $3.3 \text{ kcal mol}^{-1}$ is close to that due to the effect of the temperature on the solvent viscosity, as expected for diffusion-controlled quenching. However, in ethanol the observed effect is considerably smaller and this is attributed to the enthalpy ΔH of formation of the $(\text{UO}_2^{2+}\cdot\text{aromatic})$ complex being $0.65 \text{ kcal mol}^{-1}$. This conclusion is supported by the results from studies of the temperature dependence of fluoranthene quenching in ethanol (Fig. 2); with this molecule the static quenching is not very significant, and consequently there are no significant ground state complexes in ethanol (Table 1). Thus, as expected, the measured activation energy is much higher ($3.0 \text{ kcal mol}^{-1}$) and is close to that for a diffusion-controlled process. This value is also identical with that found in cyclohexane solutions (Fig. 2).

Table 2 presents ΔH° for the formation of complexes of UO_2^{2+} with several aromatic compounds in ethanol, together with the values of ΔG° and ΔS° ; owing to a possible contribution from dynamic quenching, the actual ΔH° may be about $0.5 \text{ kcal mol}^{-1}$ lower than given in this table. The changes in enthalpy are positive and quite small, whereas the changes in entropy are positive and relatively high. This reveals that the formation of the molecular complexes between UO_2^{2+} and aromatic hydrocarbons is mainly due to a

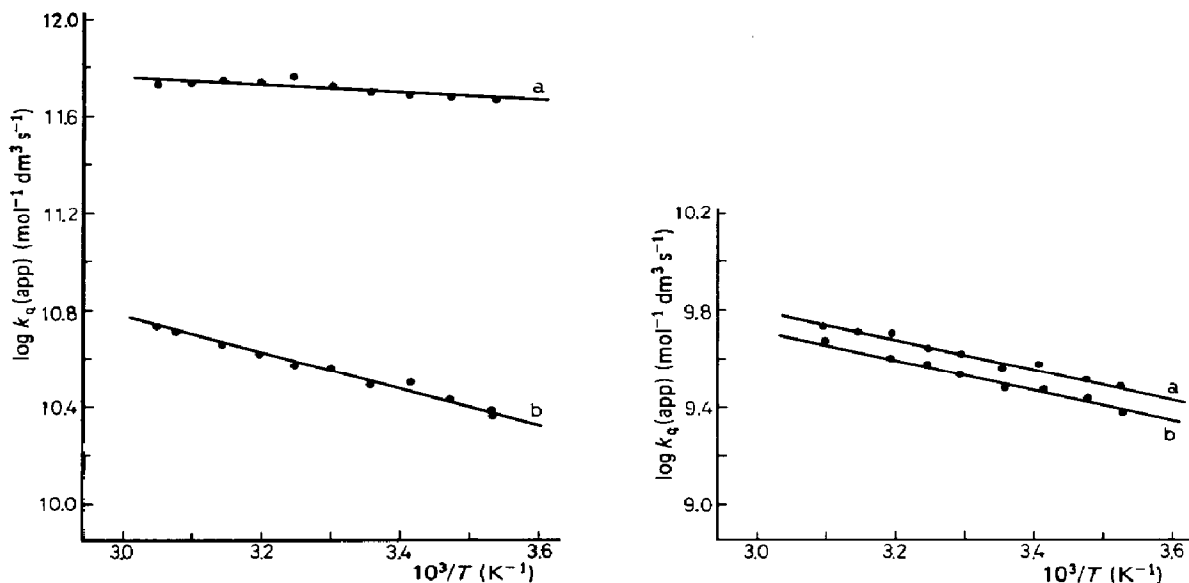


Fig. 1. Temperature dependence of the apparent quenching rate constant of azulene by UO_2^{2+} in ethanol (curve a) and 95vol.%cyclohexane–5vol.%ethanol (curve b).

Fig. 2. Temperature dependence of the apparent quenching rate constant of fluoranthene by UO_2^{2+} in ethanol (curve a) and 95vol.%cyclohexane–5vol.%ethanol (curve b).

TABLE 2

Thermodynamic parameters for (UO_2^{2+} -aromatic) complexes in ethanol at 298 K

Hydrocarbon	ΔG° (kcal mol ⁻¹)	ΔH° (kcal mol ⁻¹)	ΔS° (cal mol ⁻¹ K ⁻¹)
Benzene	-4.4	1.8	21
Azulene	-3.7	0.6	14.5
Anthracene	-3.6	0.9	15
Tetracene	-3.3	2.0	18
Perylene	-2.6	1.7	14.5

favourable entropic contribution. A positive change in entropy can be attributed largely to an increase in the entropy of the solvent molecules which were coordinated to UO_2^{2+} before the association with the aromatic molecule. The increase in freedom of the solvent molecules compensates for the decrease in entropy caused by the association of UO_2^{2+} with the aromatic molecule.

In less polar solvents, where UO_2^{2+} is less solvated, it is expected that the entropic contribution of the solvent is smaller and the complexes are less stable. This view is supported by studies of the quenching of azulene and anthracene in several cyclohexane-ethanol mixtures (Fig. 3). The apparent quenching rates decrease when the percentage of cyclohexane increases. A similar polarity effect is also observed in the quenching of azulene in alcohols: methanol, $k_q(\text{app}) = 2.2 \times 10^{11} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$; *n*-butanol, $k_q(\text{app}) = 7.5 \times 10^{10} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$; *t*-butanol, $k_q(\text{app}) = 4.0 \times 10^{10} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$.

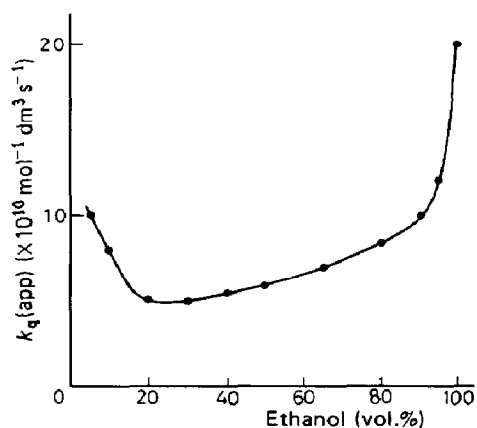


Fig. 3. Apparent rate constants of quenching of azulene by UO_2^{2+} in ethanol-cyclohexane mixtures.

3.2. Fluorescence studies at high UO_2^{2+} concentrations

At UO_2^{2+} concentrations higher than $0.005 \text{ mol dm}^{-3}$ the Stern-Volmer plots show deviations from linearity. However, such deviations depend on the nature of the solvent. For example, in 90vol.%cyclohexane-

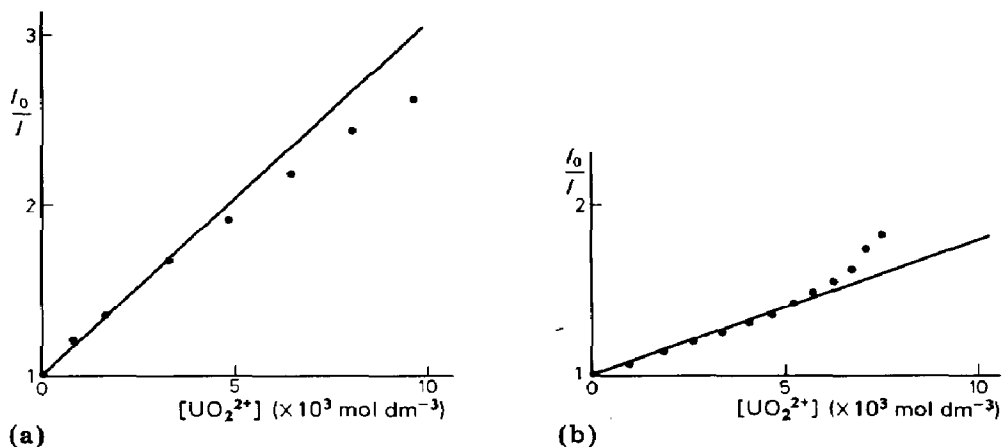


Fig. 4. Stern-Volmer plot for the quenching of azulene fluorescence by UO_2^{2+} in (a) ethanol and (b) 90vol.%cyclohexane-10vol.%ethanol.

10vol.%ethanol the Stern-Volmer plot of the fluorescence quenching of azulene possesses positive curvature, in agreement with eqn. (1). However, in pure ethanol a negative curvature is observed (Fig. 4). Multiple equilibria for complexes of the kind $((UO_2^{2+})_n \cdot \text{aromatic})$, such as have also been observed for Ag^+ with several aromatic compounds [2], can lead to negative curvatures of the Stern-Volmer plots for dynamic quenching [7, 8]. However, the contribution of the dynamic process to the overall quenching is sufficiently small to explain the effects reported in Fig. 4. In fact, negative curvatures have also been observed in ethanol in the same concentration range with benzene, benzene derivatives, anthracene, perylene and pyrene, whilst a positive curvature has been observed with fluoranthene.

The negative curvatures of the Stern-Volmer plots can be explained if, at $[UO_2^{2+}] > 5 \times 10^{-3} \text{ mol dm}^{-3}$, there is a decrease in the UO_2^{2+} -aromatic interaction, owing to the formation of new uranyl species in solution. Support for this hypothesis comes from the absorption spectra of different concentrations of uranyl nitrate in ethanol. Whereas at $[UO_2^{2+}] > 5 \times 10^{-3} \text{ mol dm}^{-3}$ the spectrum is well resolved and is independent of UO_2^{2+} concentration, at low concentrations there is a loss of structure, a decrease in the extinction coefficient by a factor of 2.2 and a red shift of 12 nm with respect to the spectrum at higher concentrations (Fig. 5). Such spectral changes can be due to ion-pair association ($UO_2NO_3^+$ or $UO_2(NO_3)_2$) and/or the presence of polynuclear species formed via nitrate ion bridging (e.g. $(UO_2)_2(NO_3)_2^{2+}$) [9]; at low concentrations the spectrum is relatively broad, possibly reflecting the presence of several molecular and ionic species resulting from uranyl nitrate, which is a weak electrolyte in ethanol [10], undergoing more significant dissociation. At high UO_2^{2+} concentrations, owing to a strong UO_2^{2+} - NO_3^- interaction, there is a decrease in the interaction of UO_2^{2+} with the aromatic molecule.

The uranyl nitrate spectra do not change within the same UO_2^{2+} concentration range in 95vol.%cyclohexane-5vol.%ethanol. There are also no

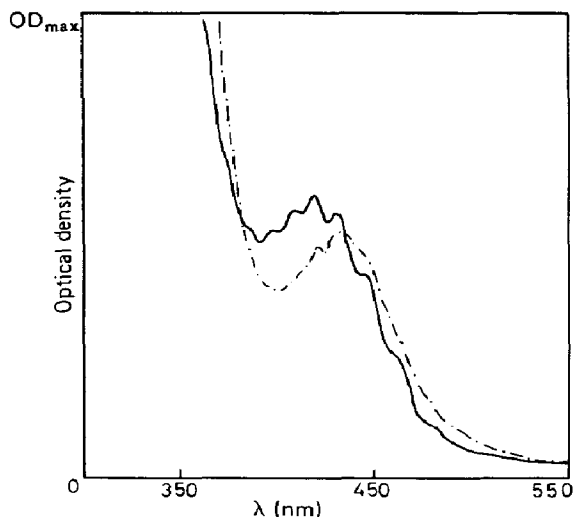


Fig. 5. Absorption spectra of uranyl nitrate in ethanol: —, $1 \times 10^{-2} \text{ mol dm}^{-3}$ ($\text{OD}_{\text{max}} = 1.0$); - - -, $1 \times 10^{-3} \text{ mol dm}^{-3}$ ($\text{OD}_{\text{max}} = 0.05$).

changes in the absorption spectra of the aromatic molecules even at high UO_2^{2+} concentrations, in both solvents.

The Stern-Volmer plots reported in Table 1 were obtained with uranyl solutions of low concentration (less than $5 \times 10^{-3} \text{ mol dm}^{-3}$) and are attributed to 1:1 complexes. When higher UO_2^{2+} concentrations are used there is a decrease in the Stern-Volmer slopes. This has been observed, for example, with azulene and anthracene.

3.3. Viscosity measurements

We have looked for further confirmation of the occurrence of these entropic interactions in ethanol solutions. The change in enthalpy for the formation of the complexes reveals that there is no strong electronic interaction between the two moieties. Consequently it is no surprise that no evidence of complex formation was found either by absorption spectroscopy or by nuclear magnetic resonance spectroscopy, which are less sensitive techniques than luminescence emission for cases where there are no strong interactions. Because the complexes have an entropic origin, however, evidence for such interactions can be sought by measuring properties which are strongly solvent dependent, such as viscosity. We have measured with great precision the viscosity η of solutions of uranyl nitrate (0.1 mol dm^{-3}) in ethanol as a function of the benzene concentration. Studies at the uranyl concentration employed for fluorescence quenching were not feasible. Measurements were undertaken at the same temperature (25°C) with solutions of benzene in ethanol. Figure 6 shows that at low benzene concentrations there is a linear variation in η with the benzene concentration. In terms of the viscosities η_r relative to the systems in the absence of benzene, $\eta_r = 1.000 - 0.089[\text{C}_6\text{H}_6]$ for UO_2^{2+} (0.1 mol dm^{-3}) in ethanol with $[\text{C}_6\text{H}_6] \leq 0.1 \text{ mol dm}^{-3}$, and $\eta_r = 1.000 - 0.068[\text{C}_6\text{H}_6]$ for pure ethanol. Since the

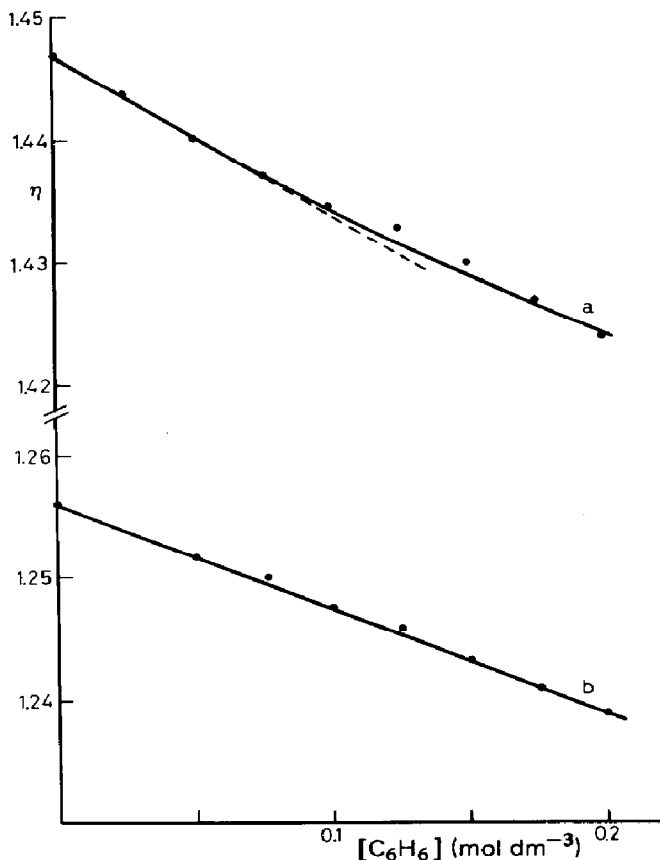


Fig. 6. Variation in the viscosity of uranyl nitrate (0.1 mol dm^{-3}) in ethanol (curve a) and of pure ethanol (curve b) as a function of benzene concentration. Linear dependences: ethanol- UO_2^{2+} , $\eta = 1.447 - 0.129[\text{C}_6\text{H}_6]$ ($[\text{C}_6\text{H}_6] < 0.1 \text{ mol dm}^{-3}$); pure ethanol, $\eta = 1.256 - 0.085[\text{C}_6\text{H}_6]$.

slopes are different we take this as evidence for a significant interaction between benzene and UO_2^{2+} . The higher decrease in η_r of solutions containing UO_2^{2+} can be attributed to a decrease in the interaction between the (UO_2^{2+} -benzene) species and the polar medium. However, when $[\text{C}_6\text{H}_6] > 0.1 \text{ mol dm}^{-3}$, there is a deviation from linearity for the viscosity of the solutions, possibly owing to the appearance of a microheterogeneity.

The fluorescence dynamic quenching of aromatic hydrocarbons by metal ions has been extensively studied and recent data reveal that it is due to the formation of a non-fluorescent complex followed by rapid inter-system crossing [11]. Such excited state complexes have a strong charge transfer character. The ground state complexes of (UO_2^{2+} -aromatic) also seem to have charge transfer character, because there is a correlation between ΔH° and the ionization energy of the excited aromatic molecules. However, the contribution of this charge transfer state to the ground state complex is quite small (about 15%) judging by the slope of Fig. 7.

Further support for a ground state interaction between UO_2^{2+} and azulene is the formation of a permanent product which is formed slowly in

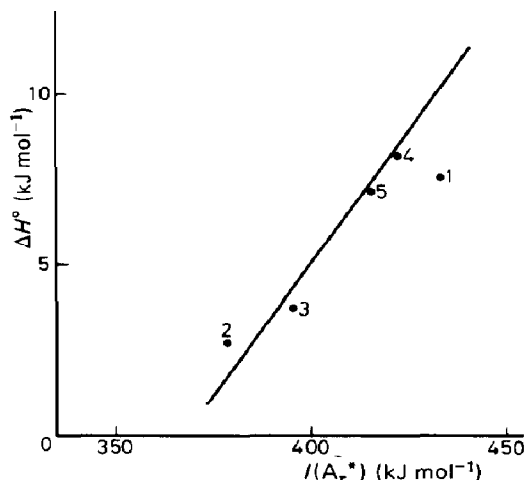


Fig. 7. Correlation between the enthalpy of formation of the $(\text{UO}_2^{2+}\cdot\text{aromatic})$ complexes and the ionization energy of the aromatic molecules: 1, benzene; 2, azulene; 3, anthracene; 4, tetracene; 5, perylene.

the absence of light and rapidly upon irradiation. We were unable to identify the product, but we were able to confirm that it contains uranium atoms.

There should be a final comment on the lack of evidence for such $(\text{UO}_2^{2+}\cdot\text{aromatic})$ ground state complexes in the studies of Matsushima and Sakuraba [4, 5]. These researchers employed aqueous acetone as the solvent and the interactions between UO_2^{2+} and the very polar H_2O molecules are strong enough to overcome any hydrophobic interactions.

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