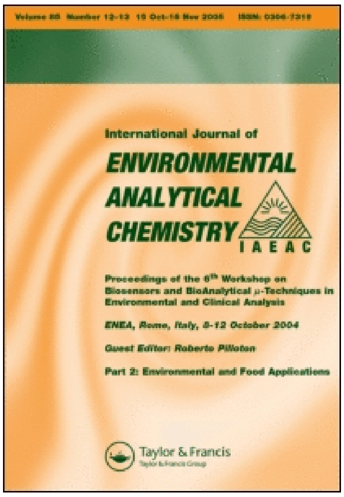

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N-OCTANOL/WATER PARTITION COEFFICIENTS OF THE ACETYLACETONATE AND MALTOLATE COMPLEXES OF Al(III), Cr(III) AND Fe(III) AND OF ALUMINUM LACTATE*

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The *n*-octanol/water partition coefficients of the neutral complexes $M(acac)_3$ (M = Al, Cr and Fe; acac = actylacetonate) and $M(malt)_3$ (M = Al and Cr; malt = 3-hydroxy-2-methyl-4-pironate) put into evidence the importance of the residual lipophilic-hydrophilic character of the metal-coordinated ligand in determining the lipophilicity of $M(acac)_3$ and the hydrophilicity of $M(malt)_3$. Aluminum lactate was also investigated and it results to be very hydrophilic.

KEY WORDS: Octanol/water partition coefficient, aluminum(III) complexes, acetylacetonate, maltolate, lactate, lipophilicity, hydrophilicity.

INTRODUCTION

Aluminum lactate ($Al(lact)_3$)[1] is being commonly used for *in vivo*[2] and *in vitro*[3] studies of the biological activity of aluminum(III). Recently, this chemical was employed in these laboratories together with the acetylacetonate (acac) and maltolate (malt = 3-hydroxy-2-methyl-4-pironate) complexes of Al(III) and Cr(III) for toxicity tests on rabbits[4] and on bacterial cultures,[5] and for membrane stability tests on erythrocytes.[6] These investigations are aimed to determine the influence of the nature of the metal coordination sphere in some biological effects of Al(III) and Cr(III) (i.e. general toxicity, genotoxicity and effects on membrane stability).

The necessity of interpreting some intriguing aspects of the results of these investigations, prompted us to experimentally evaluate the *n*-octanol/water partition coefficients of $Al(lact)_3$, $Al(acac)_3$, $Cr(acac)_3$, $Fe(acac)_3$, $Al(malt)_3$ and $Cr(malt)_3$. The relevance of these figures to the physiopathological interpretation of toxicity data stems from the generally accepted view that the *n*-octanol/water partition coefficient of a given potential toxic agent can be related to its solubility in the cell membranes.[7]

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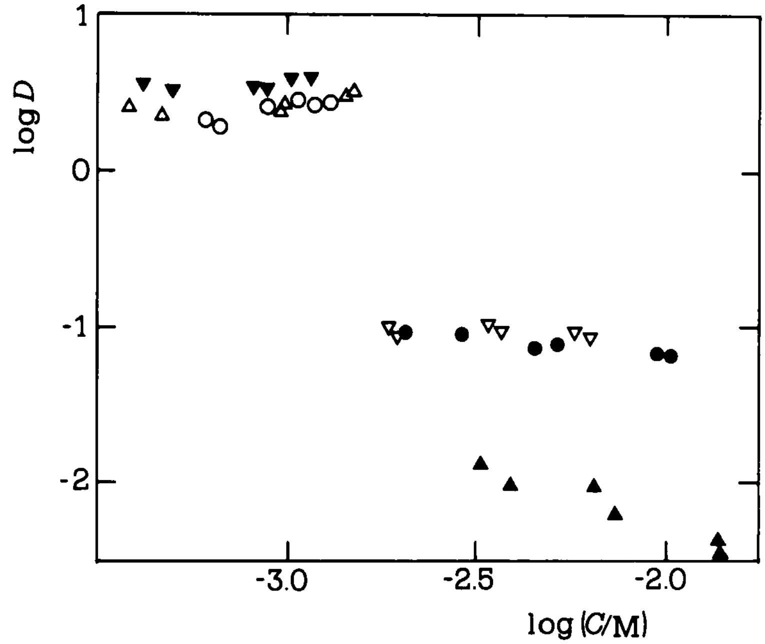

Figure 1 Dependence of the D-values on the metal complex concentration in the aqueous phase. ○ $Al(acac)_3$; ● $Al(malt)_3$; ▲ $Al(lact)_3$; ▼ $Cr(acac)_3$; ▽ $Cr(malt)_3$; △ $Fe(acac)_3$.

MATERIALS AND METHODS

$Al(lact)_3$ (Fluka) and $Cr(acac)_3$ (Schuchard) were employed as received; $Fe(acac)_3$ (Schuchardt) was recrystallized from benzene/n-heptane; $Al(acac)_3$ and $Al(malt)_3$ were prepared by literature methods.[8,9] Partition measurements were carried out by allowing the chemical (ca. 20–150 μmol) to distribute between 5 cm^3 of water and 5 cm^3 of *n*-octanol (Janssen 99%) for three days at 25.0 ± 0.1 °C with occasional stirring.[10] The various metal species were initially dissolved either in water or in *n*-octanol, according to their expected hydrophilic or lipophilic character; the analytical concentrations were determined by standard colorimetric (Al) and atomic absorption spectrophotometric (Cr and Fe) methods.

RESULTS AND DISCUSSION

The results are shown in Figure 1. The values of the stoichiometric partition ratio, D, are found to depend on the analytical concentration of each metal species, the dependence being statistically significant (F-test, level of significance ≤ 0.05). It may be observed that D increases with dilution for $D < 1$, while the opposite is true for $D > 1$. These changes are most probably due to the occurrence of equilibria,

Table 1 *n*-Octanol/water partition coefficients for tris-acetylacetonate and tris-maltolate metal complexes and for aluminum lactate at 25 °C

Species	*Conc. range* (*mM*)	K_{pc}[a]
$Al(acac)_3$	0.9–2.5	2.44 ± 0.27
$Al(malt)_3$	1.1–5.6	0.078 ± 0.009
$Al(lact)_3$	1.6–7.0	(0.0037–0.0127)[b]
$Cr(acac)_3$	0.9–3.0	3.62 ± 0.24
$Cr(malt)_3$	1.0–3.5	0.093 ± 0.005
$Fe(acac)_3$	0.7–3.3	2.70 ± 0.34

[a] Values of the partition coefficients (averages of 6 values at different concentrations). The reported uncertainties are twice the standard deviation of the average. The analytical concentration corresponds to the total (i.e. *n*-octanol plus water) volume.

[b] Range of the experimental *D* values.

such as e.g. slight dissociation of the complexes. However, in all cases but for $Al(lact)_3$, the concentration effect is rather small, and the average values of *D* can be reasonably assumed to be not far from the values of the true thermodynamic partition constant, K_{pc} (Table 1).

However, for $Al(lact)_3$, which is known to undergo rather complicated[11] and metastable[12] equilibria, the observed values of partition coefficient are likely to be appreciably different from the corresponding thermodynamic figure. In spite of this uncertainty, the present data unambiguously demonstrate the strongly hydrophilic character of $Al(lact)_3$,

While the hydrophilicity of $Al(lact)_3$, which is generally considered as a salt, matches the expected behaviour, the (moderately) hydrophilic character of $Al(malt)_3$ and $Cr(malt)_3$ deserves some further comment. These compounds are neutral and hydrolytically stable[13] metal complexes, isostructural with the corresponding acetylacetonates, which show, on the contrary, a moderately lipophilic character. The different behaviour is to be ascribed to the residual hydrophilic character of the metal-coordinated ligand, which overwhelms the lipophilic character generally expected for a neutral metal complex of organic ligands.

The importance of the residual hydrophilic-lipophilic character of the ligand in determining the solubility of the chelate complex is confirmed by the closely comparable *D* values found for the three acetylacetonates and for the two maltolates, respectively.

Acknowledgements

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