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ACTIVATION ENERGIES FOR THE LONGITUDINAL RELAXATION RATES OF THE WATER IN NORMAL AND NEOPLASTIC LUNG

Key words: lung tumors, T_1 relaxation times, water in biological samples.

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ABSTRACT

Variable temperature water T_1 relaxation times have been measured on some normal and neoplastic human lung tissues. The corresponding activation energies have been derived and a short discussion of the experimental results is given.

INTRODUCTION

In a previous work (1) we have described a correlation between tissutal water T_1 and the hystological type of tumors in human lung tissues. We have shown how, in lung epidermoid

carcinoma, the water T_1 increases with the malignancy of the neoplasm. As already found in different living tissues (2)(3):

$$T_1 \text{ tumoral tissue} \geq T_1 \text{ normal tissue}$$

has been demonstrated to be valid also in this case. This trend is subjected to an open and controversial question, present in literature, and is related to the probable origin of the water T_1 increases in tumoral samples, with regard to normal ones.

While some Authors (2) acknowledge the increased water content, others (3) evidence a structural difference of the water in normal and tumoral samples.

MATERIALS AND METHODS

Samples of lung affected by carcinoma epidermoid tumors were obtained from freshly surgered patients. Adjacent portions of normal tissues were also recovered.

Capillaries ($\varnothing = 1.5$ mm) filled with both kinds of tissues were adapted to normal NMR 5 mm tubes, containing CD_3OD for deuterium lock. The spectra were recorded on a Bruker WP80SY spectrometer at the frequency of 80.13 MHz, using a sweep width of 1000 Hz and 30 K of memory. The T_1 's were determined by I.R. method and a minimum of 20 points were collected for each measurement. The experimental data were analyzed by 3 parameters non linear regression directly on the computer. The variable temperature measurement were performed in the interval 299-330°K in 5 degrees steps.

A vacuum connected variable temperature dessicator fixed at 70° was used for the total water weight determination.

The easily removable water was determined by successive time weighting of the samples, subjected to the air stream warmed at 30°C, up to constant weight.

RESULTS AND DISCUSSION

In this short note, the aim of which is to collect more experimental informations about the origin of the water T_1 differences in both kinds of tissues, we have measured the behaviour of the water T_1 with the modification of the temperature in the interval of 299-330° K, either for distilled, but undegassed, pure water and for a number of samples of normal and tumoral lung tissues, all affected by epidermoid carcinoma.

From the linear plot of T_1^{-1} versus temperature we have calculated the activation energies of the processes involved in the water longitudinal relaxation time in the different samples.

All the data are reported in table I.

Besides the T_1 values and the activation energies, the table I also reports the total water content obtained by weighting the samples before and after a prolonged drying treatment in a vacuum at 70°C.

Furthermore, after the observation that the tumoral lung tissues appear like a mudd, while the normal ones present an elastic and compact structure, uniform watted, we have approximately estimated the fraction of easily removable water by gently blowing the samples with a tiny jet of dry air, at the temperature of 30°C, to obtain apparently dry tissues.

By comparing the weight of the samples, after this gentle treatment, with that obtained through the higher temperature treatment, the fractions of easily removable water are thus approximately determined. These fractions are also reported in the last column of the Table I.

From the results reported in the table I the following considerations are made.

In all samples the water T_1 increases in the correct way from normal to tumoral tissues, while the activation energies

TABLE I

T_1 , water content in lung tissues at 26°C and activation energies.

	T_1 (sec.)	E_a (KJ mol $^{-1}$)	weight*	P_a^{**}
	norm. tum.	norm. tum.	(gr/gr dry tissue)	norm. tum.
			norm.	
pure undegassed				
water	2.651	—	11.13	—
			—	—
Epidermoid carcinoma	1	0.828	1.139	6.32
"	2	0.781	1.020	6.79
"	3	0.854	0.875	6.37
"	4	0.769	1.012	6.07
"	5	0.783	0.875	6.49
average	0.803	0.984	6.41	10.36
				2.4
				2.94
				0.22
				0.93

* Refers to total water content after drying at 70°C. Std dev \pm 0.2.

** Refers to bulk easily removable water content at 30°C. Std dev \pm 0.02.

(E_a) follow the succession:

E_A (pure water) $\approx E_A$ (water in tumoral tissue) $> E_A$ (water in normal tissue)

The close resemblance of the activation energy of the water in its pure undergassed state with that of the tumoral tissue is quite surprising, considering the noticeable difference in the respective T_1 values.

For ultra pure and degassed water, several accurate measurements of T_1 and of E_a are reported in literature (4)(5).

In different magnetic fields and in the interval of temperature from 0 to 100°C, values of T_1 varying between 3.37 - 3.57 sec are reported with activation energy of 15.7 KJ mol⁻¹ (4).

The conclusion given by Krycknicky (5) are that the ultra pure and degassed water exists as a distribution of molecular aggregates $(H_2O)_n$ with $0 \leq n \leq 4$ hydrogen bonds.

The undegassed but distilled water, as measured by us, has both T_1 and E_a lower, in the extent of 28%, respect to the ultra pure degassed water.

While the fall of T_1 is easily understood with the presence of dissolved paramagnetic O_2 and other ions, the decrease in activation energy may be ascribed to the disruption of the higher coordinate water aggregates by dissolved substances like salts.

We believe that the close similarity between the activation energies in pure water and in tumoral tissue, the difference in the respective T_1 , and the completely different values of both parameters in normal tissues, may have their origin in the water distribution and binding at the inner-outer tissue cells surface.

The water population interacting strongly with the tumoral tissue has been estimated to be a very low fraction of the total tissue content, roughly of the order of 0.1 (see Table

1). Consequently the activation energy of the water in the native tumoral sample will be mainly that of the loosely bound water.

On the contrary, the content of easily removable water in normal tissue is estimated, by the same considerations outlined above, to be a relatively low fraction of the total water content, about 0.2 (see table 1). The activation energy, in this last case, will be then mainly determined by the water interactions with the tissue surface.

We may then derive that either in tumoral and normal cases the water fraction interacting with the tissue surface would have an activation energy of the order of $5 \approx 6 \text{ KJ mol}^{-1}$, compared to the 12 KJ mol^{-1} , obtained for the pure water.

These preliminar results thus support the opinion that a consistent contribution to the T_1 difference between normal and neoplastic lung tissue may result from the water structuration at the tissue frame, together with factors due to the total water content difference (2) and presence of salts in different concentration (6).

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