# INVESTIGATION OF TAUTOMERIC STRUCTURES OF DIALDEHYDEPOLYSACCHARIDES

**S.N. Drobchenko, L.S. Isaeva-Ivanova, A.R. Kleiner, A.V. Lomakin, V.A. Noskin**

The aldo-enol transition in oxidized dextrans is studied by UV absorption spectroscopy and electrophoretic light scattering. Absorption peaks at 267 *nm*, 240 *nm* and 290 *nm* have been attributed to aldehyde, enol and enoliation, respectively. The electrophoretic mobility of the oxidized dextran appears to be proportional to the absorption at 290 *nm* and the pH dependence of the 240 to 290 *nm* peaks ratio follows the standard titration curve. These facts are in accord with the suggested model of enol and enoliat - ions formation.The dextrans of molecular weights 2000 (Fluka AG), 40000, 60000, 70000, 11000, 500000 (Loba chemie, Fluka AG) were used. The dextrans were oxidized by sodium periodat according to method [1]. UV spectra were measured after every hour or in some experiments at high pH after every 10 minutes. All the spectra were measured againts buffer solution with the Specord M-40 spectrophotometer. The aldehyde groups were determined by Iodine number, the carboxyl groups by method [2]. The quantity of enol was determined by direct Bromine titration by Meier [3]. For determination of electrophoretic mobility (EPM)

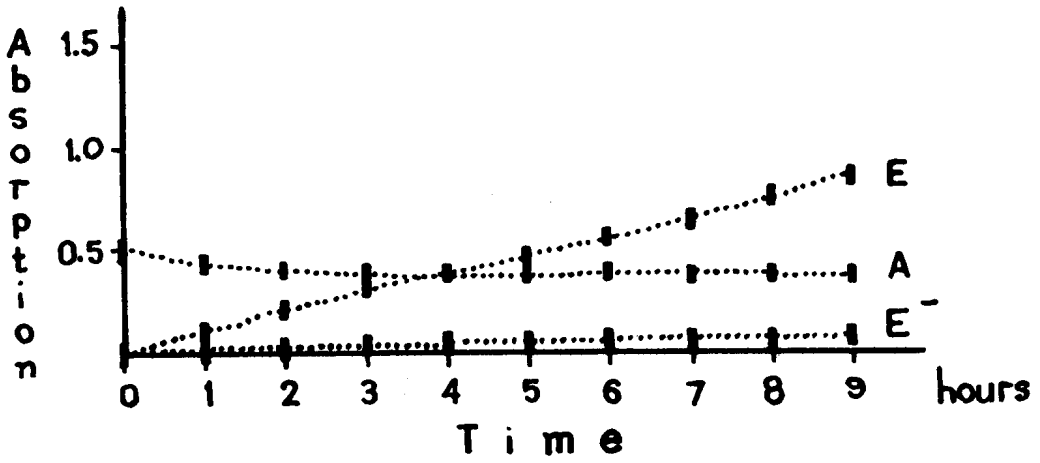


Fig.1. Absorption of aldehyde (A), enol (E) and enoliat-ion ($E^-$) groups vs time delay after pH jump for 3 to 7.5

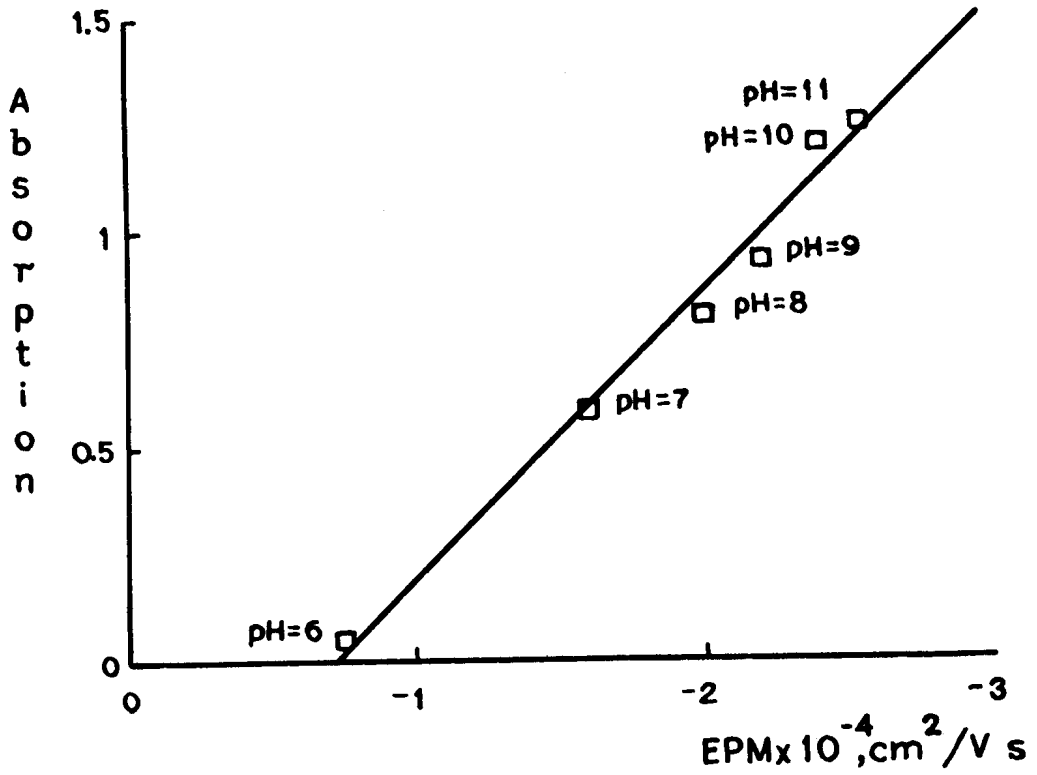


Fig.2. Dependence EPM/absorption at 290 *nm* of oxidized dextran (M.W.=500000) at different pH

the Zeta Sizer II (Malvern Instr.Ltd) and the installation designed in Molecular and Radiation Biophysics Division of the LNPI [4] were used.

The absence of UV and IR absorption of oxidized polysacharides aldehyde groups is usually explained by formation of hydrated semiacetal and gemdiol groups [1]. However, several years ago studying the interaction between oxidized dextrans and aminoalkil thiophosphates [5] we had found that dialdehydedextrans (DAD) spectra depended on pH of the solution and only within a narrow pH region (4-— 5.2) the absorption is indeed absent.

We had suggested the presence of the enol form and gave some physical and chemical arguments in favour of this suggestion in our previous works [6,7].

At the initial pH=3 there is only the aldehyde group peak at 267 *nm*. Later thepeak at 240 *nm* appears which could be ascribed to enol absorption; and at last the peak at 290 *nm* became visible together with one at 240 *nm*.

In fig.1 we have plotted corrected in this way kinetic curves of aldehyde, enol and enoliat ion groups versus time delay after pH jump for pH = 3 to 7.5:

In fig.2 we summarize the electrophoretic light scattering data in the graph where EPM measured in different conditions parallel to UV absorption are plotted against the corrected magnitude of 290 peak. So we have plotted the magnitudes of the UV absorption peaks ahainst the concurrently measured EPM to find out if any of these peaks matches the proportionality to EPM. As it can be seen in fig.2, the 290 *nm* peak appears to be in a rather explicit linear dependency with EPM. Thus, we may conclude that the absorption at 290 *nm* is due to a negatively charged group and no other charged group is present in significant amount in the oxidized dextrans.

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