

temperatures lower than 10°C. The observed $T_{1\rho}$ of methine groups diverges from the values calculated from τ_{c1} at temperatures above 35°C, indicating that the motion of methine groups has greater activation energy at temperature above 35°C. The temperature at which a break is observed in the temperature dependence is coincident with T_{mc} , described in the section of proton T_2 .

Molecular Mobility as Determined by High-Resolution NMR

Laboratory and Rotating Frame Spin-Lattice Relaxation

Times of Carbon

Figure 7 shows the typical spectra of freeze-dried γ -globulin formulation containing dextran, freeze-dried γ -globulin, and freeze-dried dextran, measured by high-resolution ^{13}C solid-state NMR (31). Peaks at 70 and 180 ppm are assigned to the dextran methine carbon and γ -globulin carbonyl carbon, respectively. The T_1 of each carbon, calculated from the signal decay, decreases with increasing temperature, indicating that relaxation occurs in the slow motional regime. The τ_c of dextran methine carbon then can be calculated from the observed T_1 according to equation (7), if the dipole-dipole interaction between carbon and proton is predominant in the relaxation process, and if the relaxation time can be expressed by a single τ_c .

$$\frac{1}{T_1} = \frac{1}{10} \gamma_C^2 \gamma_H^2 \left(\frac{h}{2\pi} \right)^2 r_{C-H}^{-6} \times \left[\frac{\tau_c}{1 + (\omega_c - \omega_H)^2 \tau_c^2} + \frac{3\tau_c}{1 + \omega_c^2 \tau_c^2} + \frac{6\tau_c}{1 + (\omega_c + \omega_H)^2 \tau_c^2} \right] \quad (7)$$

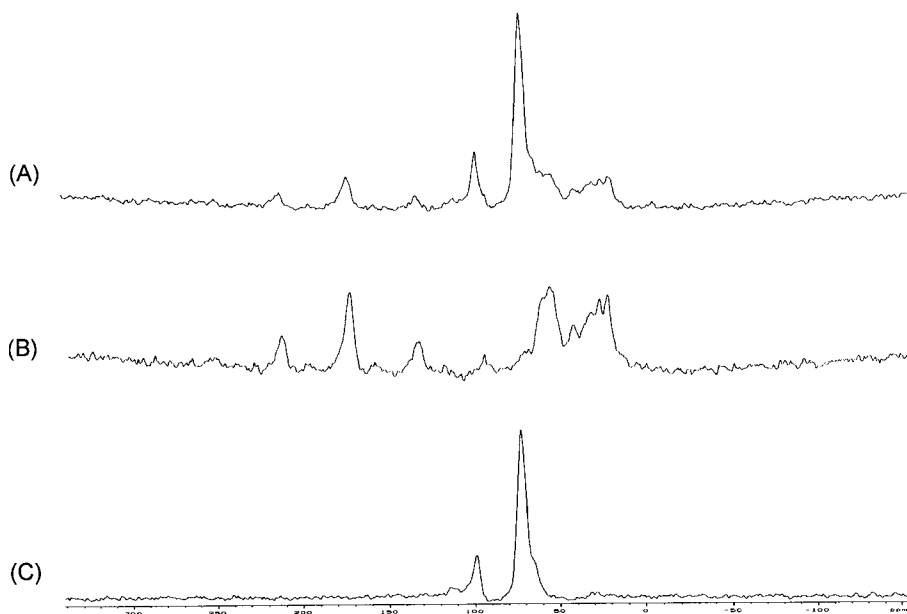


FIGURE 7 ^{13}C -NMR spectra of freeze-dried γ -globulin formulations containing dextran (A), freeze-dried γ -globulin (B), and freeze-dried dextran (C).