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Dielectric and conductivity relaxation in sodium carboxymethyl cellulose and its acid form

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We report a study on the dielectric relaxation behaviour of samples of sodium carboxymethyl cellulose and its acid form covering the frequency range 20–10^5 Hz and the temperature range 40–90°C. Treating the data in terms of an impedance formalism using the electrical modulus rather than admittance formalism using the complex dielectric constant revealed that two relaxation processes in NaCMC while its acid form, HCMC, shows only one. The high frequency process in both NaCMC and HCMC is attributed to the reorientation of the carboxymethyl groups. These results suggest that the previous assumption of lacton formatiom in HCMC seems to be untenable. The lower frequency in NaCMC is due to a conductivity relaxation. The shorter relaxation time of the latter indicates that the transport of charge carrier requries the motion of the chain segment. The effect of the degree of substitution on the dipolar relaxation in NaCMC is also discussed. Copyright © 1996 Published by Elsevier Science Ltd

INTRODUCTION

It is well known that the electric polarization in a polymer may be due to dipole alignment, rotation/motion of the main/segmental polymer chain, migration of ions within the material or injection from the electrodes. Traditionally, the complex permittivity formalism, ε^*, has been employed to describe the dielectric relaxation phenomena in polymers. In this formalism the dielectric function, ε^*, is the most direct physically meaningful quantity, under the condition that in the experiments the electric field is the undependent variable and the charge is the dependent one (Jonsher, 1983). Thus, ε^*, is a compliance. In the ε^* formalism, in the case of admittance measurements, the following relation holds.

$$\varepsilon^*(\omega) = \frac{Y^*(\omega)}{i\omega C_o} = \frac{C}{C_o} - i\frac{\sigma}{\omega C_o} \tag{1}$$

or

$$\varepsilon^*(\omega) = \varepsilon' - i\varepsilon'' \tag{2}$$

where $Y^*(\omega)$ is the measured admittance of the dielectric, C its capacitance, σ its conductance, C_o the equivalent capacitance of the free space (Jonsher, 1983), ε' is the dielectric constant and ε'' is the dielectric loss.

Sodium carboxymethyl cellulose, usually known as NaCMC, is a solid polyelectrolyte. A common method of treating the dielectric relaxation in this type of materials is to subtract from $\sigma/\omega C_o$ a contribution $\sigma_{dc}/\omega C_o$, where σ_{dc} is the limiting low frequency or dc conductivity. The frequency dispersion of the remaining part of the dielectric function,

$$\varepsilon^*_p = \varepsilon' - i\left(\varepsilon'' - \frac{\sigma_{dc}}{\omega C_o}\right) \tag{3}$$

is used to characterise the dielectric data. This method has been applied in a previous study in solid NaCMC (Rafaat *et al.*, 1993). These authors observed an ohmic conduction which does not contribute to the dielectric constant, ε', and a loss peak in the frequency range 10^2 Hz < 10^4 Hz. The latter dispersion has been attributed to the rotation of the carboxymethyl groups. However, recent work (Abel Moteeleb *et al.*, 1994) on the dielectric behaviour of NaCMC shows that NaCMC exhibits only a dielectric dispersion in the low frequency range which has been attributed to an interfacial polarization and that this dispersion disappeared when the salt is neutralised. In our opinion these previous dielectric measurements on solid NaCMC were influenced by the presence of a space charge and of a dipolar relaxation effects and that the contribution from dc conduction alone has been difficult to determine. This has been mainly due to the fact that their measurements have not shown a region of low frequency where ε' reaches a plateau value, that makes the subtraction procedure possible.

For these reasons, it seems interesting to re-investigate the different motional processes in NaCMC and its acid form. In this work the dielectric susceptibility measurements data obtained are analyzed using the electric modulus model (Fontanella *et al.*, 1992 and Federico *et al.*, 1993). One very powerful advantage of using the formalism of complex electric modulus M^* to interpret bulk relaxation properties in ion conducting amorphous solids is that variations in the very large, but low frequency, permittivity, and conductivity are minimized. In this way the familiar difficulties of electrode nature, contact and space charge effects, which appear to swamp relaxation in permittivity presentation, can be resolved, or even ignored. Our aim is to detect the conductivity and the dipolar relaxation in solid NaCMC. The effect of the degree of substitution on the dipolar relaxation process will also be discussed.

EXPERIMENTAL

Materials

The sodium carboxymethyl cellulose samples, which were kindly supplied from Hercules Inc. were purified several times by precipitation with methanol from aqueous solution and then dried at 80°C for 2 days in a vacuum oven. The degree of substitution was determined by the method of Conner and Eyler (1950) and found to be 1.2 and 0.7. The degree of polymerization, DP, was estimated for these two samples viscometrically by two independent methods, namely, those of Wirick *et al.* (1968) and Gelman(1982). A value of ca. 340 was obtained.

The acid form of carboxymethyl cellulose (HCMC) was prepared from its salt NaCMC (DS = 1.2, DP = 340) by treating 5 g of the latter with a mixture of ethanol and concentrated nitric acid (10 : 1 w/w). The mixture was stirred mechanically for 1 h, filtered, extracted with 70% aqueous methanol for 10 h using a soxhelt extractor, and rinsed with absolute ethanol followed by ether. The sample was then thoroughly dried at 80°C under vacuum for 3 days. The ash content of the sample was determined and found to be 0.03 wt% compared with a value of 22 wt% for NaCMC.

Dielectric measurements

The dielectric constant, ε', and the loss, ε'', were measured within the frequency range of 20–10 Hz over a temperature range 40–90°C using the polymer Laboratories–Dielectric Thermal Analyser (PL-DETA). A test sample was in the form of disc (33 mm in diameter and 1.8 mm in thickness) was prepared by pressing the powder sample at constant pressure of 11.76 MPa. The cell was kept dry during the measurements by guarding it with phosphorus pentaoxide and passing through it a mild stream of thoroughly dried nitrogen.

RESULTS AND DISCUSSION

The frequency dependencies of the dielectric constant, ε', and loss, ε'', of NaCMC at different temperatures is shown in Fig. 1a and b, respectively. A clear loss peak is observed in the latter figure, which shifts to higher frequencies with increasing temperature, whereas at sufficiently low frequency there is a rapid increase of both ε' and ε'' with frequency decrease. The high values of ε' and ε'' at low frequencies and relatively high temperatures make it easy to identity the effects of blocking electrodes. More specifically, in Fig. 1a the apparent dielectric constant is very large, indicating the existence of the so called 'space charge polarization' (Wintersgill *et al.*, 1989). In Fig. 1b the dielectric loss also becomes very large at low frequencies, due to the 'free charge' motion within the material. These values do not correspond, of course, to the bulk dielectric function but rather due to 'free charge' build up at the interface between the material and the electrodes. For very low frequencies there is practically time for the charges to build up at this interface before the field changes direction, giving a very large effective value of ε'. With increasing frequency there is no time for the build up of the charge at the interface but only for the build up at the boundaries of the conducting species in the material and at the ends of the conducting paths. This phenomenon leads to the so called 'conductivity relaxation'.

Figure 2 shows a plot of log σ_{ac} vs the reciprocal of absolute temperature at some selected low frequencies. The conductivity, σ_{ac}, expressed in S/cm was calculated from the totally measured loss, ε'', at a given angular frequency, ω, for a given temperature using the equation:

$$\sigma_{ac} = C_o \omega \varepsilon'' \tag{4}$$

It will be evident from this figure that at low temperatures where the dc conduction does not have any significant contribution, the apparent conductivity is strongly dependent upon frequency, again indicating the existence of a conductivity relaxation process.

To reveal the type of conduction process it is proposed that treating the data in terms of an impedance formalism using the electrical modulus, M^*, (Fontanella *et al.*, 1992 and Federico *et al.*, 1993) rather than an admittance formalism using the complex dielectric constant, ε^*, seemed to be more appropriated, especially for ion-containing system. The real and imaginary parts of the electric modulus, M'' and M'', were calculated from the equations:

$$M^* = \frac{1}{\varepsilon^*} = M + iM'' = \frac{\varepsilon'}{\varepsilon' + \varepsilon''} + i\frac{\varepsilon'}{\varepsilon' + \varepsilon''} \tag{5}$$

The electric loss modulus, M'', offers two advantages over the loss factor, ε'', for characterising low frequency processes under conditions where ε' is increasing with

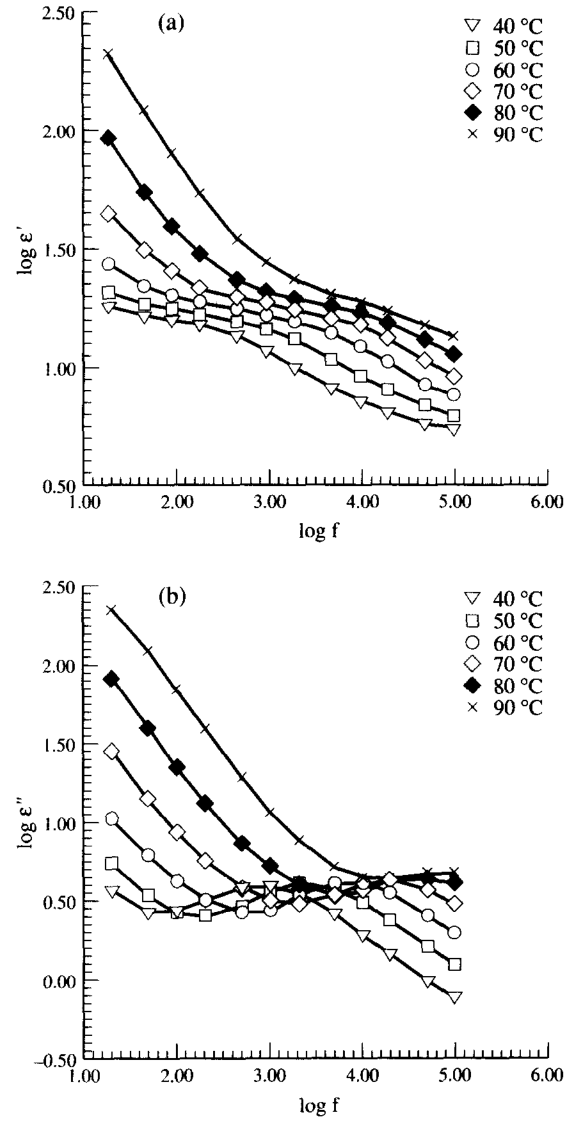

Fig. 1. Frequency dependence of the dielectric constant, ε', (a) and ε dielectric, ε'', (b) of NaCMC with DS $= 1.2$ at different temperatures.

decreasing frequency by space charge polarization, because blocking electrodes are usually used. First, the maximum in M'' will occur at a higher frequency than the maximum in ε''. Second, such a false contribution to the dielectric constant, ε', is know to be suppressed by using the electrical modulus formalism (Fontanella *et al.*, 1993 and Mclin *et al.*, 1992). These points are illustrated in Fig. 3 where the electrical loss modulus, M'', for NaCMC were plotted against log f at different temperatures. Taking into consideration that the complex dielectric and the complex modulus contain the same information a new relaxation process is defined in the low frequency range (20–1000 Hz). This is a conductivity relaxation process and might tentatively be attributed to cations blocked in clusters. This is in agreement with the cluster model suggested by Datye *et al.* (1984). Accordingly, because of the micro-structural heterogeneity of the polyelectrolyte NaCMC involving cluster formation, in which there are bound and unbound ions (the latter being attached to the backbone of the polymer), ions travel by hopping between clusters. These clusters could therefor be seen as sodium reservoirs scattered inside the bulk ployelectrolyte. It can be also seen that the conductivity relaxation peaks are shifted towards higher frequency as the temperature is increased. This is because of the enhancement of the ion transport process. This relaxation can be characterized by a time constant, $\tau = 1/2\pi f$ where f is the peak frequency of the conductivity relaxation. It is well known that the reciprocal of relaxation time is related to the mobility of charge carriers (Bard *et al.*, 1980 and Hamaide *et al.*, 1993): the longer, τ, the slower the ionic motion. The value of the relaxation time for this relaxation lie in the range 1.5×10^{-4} s, which is longer than values usually observed in typical electrolytes (Hamaide *et al.*, 1990).

Figures 1a and 3 shows that either in using the measured dielectric loss, ε'', or the corresponding loss modulus, M'', a high frequency relaxation process is observed. This process presumably involves a dipolar activity and could be associated with the co-operative motion of the side group, probably the —OCH_2COONa groups and could be affected by the number of these groups. However, a comparison of the results obtained for sample with lower DS (DS $= 0.7$) shown in Figs 4a and b with those of higher DS shown in Fig. 1b and Fig. 3 (noting that both having the same M_w) indicate that a decrease in the DS does not result in a decrease of the peak heights. Such behaviour is in agreement with that observed previously (Rafaat *et al.*, 1993) and can be accounted for in the basis that, although the magnitude of the loss increases with the concentration of the concerned dipolar groups in a chain, it is chiefly governed (Yager *et al.*, 1942) by interchain interactions. This means that, the interchain forces constrain the concerned dipole motion despite the higher proportions of groups of higher dipole moments in the sample with DS $= 1.2$ than in sample with DS $= 0.7$. This is in support with the hypothesis (Yager *et al.*, 1942) that it is not only a matter of concentration and dipole moment of groups along the chain that affect the magnitude of the peak height. But is also chiefly a matter of interaction between adjacent chains. Since the interchain interactions depend on the uniformity of distribution of the —OCH_2COONa groups, one expects that the higher the DS the more is uniformity of distribution of these groups. This may account for the broader absorption peaks observed in sample with lower DS compared to sample with higher DS. In the former the interactions between chains include hydrogen bonding, dipole–dipole, ion–dipole and dispersion forces.

The frequency dependencies of the dielectric constant, ε', and the dielectric loss, ε'', of the acid form of carboxymethyl cellulose, HCMC, at different

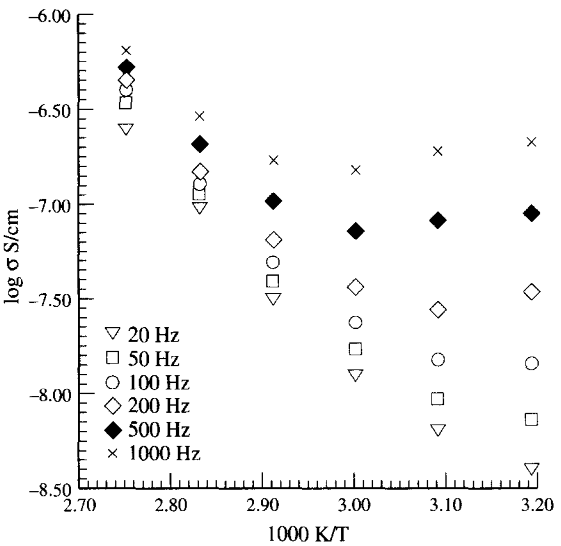

Fig. 2. Dependence of the apparent conductivity, σ_{ac}, S/cm of NaCMC on reciprocal of the absolute temperature at different frequencies.

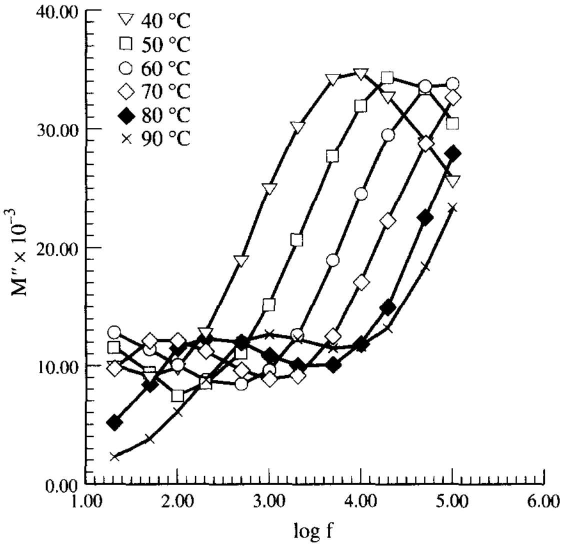

Fig. 3. Frequency dependence of electric loss modulus, M'', of NaCMC with DS = 1.2 at different temperatures

temperatures are shown in Figs 5a and b. Proposing, in an approximate way, that the replacement by hydrogen ions of all sodium ions has been practically achieved, the following comparison is made between the results of the acid form of CMC and those of its salt (see Fig. 1):

(1) At a given temperature, HCMC exhibits higher values of both ε' and ε'', compared to the sodium salt, over the whole frequency range investigated (20–10^5 Hz);

(2) No loss peaks are discernible up to the highest available frequency (10^5 Hz), which is not the case for NaCMC;

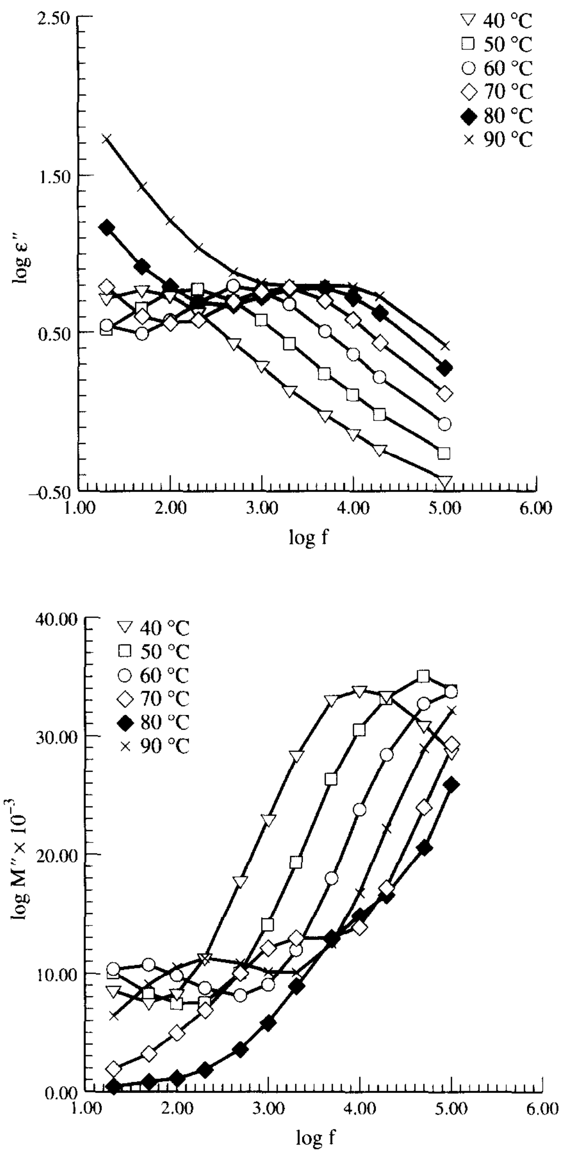

Fig. 4. Frequency dependence of the dielectric loss, ε'', (above) and the electric loss modulus, M'', (below) of NaCMC with DS = 0.7 at different temperatures.

(3) Both the dielectric constant, ε', and the dielectric loss, ε'', rise steeply in a manner similar to that observed in the case of NaCMC.

Since the high frequency process in NaCMC ascribed to the co-operative motion of the side groups (—OCH_2COONa), which disappears in HCMC, one might infer that this is a justification of the very earlier theory of Chowdhury, (1929). This theory assumes that cellulose derivatives bearing — COOH groups form lactone rings with the unreacted hydroxyl groups in the cellulose molecules upon drying. Consequently, if one accepts the above assumption of lactone formation, it then follows that the diminishing of the —OCH_2COOH groups and the consequent absence of co-operative motions of these groups, result in the disappearance of the loss peaks within the high frequency interval (10^3–10^5 Hz). Whilst this interpretation seems to be acceptable for the invisibility of the expected high-frequency process in analogy with the sodium salt, it is interesting to consider the observed large dispersions of the storage component, ε', and the rapid decrease in the loss component, ε, in the low-frequency range (again see Figs 1a and 1b). Since high values of both ε' and ε'', in the limits where the frequency approaches zero, together with the strong low-frequency response, are frequently observed in charge-carrier dominated systems (Jonsher, 1983), therefore the above suggestion of lactone formation to account for the disappearance of the loss peaks seems untenable. To see whether the dielectric response in the investigated low-frequency range is merely a direct-current conduction mechanism, or simultaneously accompanied by another different mechanism arising from the presence of rotatable dipolar species, the method of the complex modulus ($\varepsilon^* = 1/M^*$) was adopted. Thus a plot of the loss modulus, M'', vs the frequency at different temperatures was given in Fig. 6. This figure reveals a dielectric relaxation process presumably involving dipolar activity, which could be associated with the rotation of carboxymethyl (—OCH_2COOH) groups. The fact that this relaxation is observed at a lower frequency with a high activation energy of dipole relaxation (ca. 120 kJ/mol) compared to that found in NaCMC (ca. 111 kJ/mol), suggests that the orientational freedom of the side groups is restricted owing to the hydrogen bonding between neighbouring parallel chains.

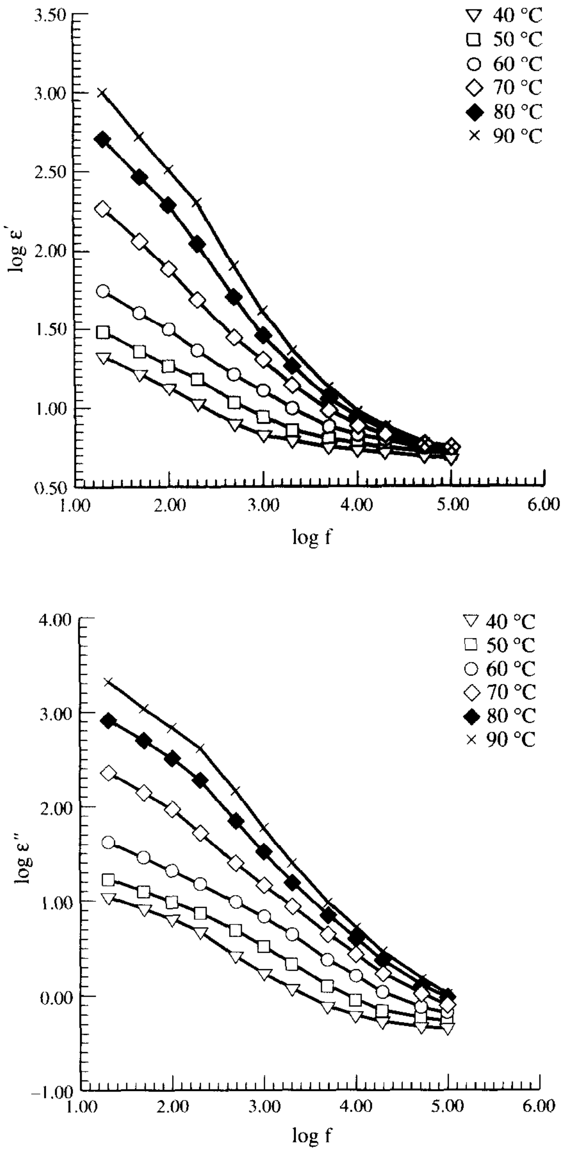

Fig. 5. Frequency dependence of the dielectric constant, ε', (above) and dielectric, ε'', (b) of HCMC with DS = 1.2 at different temperatures.

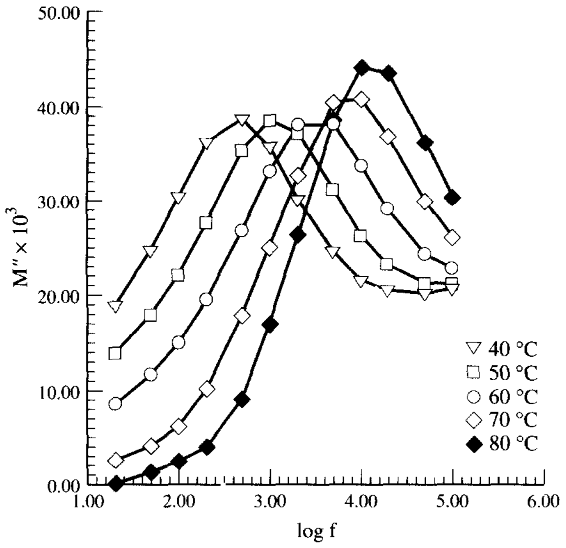

Fig. 6. Frequency dependence of electric loss modulus, M'', of HCMC with DS = 1.2 at different temperatures.

It is worth mentioning that, NaCMC is distinguishably heterogeneous in the micro-structural scale by virtue of its cluster formation, leading to an ionic interfacial polarization arising from the accumulation of ionic charges at the boundaries of the underlying cluster morphology provided of course that the mobility of the ions under these circumstance are of short-range displacements.

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