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Permeation of water as a tool for characterizing the effect of solvent, film thickness and water solubility in cellulose acetate membranes

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Abstract

Cellulose acetate membranes have been used in many applications; of particular interest are reverse osmosis systems, and as a neutral matrix for incorporation of different polymers (e.g., conducting polymers), inorganic ions (e.g., lanthanides) and organic (e.g., pharmaceutical) compounds. The properties of the new polymers derived from cellulose acetate or blends depend on those of cellulose acetate. This work presents an attempt to find links between thermodynamic and kinetic properties of cellulose acetate membranes in equilibrium with water. Water diffusion coefficients in cellulose acetate membranes are reported, measured with a simple water permeation technique. The comparison of these values with the percentage of water uptake and polymer thickness leads to interesting conclusions related with different polymer properties.
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1. Introduction

The study of transport properties in membranes of cellulose acetate (CA) and its derivatives has attracted the attention of many researchers due to the broad applications of these polymers in areas such as pharmacology [1], wastewater treatment [2], artificial organs [3], and liquid chromatography [4]. The use of cellulose acetate for these different goals remains an interesting problem [5–7].

It is well known that the diffusion processes of different solutes and/or solvents [8–11] in CA membranes depends on the degree of acetyl substitution [9], film thickness [12,13], structure [3], polymerization conditions, etc. Petropoulos et al. also found that the diffusion of different solvents in cellulose acetate membranes depends on stress and macromolecular orientation [14,15].

The effect of water sorption and diffusion in cellulose and cellulose acetate with different degrees of substitution were studied in [16]. Thermodynamic parameters of the polymer in aqueous solutions were calculated and characteristics of clustering and diffusion coefficients

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were estimated. Water diffusion in cellulose and water-soluble cellulose acetate derivatives was shown to be primarily controlled by thermodynamic affinity, associated with hydrophilic hydration as well as by structural changes as induced by sorption. As the degree of substitution of cellulose acetates increases, thermodynamic affinity towards water decreases. Water clustering was shown to be a main reason for decreased average diffusion coefficients [16].

In addition to all these applications, cellulose derivatives can be used as polymeric supports. We have been particularly interested in their application for supporting conjugated organic polymers, such as polyaniline [17,18], to be used as hole transport [19,20] layers in multilayer polymeric and organic light emitting diodes (LEDs). These multicomponent systems frequently suffer the partial incompatibility of the various components, leading to phase separation. The problem can frequently be solved by changing solvent and cellulose acetate concentration. This work shows the analysis of the effect of solvent and cellulose acetate content on the water diffusion coefficient. The variation of water diffusion coefficient is discussed on the basis of polymer structural properties in addition to water equilibrium behaviour in CA. It is very difficult to separate the thermodynamics of water sorption from the kinetic properties, that is, from the diffusion of water [21]. Our objective is to develop an equation linking thermodynamic and kinetic parameters.

2. Experimental

2.1. Membranes

Cellulose acetate membranes were prepared using CA purchased from Aldrich—Spain, with a weight-average molecular weight of 30,000 and degree of substitution of 39.8% acetyl groups. Different weights of CA were dissolved in tetrahydrofuran (Merck) (THF) or acetone (Panreac, pro-analysis) at 25 °C, with constant stirring during 24 h. The solution was then deposited on a flat glass support and spread out with a Braive film applicator to produce membranes of specified thickness. After complete evaporation of the solvent at room temperature, the membrane was removed from the glass support with the help of water.

Different samples of each membrane were cut and immersed in water. They remained in equilibrium with water until the weight of the sample reached an equilibrium value M_{eq}. Subsequently, membranes were placed inside a vacuum oven at 100 °C until constant weight, M_0. The weight/weight (w/w) water concentration in the membrane, C_w, was calculated from

$$C_w = (M_{eq} - M_0)/M_0. \tag{1}$$

All gravimetric measurements on water sorption were measured to ±0.1 mg using an ADA 120LE balance.

2.2. FTIR

Membranes were characterized by their infrared spectra using a ATI Mattson Genesis Series FTIR spectrometer. Polymer samples ($\approx$10 μm thickness) were cut from a membrane. Some samples were dried at 60 °C during several days before recording the spectra.

2.3. Scanning electron microscopy

Morphology of the cellulose acetate films (thickness around 20 μm), prepared with different solvents, was analyzed using a Jeol/Scanning Microscope, model 5310 under low vacuum, operating at 20 kV.

2.4. X-ray scattering analysis

The degrees of crystallinity of the polymeric films were evaluated using a Philips, model X-Pert X-ray diffractometer operating at 40 kV, using Co as radiation source and a graphite filter. The scans were obtained using a scan step size of 0.025° with a scan step time of 0.5 s.

2.5. Differential scanning calorimetry

The samples were accurately weighed (1–3 mg) and cut from films prepared as described above. To remove the residual solvent, the films of pure polymers and blend were dried at reduced pressure for, at least, one day at ambient temperature. Differential scanning calorimetry (DSC) measurements were performed using a Shimadzu differential scanning calorimeter, *DSC-50* model, at a heating rate of 10 °C min^{-1}, in a nitrogen atmosphere with a flow rate 20 ml min^{-1}. The thermograms were obtained using a cycle of heating from ambient temperature to 300 °C and subsequently cooling to room temperature.

2.6. Water permeation

A previously described technique [22] was used to measure the diffusion coefficient of water in different CA membranes. A cell (Fig. 1) with two compartments, A completely filled with distilled water, and B with poly(ethylene glycol), has a membrane 19.50 mm in diameter separating them. A capillary positioned in the upper side of the cell measures the variation of water volume during diffusion studies. Poly(ethylene glycol) (molecular weight 400, Fluka, *purum*) in compartment B, continuously stirred, maintains the concentration of water in the bottom of the membrane equal to zero.
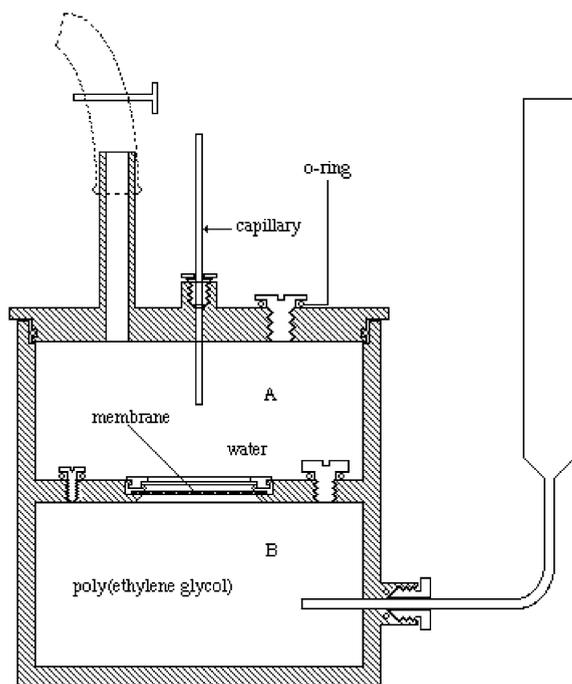
Fig. 1. Schematic representation of the cell developed to measure the integral diffusion coefficients of water in membranes.

Fig. 2. IR spectra of CA films ($l = 10\,\mu m$) prepared using different solvents: acetone (a) and THF (b). Figs. 1 and 2 represent the films dried and in equilibrium with water, respectively.

To achieve the equilibrium quickly, all the membranes were immersed in water 24 h before initiating each experiment.

The water diffusion coefficients, D_w, were calculated from the following adaptation of Fick's first law equation:

$$\rho_0 \mathrm{d}h/\mathrm{d}t = C_w D_w (s_m/a_c) l^{-1}, \tag{2}$$

where ρ_0 is the water density, $\mathrm{d}h/\mathrm{d}t$ is the variation of the height of column of water in the capillary tube with time, C_w is the water concentration in the membrane surface in contact with water phase, s_m is the area of membrane surface, and a_c is the capillary area.

3. Results and discussion

3.1. Effect of solvent on the cellulose acetate structure

Fig. 2 shows IR spectra of CA membranes in THF and acetone before and after equilibrium with water. The characteristic CA bands at 1740, 1360, 1230, and 1040 cm^{-1} are clearly observed. No alterations are found in the IR spectra with CA concentration. In the presence of water, the CA/THF IR-spectrum shows broader and stronger bands (b2) than in its absence (b1). However, such alterations are only due to the presence of water; no structural alteration (as may be ex-
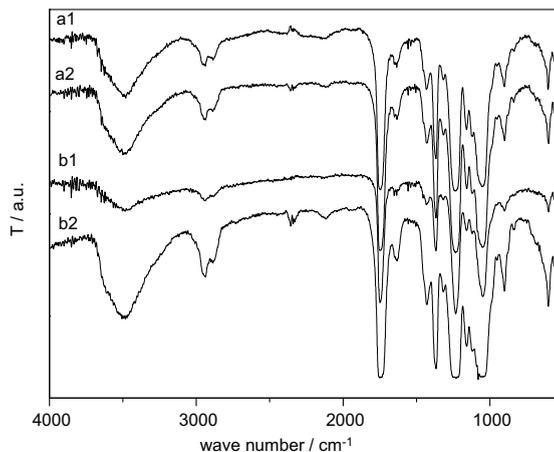
pected, for example, for hydrolysis) is found. The effect of water absorption on the IR spectra of CA/THF film is much more marked than in CA/acetone film.

The effect of the solvent used to prepare the films on the structure of CA membranes can also be found in the analysis of calorimetric thermograms (Fig. 3). The CA (acetone) membrane shows an expected melting point at 229 °C. However, this melting point is not observed when THF is used to prepare the membrane. This suggests that CA membranes prepared with acetone have a structure with a higher degree of crystallinity; the more amorphous structure of CA/THF film found by DSC is in agreement with increased water sorption by IR. In
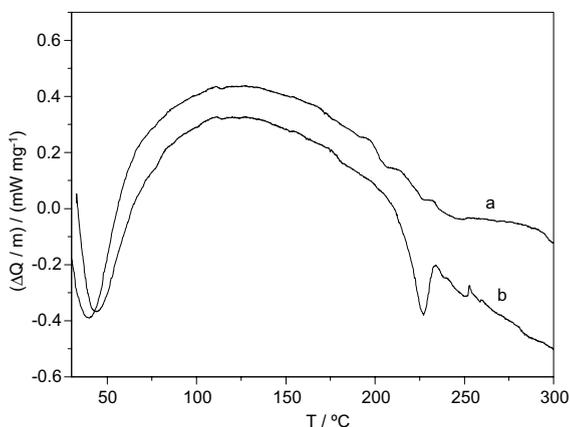

Fig. 3. Differential scanning calorimetry scans of cellulose acetate films with different solvents: (a) THF and (b) acetone. Endothermic transitions are down.

fact, sorption of water by the amorphous structure is likely to change the physical properties (for example, relaxation and swelling) of the CA structure.

3.2. Effect of solvent on the crystallinity and morphology of cellulose acetate membranes

The degree of crystallinity of CA membranes was evaluated qualitatively using X-ray diffraction by determination of the area of the scattering peaks presented in Fig. 4. Broad peaks are observed with both CA/THF and CA/acetone suggesting very low degrees of crystallinity. However, the peak with the CA/acetone membrane is slightly more structured and about pattern is three times higher than that observed in CA/THF. This result agrees with the DSC analysis and, confirms that while the acetone cast CA membranes have a very low degree of crystallinity, this is still higher than the essentially amorphous CA/THF membranes are.

The morphology of CA membranes surface, which is also an important feature to the water sorption and mobility, was analyzed by SEM. Fig. 5 shows the effects of casting from different solvents on the surface structure/morphology.

In CA/THF film the degree of porosity is very high and homogeneous throughout the analyzed surface. The pore sizes are quite heterogeneous, with the larger ones reaching 1.6 μm of diameter. In contrast, the surface of CA/acetone film shows fewer, and generally smaller pores, with a maximum size around 1.0 μm.

3.3. Effect of solvent and CA concentration on the percentage of water uptake

As pointed out in the Introduction, it is impossible to draw conclusions about water solubility using just ki-
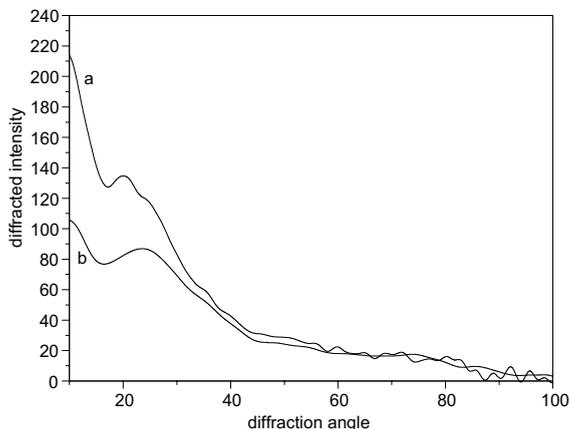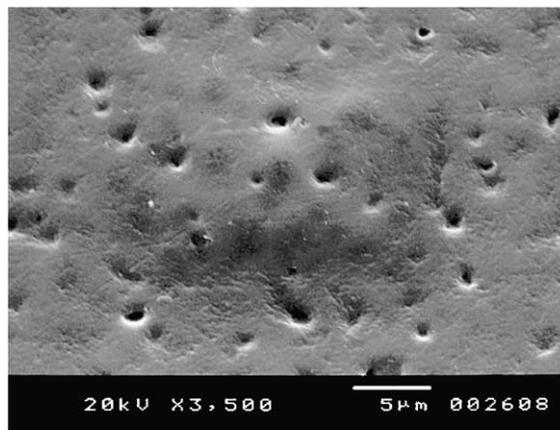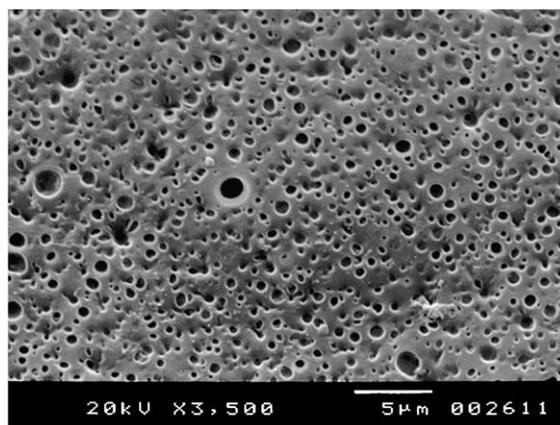

(a)

(b)

Fig. 5. SEM micrographs of cellulose acetate films prepared with different solvents: (a) acetone, and (b) THF.

netic data. Furthermore, both factors can be influenced by a number of parameters. Some of these which are relevant to our work, are solvent (acetone or THF), thickness, and cellulose acetate concentration used for film formation. The effect of all these parameters will be studied and discussed. Experimentally, there are two ways of changing the thickness of a membrane, prepared as described in Experimental Section: (a) increasing the height of the mould used to prepare the membrane and (b) increasing the CA concentration.

In the following discussion we consider all the processes together.

The study of the response of polymer density and water uptake to the alteration of polymer structure by solvent was carried out. Analyzing the density of the different membranes, we found that the CA polymer density is higher when acetone is used as solvent, in agreement with the other results on the higher degree of crystallinity. For CA 15% (w/v), the density of CA (acetone) is equal to $1.16 (\pm 0.2)$ g cm^{-3} (for a membrane

Fig. 4. X-ray diffraction of cellulose acetate films prepared using acetone (a) and THF (b).

thickness of 20 μm), whilst for the CA(THF) membrane, with the same thickness, the density decreases to 0.73 (±0.05) g cm^{-3}. Decreasing the CA concentration and/or increasing the membrane thickness, the density also decreases in CA/THF systems. For example, the density decreases from 0.73 to 0.52 g cm^{-3} ($l = 70$ μm) when the CA concentration decreases from 15% to 10% (w/v CA/THF). However, in the case of CA/acetone systems the density is almost independent of the CA concentration and increases with the membrane thickness (e.g., d(CA 5%, acetone) = 0.82 (±0.08) g cm^{-3} and $l = 0.015$ mm to d(CA 15%, acetone) = 1.22 (±0.11) g cm^{-3} and $l = 0.025$ mm).

Figs. 6 and 7 show the effect of solvent, cellulose acetate concentration and membrane thickness on the percentage of water uptake.

The experimental results of C_w as a function of membrane thickness were analyzed using a least-squares method. The fitting equations which best correspond to the observed weight/weight water concentration as a function of membrane thickness for CA prepared with THF and acetone are $C_w = 0.18$ (±0.04) + 26.31 (±19.02) × exp[−l/0.0042 (± 0.0008)] with 0.015 mm < l < 0.049 mm and $C_w = 0.16$ (±0.02) + 0.69 (±0.27) × exp[−l/0.011(±0.004)] to 0.012 mm < l < 0.065 mm, respectively.

From Figs. 6 and 7 we may conclude that (i) the percentage of water uptake as a function of membrane thickness does not depend on the cellulose acetate content; (ii) the percentage of water uptake is of same order of magnitude for different solvents and for similar thicknesses; and (iii) C_w is higher when the thickness decreases. We must point out in addition that the water sorption is not accompanied by membrane swelling.
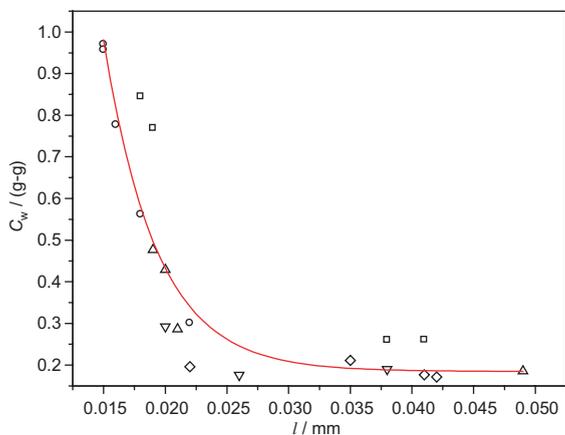

Fig. 7. Effect of thickness, l, and cellulose acetate content on the percentage of water uptake (C_w), of cellulose acetate/acetone membranes, at 25 °C: (●) CA 5% (wt/v); (▲) CA 10% (wt/v); (♦) CA 15% (wt/v).

Such behaviour can be explained by the predominant role of the polymeric surface on the sorption process. In the more porous surface structure (CA/THF), the percentage of water sorption is slightly higher than in the case of CA/acetone, in particular for membranes less than 0.025 mm. However, at membrane thicknesses above 0.025 mm very small differences existing in CA prepared from the different solvents. Therefore, as thickness increases, the bulk structure plays a more important role, and other properties must be taken into account. One of them is the structural organization (polymer density) of the polymers as discussed earlier.
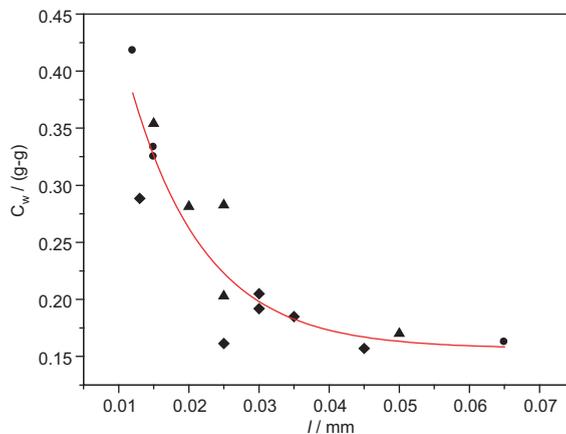

Fig. 6. Effect of thickness, l, and cellulose acetate content on the percentage of water uptake (C_w), of cellulose acetate/THF membranes, at 25 °C: (□) CA 1% (wt/v); (○) CA 5% (wt/v); (△) CA 10% (wt/v); (◇) CA 15% (wt/v); (▽) CA 20% (wt/v).
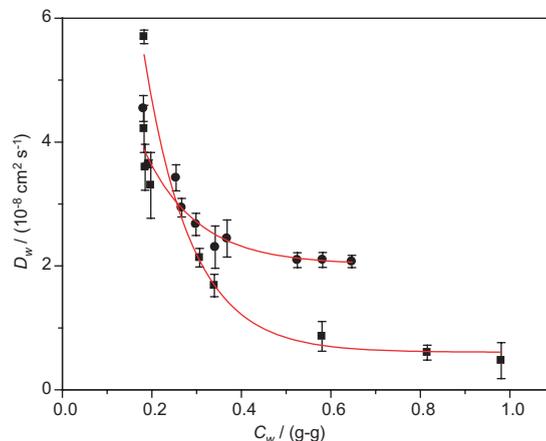

Fig. 8. Effect of weight–weight water concentration, C_w, on the diffusion coefficient of water, D_w, in cellulose acetate membranes: (■) in THF and (●) in acetone.

Table 1
Summary of the effect of solvent, thickness and water solubility on the cellulose acetate properties, as seen by different experimental techniques

Technique	Acetone	THF	Conclusion
FTIR	Little effect of water on the spectrum	Marked effect of water on the spectrum	More hydrophilic character of CA (THF)
DSC	Partial crystallinity	Amorphous	In favour of more hydrophilic character of CA (THF)
X-ray	Partial crystallinity	Amorphous	In favour of more hydrophilic character of CA (THF)
SEM	Single pores	Developed porosity	In favour of more hydrophilic character of CA (THF)
C_w dependence on thickness	Decrease approaching constant value	Decrease approaching constant value	Predominated surface contribution or thin membranes are not structured
D_w dependence on C_w	Exponential decrease		Typical for cellulose acetate (cluster formation, etc.)
		Sharper decrease	More hydrophilic character of CA (THF)

3.4. Water diffusion coefficients

Fig. 8 shows the effect of the casting solvent (THF and acetone) and water sorption uptake on the water diffusion coefficients of cellulose acetate membranes. The water diffusion coefficients were calculated using, at least, 3 different experiments. The water concentration, C_w, was calculated using the fitting equations of C_w as a function of l, described in the previous section, by measuring the membrane thickness of the polymeric samples used in the water permeation experiments.

From the analysis of the experimental results shown in Fig. 8, there is an exponential decrease of the water diffusion coefficient with an increase of water concentration. The equations that best fit these data are $D_w \times 10^8 = 0.58(\pm 0.11) + 26.9(\pm 3.8) \times \exp(-C_w/0.106 (\pm 0.009))$, $R^2 = 0.96$, and $D_w \times 10^8 = 2.02(\pm 0.09) + 8.7(\pm 2.7) \times \exp(-C_w/0.12(\pm 0.02))$, $R^2 = 0.96$, for CA/THF and CA/acetone, respectively. We can also observe that comparing the nominal water diffusion coefficients for both membranes, D_w is higher for CA/acetone membranes, at $C_w < 0.24$ (g–g). However, at C_w below 0.25 (g–g) a sharp decrease of D_w with C_w, is observed for CA/THF. These results cannot be explained by the surface properties, indicating that some other parameter must be involved. The diffusion of any solute in polymeric membranes depends both on the membrane surface and on the spongy structure of the polymeric matrix. It is known [12], that cellulose acetate membranes with a larger as-cast thickness give more permeable spongy structures, which lead to higher values of diffusion coefficients. Such an explanation is in agreement with the general ideas expressed in the previous section. Generally, amorphous polymers with an anisotropic distribution have a much more compact structure and, consequently, a lower water diffusion coefficient. This is what is observed in the CA/THF membranes.

We may conclude that the water solubility is the major parameter influencing the water diffusion kinetics.

In CA/acetone system, the decrease of D_w with C_w is smooth, suggesting that two major effects are influencing the water transport in CA/acetone membranes: the equilibrium water concentration and the polymer thickness. In this case, not only the bulk structure but also the surface resistance is important.

4. Concluding remarks

An approach has been developed to modulate and understand transport properties of cellulose acetate membranes using different solvents and initial concentrations. Table 1 summarizes the influence of structure and other different properties on the water kinetics as seen by different techniques.

The effect of solvent is shown to produce cellulose acetate membranes of different bulk and surface structures. Membranes obtained from cellulose acetate in THF are more amorphous than those obtained from cellulose acetate solution in acetone. This can be a consequence of anisotropic distribution of the polymeric skeleton. Difference in structure defines difference in water sorption and mobility in favour of more hydrophilic character of matrices obtained from THF solution. Membrane thickness is shown to be a simple and efficient probe to control polymer structure and transport properties.

Acknowledgments

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