

Thermodynamic studies of inclusion complex formation between alkylpyridinium chlorides and β -cyclodextrin using conductometric method

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Abstract Thermodynamics on inclusion complexation of β -cyclodextrin (β -CD) with n -alkylpyridinium chlorides (C_n PC, $n = 12, 14, 16$) were measured by conductivity technique to evaluate the effects of chain length of C_n PC and temperature. The data obtained indicate that inclusion complexes S(CD) and S(CD)₂ had formed between surfactant and β -CD in aqueous solution. Investigation showed that the K_1 (first equilibrium constant) for S(CD) formation is greater than K_2 (second equilibrium constant) for S(CD)₂ formation. It has been found that C_{12} PC forms only the 1:1 complex, while C_{14} PC and C_{16} PC form 1:1 and 1:2 complexes. Thermodynamic parameters of the complexation, i.e. ΔG° , ΔH° and ΔS° have been also calculated. The large values of ΔG° indicate that complexation between surfactant and β -CD is very favorable.

Keywords Inclusion complex ·
Alkylpyridinium chlorides · Cyclodextrin ·
Conductometry · Thermodynamic parameters

Introduction

Cycloamyloses (cyclodextrins, CDs) are doughnut-shaped molecules, formed from D(+)-glucose units linked in a

cycle. Because the interior of the doughnut predominantly contains CH groups, it provides a relatively hydrophobic environment into which nonpolar molecules can be trapped. CDs can give beneficial modifications of guest molecules not otherwise achievable. Because they are practically nontoxic, they are added into pharmaceuticals and foods. The hydrophobic effect has been implicated as one of the key factors contributing to the relatively strong, noncovalent complexes that are formed between β -CD and apolar guest molecules. β -CD shows amphiphilic character due to an apolar cavity and a hydrophilic annulus consisting of a number of hydroxyl groups. Surfactants and cyclodextrins are known to form inclusion compounds in which the hydrophobic chain of the surfactant resides in the hydrophobic environment of the interior of the cyclodextrin [1–5]. Indeed, the ability of cyclodextrins to modify the physicochemical properties of such aqueous solutions has been used to study their complexation behavior with surfactants, and a variety of experimental techniques have been used for this purpose. These techniques include UV–Vis and fluorescence spectroscopy [6, 7], conductivity [8–11], potentiometry [12–16], surface tension [17], NMR [3, 18], volumetric [19, 20]. In order to gain a better understanding about the binding events, theoretical methods were used to study the CD complexes [21, 22].

In the present paper, the inclusion complex formation interaction between β -cyclodextrin and a homologous series of n -alkylpyridinium chlorides (C_n PyC, $n = 12, 14, 16$) are analyzed by electrical conductivity measurement. The effect of the chain length of the n -alkylpyridinium chlorides upon the interaction with β -cyclodextrin solution is studied. Conductometric measurements were undertaken to determine the stoichiometry and association constants of cyclodextrin-surfactant inclusion complexes in the pre-CMC concentrations (CMC = Critical Micelle Concentration) at

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different conditions. Also, thermodynamic quantities have been evaluated using mass action model and temperature dependence of complexation constants.

Experimental

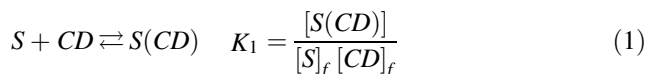
β -Cyclodextrin (β -CD) was obtained from Fluka and used as supplied. The water content of the cyclodextrin, determined by thermogravimetric analysis, was approximately 13.0%. The hydration water of the β -CD was taken into account in the preparation of the solutions, that were prepared by weight. Dodecylpyridinium chloride ($C_{12}PC$) and tetradecylpyridinium chloride ($C_{14}PC$) and hexadecylpyridinium chloride ($C_{16}PC$) were obtained from Aldrich and they were used without further purification.

Conductance measurements were carried out with a WTW conductometer (Model Inolab Cond. Level 1, Germany) and a dip-type conductivity cell with platinum black electrode (cell constant = 0.109 cm^{-1}) was used. The conductivity cell was calibrated with 0.01 M solution of analytical-grade KCl (Merck) in thrice distilled deionized water. In all measurements, the cell was thermostated at the desired temperature $\pm 0.1\text{ }^\circ\text{C}$ using a Grant thermostat-circulator water bath (model W28, England) water-bath circulator. In a typical experiment, a surfactant solution was placed in the conductivity cell; then, a known amount of the concentrated β -CD solution were added in a stepwise manner using a calibrated micropipette. The conductance of the solution was measured after each addition.

Results and discussion

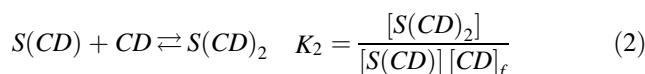
In the evaluation of the complexation constants as discussed above the following assumptions are made: (i) β -CD does not associate in water; (ii) there is no interaction between β -CD and counter ion (Cl^-) to any extent; (iii) each complex only contains one surfactant ion [16].

In the first instance it is necessary to check whether the surfactant (S) and corresponding cyclodextrin (CD) form a 1:1 complex with the following equilibrium constant:



where $[S]_f$, $[CD]_f$ and $[S(CD)]$ are free surfactant monomer concentration, free CD concentration and 1:1 stoichiometric complex concentration, respectively.

If the second equilibrium proceeds, we should consider a 2:1 stoichiometry for complex formation. In this case, an amount of the complex $S(CD)_2$ is formed according to:



where $[S(CD)_2]$ is the concentration of 2:1 complex. According to the law of conservation of mass, it could be stated:

$$[S]_t = [S]_f + [S(CD)] + [S(CD)_2] \quad (3)$$

$$[CD]_t = [CD]_f + [S(CD)] + 2[S(CD)_2] \quad (4)$$

where $[S]_t$ and $[CD]_t$ are total surfactant and cyclodextrin concentrations, respectively. In this case, the observed specific conductance could be expressed as:

$$\kappa_{\text{obs}} = \kappa_S + \kappa_{S(CD)} + \kappa_{S(CD)_2} \quad (5)$$

where κ_S , $\kappa_{S(CD)}$ and $\kappa_{S(CD)_2}$ are surfactant and the complexes (1:1 and 2:1) specific conductances, respectively.

Taking into account the definition of molar conductivity, by combining Eqs. 1–5, Eq. 5 can be re-written as:

$$\Lambda_{\text{obs}} = \frac{(\Lambda_S + \Lambda_{S(CD)} K_1 [CD]_f + \Lambda_{S(CD)_2} K_1 K_2 [CD]_f^2)}{(1 + K_1 [CD]_f + K_1 K_2 [CD]_f^2)} \quad (6)$$

where Λ_{obs} is the observed molar conductivity. Using the Eqs. 1–4:

$$K_1 K_2 [CD]_f^3 + (K_1 - K_1 K_2 [CD]_t + 2K_1 K_2 [S]_t) [CD]_f^2 + (1 + K_1 [S]_t - K_1 [CD]_t) [CD]_f - [CD]_t = 0. \quad (7)$$

The free cyclodextrin concentrations, $[CD]_f$, were calculated by means of a Newton–Raphson procedure. Once the value of $[CD]_f$ had been obtained, the concentrations of all other species involved were calculated by using the estimated values of the formation constants at the current iteration step of the program. For evaluation of the formation constants from the molar conductivity versus $[CD]_f/[S]_t$ mole ratio data, a non-linear least-square curve fitting program KINFIT [23] was used. The program is based on the iterative adjustment of calculated conductance to the observed values. Adjustable parameters are stepwise formation constants of all complexes present (K_1 , K_2) and the corresponding molar conductances ($\Lambda_{S(CD)}$, $\Lambda_{S(CD)_2}$).

The procedure used for the evaluation of K_1 and K_2 values from the experimental data is as follows. The free cyclodextrin concentrations, $[CD]_f$, were calculated by means of a Newton–Raphson procedure. When the value of $[CD]_f$ had been obtained, the concentrations of other species involved are calculated from the corresponding mass balance equations by using the estimated values of the formation constants at the current iteration step of the program. Refinement of the parameters was continued until the sum-of-squares of the residuals between calculated and

observed values of the the conductance for all experimental points was minimized. The output of program KINFIT comprises the refined parameters, the sum-of-squares and the standard deviation of the data [9]. All the calculated formation constants are summarized in Table 1.

Figures 1, 2, and 3 show Λ_{obs} as a function of β -CD concentration for $C_{12}\text{PC}$, $C_{14}\text{PC}$ and $C_{16}\text{PC}$ solutions at a constant concentration of each surfactant ($1.0 \times 10^{-4} \text{ mol dm}^{-3}$) and different temperatures. A sample computer fit of the molar ratio data is shown in Fig. 4. These plots show how Λ_{obs} is affected by an increasing in the β -CD concentration. The molar conductance decreased sharply as β -CD was added presumably because the surfactants ions having been complexed by β -CD were less effective as a charge carrier. As shown in Figs. 1, 2, and 3, in all cases, there is a gradual decrease in the molar conductance with an increase in the β -CD concentration. This behavior indicates the lower mobility of the complexed surfactants compared to the solvated ones. At a certain concentration in β -CD, this linear decrease of molar conductance with β -CD concentration shows a change in gradient of slope. The stoichiometry at which this halt occurred were 1:1 for β -CD: $C_{12}\text{PC}$, 1:1.2 for β -CD: $C_{14}\text{PC}$ and 1:1.3 for β -CD: $C_{16}\text{PC}$. This indicates that the inclusion complex of β -CD with $C_{12}\text{PC}$ is only 1:1, while in the cases of $C_{14}\text{PC}$ and $C_{16}\text{PC}$ the chief inclusion complex is 1:1 with possibly a little 2:1 complex also present.

The obtained results for $C_{14}\text{PC}$ and $C_{16}\text{PC}$ showed that $K_1 \gg K_2$ which indicates that the formation of 1:1 stoichiometric complex predominate rather than 2:1 ones. The cyclodextrin structure is such that the inside of the cavity is covered with CH_2 groups thus providing a hydrophobic

Table 1 The formation constants for the inclusion complexes between $C_n\text{PyC}$ and β -CD at various temperatures

| Surfactant | t (°C) | K_1 ($\text{mol}^{-1} \text{ dm}^3$) | K_2 ($\text{mol}^{-1} \text{ dm}^3$) | Sum square |
|-------------------|----------|--|--|------------|
| $C_{12}\text{PC}$ | 25 | 17,220 | – | 0.88 |
| | 30 | 13,731 | – | 0.19 |
| | 35 | 12,238 | – | 0.27 |
| | 40 | 7,302 | – | 1.56 |
| $C_{14}\text{PC}$ | 20 | 78,320 | 29 | 0.15 |
| | 25 | 67,518 | 94 | 0.10 |
| | 30 | 60,588 | 61 | 0.04 |
| | 35 | 55,127 | 66 | 0.15 |
| $C_{16}\text{PC}$ | 40 | 50,664 | 83 | 0.63 |
| | 20 | 104,948 | 919 | 0.89 |
| | 25 | 93,749 | 356 | 0.30 |
| | 30 | 82,737 | 1,523 | 0.12 |
| | 35 | 76,664 | 920 | 0.14 |
| | 40 | 57,511 | 99 | 0.15 |

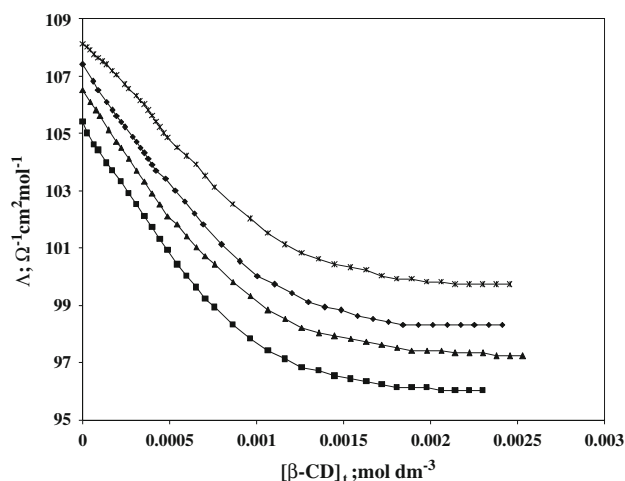


Fig. 1 Molar conductivity of $1 \times 10^{-4} \text{ mol dm}^{-3}$ $C_{12}\text{PC}$ with added β -CD at (■) 25 °C, (▲) 30 °C, (◆) 35 °C and (*) 40 °C

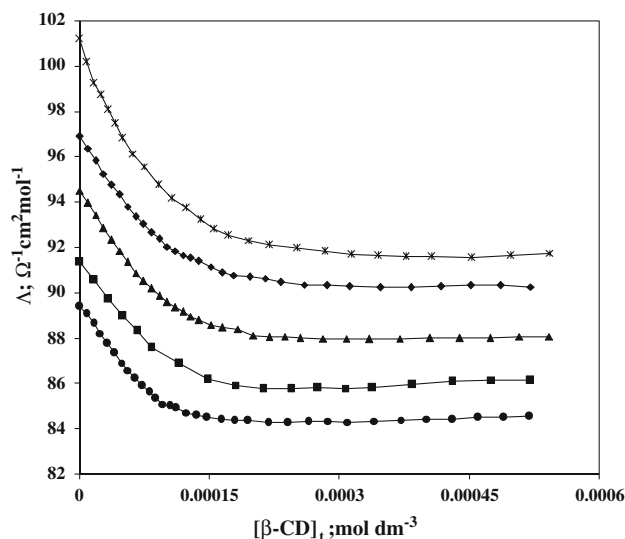


Fig. 2 Molar conductivity of $1 \times 10^{-4} \text{ mol dm}^{-3}$ $C_{14}\text{PC}$ with added β -CD at (●) 20 °C, (■) 25 °C, (▲) 30 °C, (◆) 35 °C and (*) 40 °C

environment that is favorable to interact with the hydrocarbon chain of surfactant. X-ray crystallography shows that the depth and inner diameter of β -CD are 7.8 and 7.8 Å, respectively. The length, l , and diameter, d , of structural alkyl group with formula C_nH_{2n+1} are calculated from the following equations [4, 9]:

$$l(\text{Å}) \approx 1.5 + 1.265(n - 1) \tag{8}$$

$$d(\text{Å}) \approx \left[\frac{34.89 + 34.25(n - 1)}{1.5 + 1.265(n - 1)} \right]^{1/2} \tag{9}$$

For $C_{12}\text{PC}$, $C_{14}\text{PC}$ and $C_{16}\text{PC}$ that have 12, 14 and 16 carbon atoms in their alkyl chain, using Eq. 8, give the length of the chain as 15.42, 17.95 and 20.5 Å,

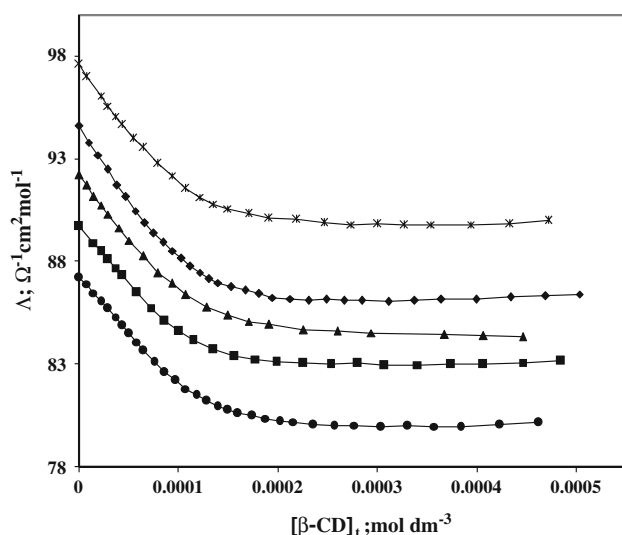


Fig. 3 Molar conductivity of 1×10^{-4} mol dm $^{-3}$ C $_{16}$ PC with added β -CD at (●) 20 °C, (■) 25 °C, (▲) 30 °C, (◆) 35 °C and (*) 40 °C

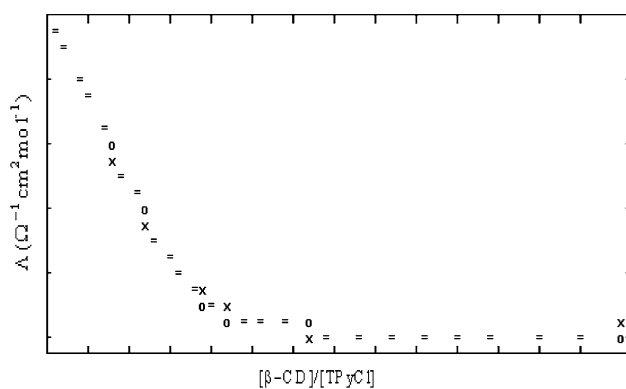


Fig. 4 Computer fit of the molar conductance-mol ratio for the β -CD and C $_{14}$ PC system at 20 °C: (x) experimental point, (o) calculated point, (=) experimental and calculated points are the same within the resolution of the plot

respectively. Also, using Eq. 9, give the diameter as approx. ≈ 5.17 Å for all surfactants. Comparison of these values with the structural characteristics of β -CD show that there is a good match fitting between β -CD cavity and surfactant alkyl chain. On the other hand, there is the possibility for simultaneous entry of two β -CD molecules in the length of the C $_{14}$ PC and C $_{16}$ PC chain, but this is not occurred for C $_{12}$ PC.

The obtained values of K_1 and K_2 from fitting of data have been used for the calculation of the thermodynamic parameters such as ΔG° , ΔH° and ΔS° . The Gibbs free energy of each step complex formation could be calculated from the following equation:

$$\Delta G^\circ = -RT \ln K. \quad (10)$$

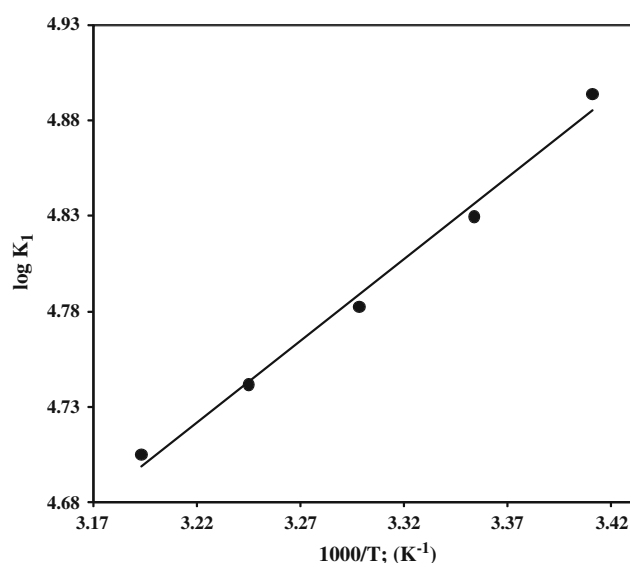


Fig. 5 A typical plot of $\log K_1$ vs. $1/T$ for C $_{14}$ PC/ β -CD inclusion complex formation

The enthalpy of complexation was obtained from the temperature dependence of the complexation constant (K) using the van't Hoff relation (see Fig. 5) and finally the ΔS° values could be obtained from the following equation:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (11)$$

The obtained results are listed in Table 2. The negative values of ΔH° could be attributed to attraction between hydrocarbon chain of the surfactant and hydrophobic interior of β -CD. The results also indicate that $-\Delta G^\circ$ at various temperatures increases steadily with increasing alkyl chain length of the surfactants. The results demonstrate that the longer chain surfactants lead to a greater association constant with β -CD, which concerned with hydrophobicity of cyclodextrin cavity.

Molecular-level interpretations of linear enthalpy-entropy compensation have been built on the inference that such behavior constitutes evidence for a dominant mechanism throughout the correlated series. Recently, the last two factors are considered to be the minor driving forces for inclusion complexation [1]. C $_n$ PC and β -CD do not have the site for the hydrogen bonds and the ionic groups, respectively. Thus, the hydrogen bonds and the electrostatic interaction do not participate in the driving force of inclusion complexation between C $_n$ PC and β -CD. The arguments mainly center on hydrophobic and van der Waals interactions.

As can be seen from Table 2, the inclusion complexes for the first step of C $_{14}$ PyCl and C $_{16}$ PyCl with β -CD are exclusively exothermic and mostly enthalpy driven with varying positive entropic contributions. From studies of the

Table 2 The calculated values of thermodynamic parameters for complexation between C_n PC and β -CD at various temperatures

| Surfactant | t (°C) | K_1 (mol ⁻¹ dm ³) | ΔG_1° (kJ/mol) | ΔH_1° (kJ/mol) | ΔS_1° (J mol ⁻¹ K ⁻¹) | K_2 (mol ⁻¹ dm ³) | ΔG_2° (kJ/mol) |
|--------------------|----------|--|-----------------------------|-----------------------------|---|--|-----------------------------|
| C ₁₂ PC | 25 | 17,220 | -24.18 | -41.59 | -58.41 | - | - |
| | 30 | 13,731 | -24.02 | | -57.98 | - | - |
| | 35 | 12,238 | -24.12 | | -56.72 | - | - |
| | 40 | 7,302 | -23.16 | | -58.86 | - | - |
| C ₁₄ PC | 20 | 78,320 | -27.46 | -16.43 | 37.66 | 29 | -8.21 |
| | 25 | 67,518 | -27.56 | | 37.36 | 94 | -11.26 |
| | 30 | 60,588 | -27.75 | | 37.37 | 61 | -10.36 |
| | 35 | 55,127 | -27.97 | | 37.46 | 66 | -10.74 |
| | 40 | 50,664 | -28.21 | | 37.62 | 83 | -11.51 |
| C ₁₆ PC | 20 | 104,948 | -28.18 | -16.04 | 41.39 | 919 | -16.63 |
| | 25 | 93,749 | -28.38 | | 41.37 | 356 | -14.56 |
| | 30 | 82,737 | -28.54 | | 41.22 | 1,523 | -18.47 |
| | 35 | 76,664 | -28.82 | | 41.44 | 920 | -17.48 |
| | 40 | 57,511 | -28.54 | | 39.88 | 99 | -11.96 |

thermodynamics of the β -CD/surfactant interaction, we conclude that there is a significant contribution from the classical hydrophobic effect but this contribution is reduced by predominant binding forces characterized by negative enthalpy and entropy changes. Using the simple qualitative argument that a surfactant strongly bound within the β -CD cavity has lost some freedom of motion, one expects it to have lower entropy than if it were weakly bound within the cavity. The values of the entropy change ΔS° are positive and decrease with increasing alkyl chain length of the surfactants. This indicates that the degrees of freedom of the surfactant included in the β -CD cavity become lower with increasing alkyl chain length of the surfactants [24–26].

However, ΔH° and ΔS° were both negative in C₁₂PC/ β -CD system. The signs of ΔH° and ΔS° for inclusion complexation of β -CD are inconsistent with those for the hydrophobic interaction process. The negative values of both ΔH° and ΔS° are attributed to other factors [27].

The rationalization of ΔH° and ΔS° values, while of interest for understanding the molecular details and driving forces involved in complex formation, is necessarily somewhat speculative, and it must be realized that other factors such as the displacement of high-energy water from within the β -CD cavity, or structural changes of the β -CD molecule may contribute to ΔH° and ΔS° for the surfactant binding [28, 29].

The value of ΔS° is affected by several phenomena. Hydrophobic effects that can be mainly attributed to the hydrophobic interaction between the alkyl chain and the inner wall of the CD molecule, and partly to the release of water molecules from the alkyl chain of the surfactant and the cavity of the CD during the penetration process, is one of the most important factors.

Conclusion

Based on conductometry measurements, the interaction between n -alkylpyridinium chlorides (C_{*n*}PC, $n = 12, 14, 16$) and β -CD were studied. The association constants and also stoichiometry of inclusion complexes were determined using non-linear least-square curve fitting program KINFIT. The program is based on the iterative adjustment of calculated conductance to the observed values. Comparison of the length and volume surfactants with the structural parameters for β -Cyclodextrin show that there is the possibility for simultaneous entry two β -Cyclodextrin molecules in the length of the C₁₄PC and C₁₆PC chains, but it is not occurred for C₁₂PC.

The larger value of K_1 with respect to K_2 predicts the preferability of 1:1 complex. The calculated thermodynamic parameters show that the Hydrophobic effects that can be mainly attributed to the hydrophobic interaction between the alkyl chain and the inner wall of the CD molecule, and partly to the release of water molecules from the alkyl chain of the surfactant and the cavity of the CD during the penetration process, is one of the most important factors.

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