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The effect of oxygen carriers on gas transport through polysiloxane and ethylcellulose membranes

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Three cobalt Schiff-base complexes were synthesized and added into poly(dimethylsiloxane) (PDMS) and ethyl cellulose (EC) membranes as oxygen carrier. The influences of oxygen carrier concentration and temperature on the gas permeability and selectivity of the membranes were studied and the effects of oxygen carrier concentration on the oxygen facilitated transport, on the polymer chain flexibility as well as on the free volume in the membranes were discussed. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: cobalt Schiff-base complex; oxygen carrier; facilitated-transport oxygen-enriched membrane)

INTRODUCTION

Because the addition of oxygen carrier in an oxygen-enriched membrane is a possible method for the simultaneous enhancement of oxygen permeability (P_{O_2}) and selectivity (α, $\alpha = P_{O_2}/P_{N_2}$), much effort has been expended on research into facilitated-transport of oxygen in a polymer membrane containing oxygen carrier since the 1980s[1–4]. Tsuchida and his coworkers have reported the simultaneous increase of P_{O_2} and α using oxygen carrier in polyacrylate membranes specially in the case of low gas pressure in the upstream side[5–7]. Delaney and Reddy synthesized styrene copolymers with grafted Co(II) Schiff-base complexes and found that a high selectivity can be maintained even at high oxygen pressures[8]. The mechanism and theoretical modes for facilitated-transport of molecular oxygen in a solid membrane containing oxygen carrier were also discussed in the literature[2,3,9].

Because of the excellent permeation property of poly(dimethylsiloxane) (PDMS) and the good mechanical properties as well as fine oxygen selectivity of ethyl cellulose (EC), much work has been done on the study of oxygen enriched membranes using these two polymers as the matrix, but little attention was paid to the research on the oxygen facilitated-transport in these membranes containing oxygen carriers.

In this paper, the permeabilities of PDMS and EC oxygen-enriched membranes containing different Schiff-base cobalt complexes as oxygen carrier were measured and the dependencies of the permeability and selectivity on the temperature and oxygen carrier concentration were studied.

EXPERIMENTAL

Materials

The synthesis of (*N,N*′-disalicylideneethylenediamine) cobalt(II) (CoS) and cobalt di-(3-methoxysalicylal tertbutylamine)(CoST) are reported in the literature[10–13].

Poly[(methyl acrylate)-*co*-(4-vinylpyridine)] (PMAVp) was prepared by the radical copolymerization of 40 g methyl acrylate with 8.7 g 4-vinylpyridine in 120 ml methanol at 60°C for 8 h using 2,2′-azobisisobutyronitrile (AIBN) as initiator. The monomer molar ratio of methyl acrylate to 4-vinylpyridine was 0.85/0.15. The molar ratio of methyl acrylate unit to 4-vinylpyridine unit in the synthesized PMAVp was about 0.65/0.35, calculated from the elementary analysis results of the copolymer. The molecular weight of the copolymer was 95 000 measured using a gel permeation chromatograpy (g.p.c.) instrument. (MAXIMA 820 GPC). The result of differential scanning calorimetry (d.s.c.) measurement of the obtained PMAVp showed that the copolymer had only one wide glass transition and the glass transition temperature of 32°C was between the glass transition temperatures of poly [methyl acrylate](6°C) and poly[4-vinylpyridine] (142°C); this means that the synthesized copolymer is possibly a random copolymer. No further study was carried out on whether it was a head-to-head or a head-to-tail copolymer.

The dark red polymer complex PCoS solution was prepared by adding the red complex CoS to the light yellow PM AVp chloroform solution while strong stirring. The molar ratio of the pyridine group to CoS in PCoS was 1/1 (*Figure 1*).

Membranes

The chloroform solution of PDMS or EC with oxygen carrier was carefully cast on a glass plate. After the solvent was volatilized at room temperature, the membrane was

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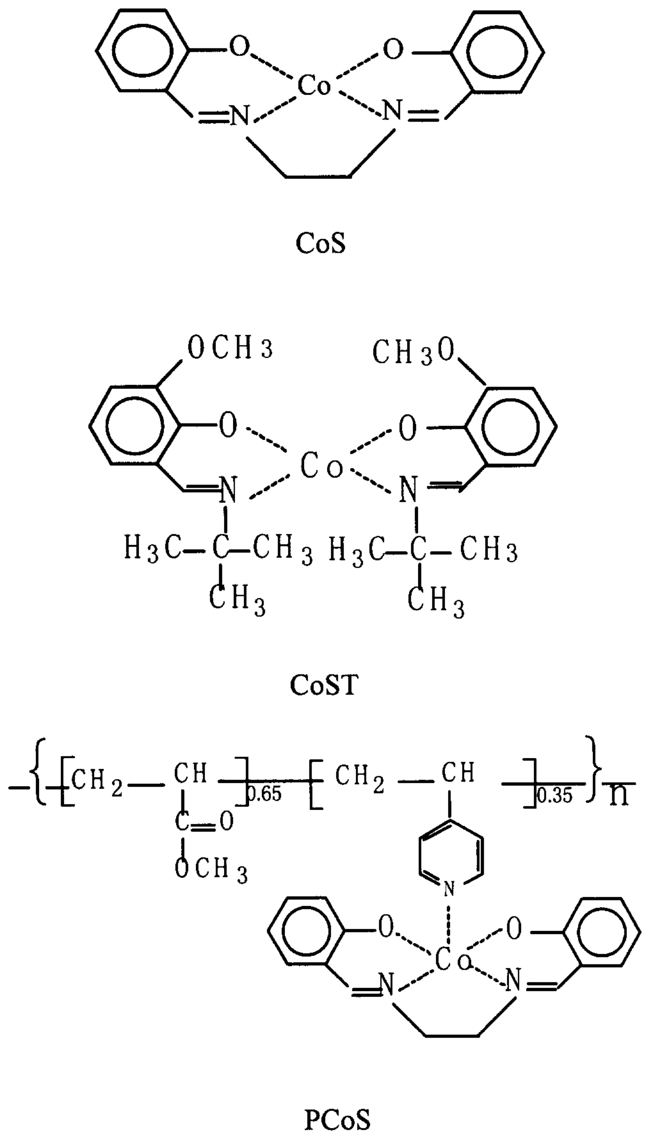

Figure 1 The structure of oxygen carriers

then dried in vacuum (10 mmHg) at room temperature for 24 h to yield a transparent membrane. The thicknesses of PDMS and EC membranes were about 170 μm and 60 μm respectively.

For all PDMS membranes, the polymer concentration was 25% in casting solution, and the solvent volatilization time was 12 h. For EC–CoS and EC–CoST membrane systems (including pure EC membrane), the polymer concentration was 2.5% in casting solution, and the solvent volatilization time was 12 h. As to the EC–PCoS membrane system (including pure EC membrane), the polymer concentration was 1.5% in casting solution, the solvent volatilization time was 24 h since PCoS is a viscous polymer complex solution.

Permeation measurement

Gas permeability was measured using a permeation apparatus with a stable thermostat in the chamber (K-3 I SN, Rika Seiki Inc.). The permeability was calculated from the slope of the steady-state straight line of the permeation curve.

RESULTS AND DISCUSSION

Effect of oxygen carrier concentration

The addition of oxygen carrier into a solid polymeric membrane can influence the gas permeation property of the membrane in three aspects:

(1) The essential function of oxygen carrier is to facilitate the transport of oxygen in the membrane. This comes from the reversible reaction of oxygen carrier with molecular oxygen, as shown in equation (1).

$$BCo + O_2 \rightleftharpoons BCoO_2 \qquad (1)$$

where BCo is the cobalt Schiff-base oxygen carrier. This facilitated transport of oxygen could increase the oxygen permeability.

(2) The oxygen carrier may act as a plasticizer in the polymer membrane leading to increase of oxygen and nitrogen permeabilities.

(3) Part of the oxygen carrier may form complexes with the oxygen atoms in the polymer chain of the membrane matrix after the addition of oxygen carrier, leading to lower flexibility of the chain, or the oxygen carrier may occupy some gas permeation channels in the polymer matrix so decreasing the free volume of the membrane. Both the effects can reduce the oxygen and nitrogen permeabilities.

The oxygen permeation can be divided into two terms: $P_{O_2,M}$, which depends only on the properties of the matrix such as polymer chain flexibility, free volume and so on, is the permeation through the membrane matrix; the other term, $P_{O_2,C}$, which depends on the oxygen carrier concentration, upstream pressure, reaction equilibrium constant and reverse reaction constant of equation (1), is the permeation through the reversible reaction of the oxygen carrier with the molecular oxygen[14]. On the other hand, the nitrogen permeation of a membrane containing oxygen carrier depends only on the properties of the membrane matrix such as chain flexibility and free volume in the membrane. Because the chain flexibility and the free volume of membrane matrix could be changed by the addition of the oxygen carrier, it could not be assumed that the nitrogen permeability P_{N_2} and the term of oxygen permeability through the membrane matrix $P_{O_2,M}$, would be equal to the P_{N_2} and P_{O_2} of the reference membrane containing no oxygen carrier, therefore it is difficult to exactly measure the values of $P_{O_2,M}$, and $P_{O_2,C}$, experimentally.

Figures 2 and 3 show the relationship between the gas permeability and the concentration of oxygen carrier. The oxygen and nitrogen permeabilities. are sensitive to the membrane preparation conditions such as the viscosity and polymer concentration of casting solution, the solvent volatilization time and temperature, membrane drying time and temperature, the vacuum and so on. To avoid the possible deviation, the membranes containing different oxygen carrier concentration (including zero concentration) were made in one batch for a given polymer and a given oxygen carrier. It can be seen from the PDMS–CoS curves and PDMS–CoST curves in *Figure 2* that the difference between the measured values of oxygen permeability as well as the difference between the measured values of nitrogen permeability at zero oxygen carrier concentration is small, although the two membranes were prepared under the same conditions but in different batches. These differences are also small in the EC–CoS curves

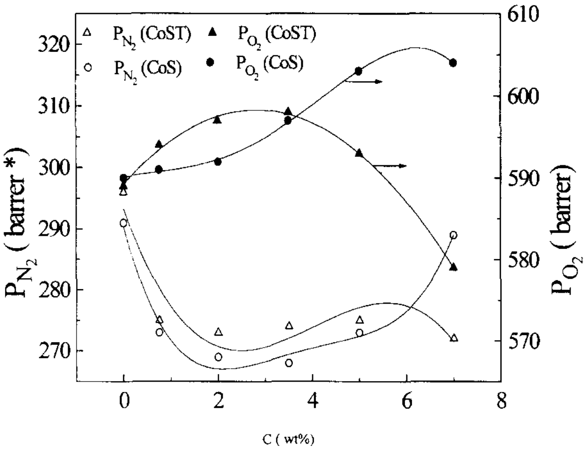

Figure 2 Permeability as a function of oxygen carrier concentration in PDMS membranes (temperature 20°C; upstream gas pressure 1.01 × 10^5 Pa; 1 barrer = 10^{-10} cm^3 (STP)

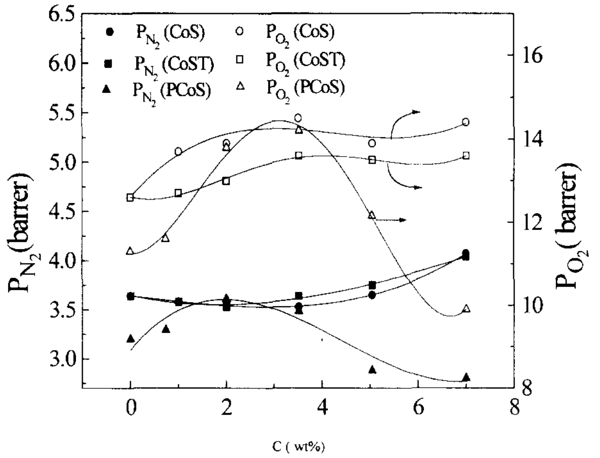

Figure 3 Permeability as a function of oxygen carrier concentration in EC membranes (temperature 30°C; upstream gas pressure 1.01 × 10^5 Pa; the concentration of PCoS was calculated on the basis of the PMAVp/CoS complex, the CoS weight content in PMAVp/CoS complex is 55.1%)

and EC–CoST curves shown in *Figure 3*. The PCoS is a polymer complex and the addition of PCoS in the casting solution should increase the solution viscosity. Therefore the membrane preparation condition for EC-PCoS membrane system is different from that for EC-CoS and EC-CoST membrane systems (see Section 2). The relatively low oxygen and nitrogen permeabilities at zero oxygen carrier concentration in EC–PCoS curves, compared with those in the EC–CoS and EC–CoST curves (*Figure 3*), are possibly caused by the different membrane preparation conditions of the EC–PCoS membrane system from those of the EC–CoS and EC–CoST membrane systems.

As discussed above, the variation of P_{N_2} with the oxygen carrier concentration reflects the changes of the polymer chain flexibility and the free volume in the membrane with the addition of oxygen carrier. For the PDMS membrane (*Figure 2*) and the EC membrane (*Figure 3*) with CoS and CoST as oxygen carrier, P_{N_2} decreases with the concentration of oxygen carrier in the low concentration range (<3.5%), which means that the term of oxygen permeability through the membrane matrix $P_{O_2,M}$ decreases also with the concentration of oxygen carrier in the low concentration range. But the total P_{O_2} increases with the concentration of oxygen carrier in the same concentration range (< 3.5%), which implies a significant value of the term of oxygen permeability through the reversible reaction of oxygen carrier with molecular oxygen $P_{O_2,C}$ in the low oxygen carrier concentration range. This high value of $P_{O_2,C}$ can be also seen from the high slope of P_{O_2} for PCoS as oxygen carrier in an EC membrane in the low concentration range (*Figure 3*). In the high oxygen carrier concentration range the facilitated-transport of oxygen caused by the reversible reaction of oxygen carrier with molecular oxygen is not so significant (*Figures 2 and 3*). This behaviour of oxygen carrier, that in the high oxygen carrier concentration range the oxygen permeability decreases with increasing oxygen carrier concentration, was also reported in the literature and may be explained by the dimer formation of oxygen carrier in the high oxygen carrier concentration range[15,16].

The relationship between gas selectivity and concentration of oxygen carrier is shown in *Figures 4 and 5*. The selectivity increases at first, to reach a maximum value, and then decreases with increasing oxygen carrier concentration. For the PDMS membrane, the maximum α was reached in the oxygen carrier concentration range from 2.0% to 5.0% for CoS as oxygen carrier, and from 1.5% to 3.0% for CoST as oxygen carrier (*Figure 4*); For EC membrane the maximum α was reached in the concentration range from 3.0% to 4.0% for PCoS and CoST as oxygen carrier, and from 2.5% to 3.5% for CoS as oxygen carrier (*Figure 5*).

From the relationships between oxygen permeability, selectivity and the concentration of oxygen carrier, it can be seen that P_{O_2} and α can increase simultaneously with the addition of oxygen carrier into the membrane. There is a concentration range of oxygen carrier in which optimum membrane properties (high P_{O_2} and α) can be obtained. This concentration range is about from 2.5% to 4.0% for EC membranes containing CoS, PCoS, CoST as oxygen carriers. For PDMS membrane this range is about from 4.0% to 5.5% for CoS as oxygen carrier, and from 1.5% to 3.5% for CoST as oxygen carrier.

It is necessary to point out that in this paper the selectivity values were calculated on the basis of the ratio of oxygen permeability to nitrogen permeability for pure gases, which may be different from the true selectivity for mixed gases, since each gas may affect the permeation of the other. This difference is even more likely in facilitated transport membranes, for the complex formed by the oxygen with the carrier may affect the permeation of nitrogen.

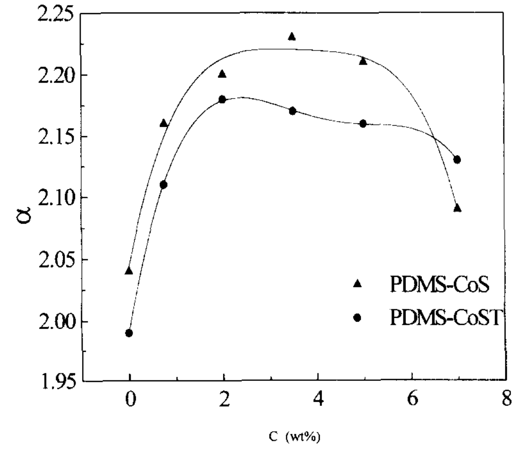

Figure 4 Relationship of selectivity with oxygen carrier

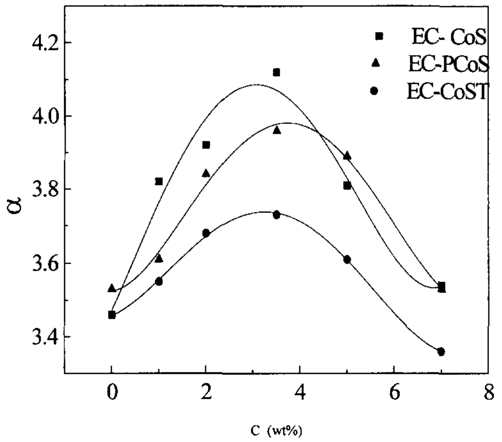

Figure 5 Relationship of selectivity with oxygen carrier

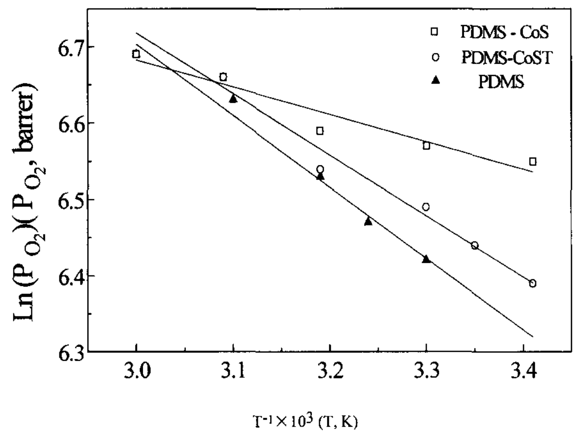

Figure 6 Plots of Ln(P_{O_2}) *versus* 1/*T* for PDMS membranes

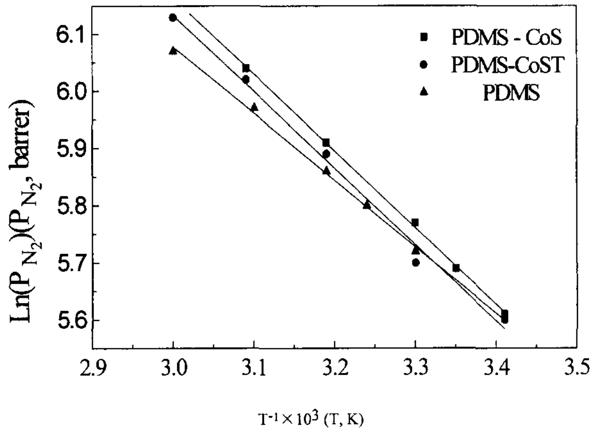

Figure 7 Plots of Ln(P_{N_2}) *versus* 1/*T* for PDMS membranes

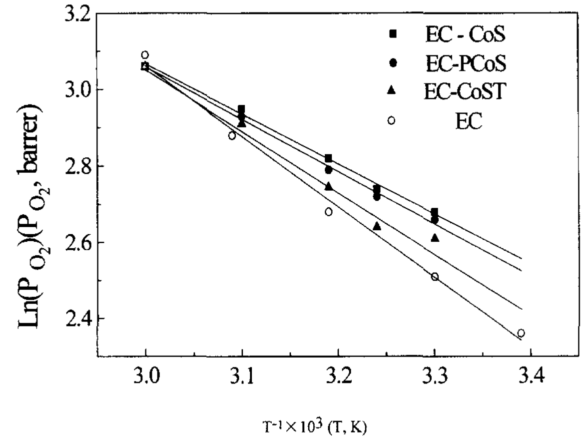

Figure 8 Plots of Ln(P_{O_2}) *versus* 1/*T* for EC membranes

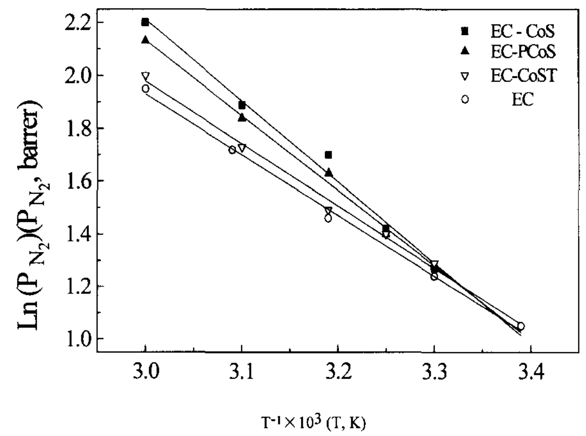

Figure 9 Plots of Ln(P_{N_2}) *versus* 1/*T* for EC membranes

Effect of temperature

According to gas permeation theory, the permeability can be defined as:

$$P = DS \tag{2}$$

where D is the diffusion coefficient and S is the solubility coefficient[17]. D and S can be expressed by the Arrhenius equation as:

$$D = D_O \exp(-E_d/RT) \tag{3}$$

$$S = S_O \exp(-H_S/RT) \tag{4}$$

where E_d is the apparent activation energy for diffusion and H_S is the heat of solution, D_O and S_O are constants for a given gas and polymer.

From equations (3) and (4), equation (5) can be obtained as:

$$DS = D_O\, S_O \exp[-E_d + H_S)/RT] \tag{5}$$

or

$$P = P_O \exp(-E/RT) \tag{6}$$

as $P_O = D_O S_O$ and $E = E_d + H_S$. Here E is the apparent activation energy for permeation. From equation (6) it is known that there is a linear relation between Ln(P) and 1/T′ and the apparent activation energy for permeation (E) can be calculated from the slope of the line.

The dependencies of Ln(P) on 1/T in the temperature range from 20°C to 60°C are shown in *Figures 6–9* (the oxygen carrier concentration was kept constant as 3.5% for all facilitated-transport membranes). The negative slopes for all lines in *Figures 6–9* mean that P_{O_2} and P_{N_2} increase with increasing temperature for all membranes. In all cases the lines of Ln(P_{O_2}) and Ln(P_{N_2}) of facilitated-transport membranes containing oxygen carrier are above the corresponding lines of the reference membrane containing no oxygen carrier. The Ln(P_{O_2}) difference between membranes containing oxygen carrier and reference membranes containing 110 oxygen carrier increases with increasing 1/T for all oxygen carriers in the two Polymer matrixes (*Figures 6, and 8*), but in contrast this difference of Ln(P_{N_2}) for all oxygen carriers decreases with

Table 1 The measured apparent activation energy

Membranes	E_{O_2}(KJ/mol)	E_{N_2}(KJ/mol)	E_α(KJ/mol)
PDMS	7.86	9.23	−1.32
PDMS-CoST	6.64	10.8	−4.16
PDMS-CoS	6.51	11.2	−4.69
EC	15.5	19.4	−3.90
EC-CoST	13.4	19.6	−6.20
EC-PCoS	12.0	21.6	−9.60
EC-CoS	10.3	24.4	−14.1

The E_{O_2} decreases and E_{N_2} increases after the addition of oxygen carrier into the membrane for both polymer matrixes. The negative $E\alpha$ means that a higher α can be obtained at lower temperature.

increasing $1/T$ (*Figures 7, and 9*), which implies that more effective oxygen facilitated-transport and higher selectivity can be obtained at lower temperature in the systems studied.

The measured apparent activation energies of oxygen permeability, nitrogen permeability and selectivity are listed in Table 1.

The E_{O_2} decreases and E_{N_2} increases after the addition of oxygen carrier into the membrane for both polymer matrixes. The negative E_α means that a higher α can be obtained at lower temperatures.

CONCLUSION

The oxygen permeability and the selectivity can increase simultaneously with the addition of oxygen carrier into the membrane for the systems studied in this paper. The oxygen carrier in the membrane not only facilitates the oxygen transport but also affects the polymer chain flexibility and free volume of the membrane. There is a concentration range of oxygen carrier, in which the membrane with the oxygen carrier has optimum permeation properties (high P_{O_2} and α simultaneously). The apparent activation energy of oxygen permeability decreases and the apparent energy of nitrogen permeability increases after the addition of oxygen carrier into the membrane. A more effective oxygen facilitated transport and higher selectivity can be obtained at lower temperatures.

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