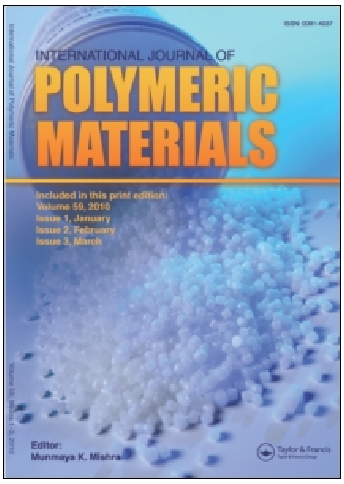

International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

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To cite this Article Andrade, L. , Amaral, L. Q. and Akcelrud, L.(1997) 'The Solubility Parameter of Chlorosulfonated Polyethylene', International Journal of Polymeric Materials, 35: 1, 1 — 12

To link to this Article: DOI: 10.1080/00914039708039748

URL: http://dx.doi.org/10.1080/00914039708039748

Intern. J. Polymeric Mater., 1997, Vol. 35, pp. 1-12
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The Solubility Parameter of Chlorosulfonated Polyethylene

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(Received 8 March 1996; In final form 14 March 1996)

The solubility parameter (δ) of chlorosulfonated polyethylene-Hypalon™ 45 was determined by means of theoretical calculations, equilibrium swelling and turbidimetric techniques. The average repeating unit of the polymer was determined from chlorine and sulphur determinations and from NMR and thermal degradation data. Calculated δ from the individual contributions of atoms and groups yielded $\delta = 9.46$ $(\mathrm{cal/cm^3})^{1/2}$. Equilibrium swelling measurements gave $\delta = 7.2 \pm 1.9$ $(\mathrm{cal/cm^3})^{1/2}$ and turbidimetric measurements $\delta = 7.4 \pm 1.9$ $(\mathrm{cal/cm^3})^{1/2}$. The latter technique also made it possible the determination of the spatial components of δ: dispersive $\delta_d = 7.2 \pm 1.7$ $(\mathrm{cal/cm^3})^{1/2}$, dipolar $\delta_p = 0.9 \pm 0.3$ $(\mathrm{cal/cm^3})^{1/2}$ and hydrogen bonded $\delta_h = 1.4 \pm 0.3$ $(\mathrm{cal/cm^3})^{1/2}$.

Keywords: Chlorosulfonated polyethylene; Hypalon™ 45; Swelling equilibrium; Turbidimetric titration; Solubility parameter

INTRODUCTION

Chlorosulfonated polyethylene was introduced as a synthetic rubber in 1952. After crosslinking the product is characterized particularly by good resistance to ozone attack and color retention during light exposure. These good weathering properties along with heat and flame resistance make it a valuable material to shearing many types of wire and cables [1]. There are five grades of chlorosulfonated polyethylene currently available under the trade names of Hypalon™ 20, 30, 40, 45 and 48, by Du Pont. These are obtained from high density polyethylene by reacting with gaseous chlorine and sulphur dioxide in a chlorinated solvent at 70–75°C in the presence of ultraviolet radiation. The chlorine and sulfonyl chloride groups in the chain are responsive to a variety of curing systems which can be classified into two categories: in the first the chains are linked together by means of classical sulphur based vulcanization or reacting with appropriate curing agents [2]. In the second the crosslinking is accomplished through the exposure of the polymer to an electron beam, which dose is within the 5 to 50 Mrad range. The simplicity of latter has made it useful industrially since the last 20 years.

The motivation of our work was to evaluate the relationships between dose intensity and crosslinking density in the irradiation of Hypalon™ 45. We also aimed to find out if some other reactions could be occurring simultaneously, particularly degradation, and the effects of irradiation in the polymer morphology as well.

In order to provide information about crosslinking density, to be determined through equilibrium swelling measurements, the knowledge of the solubility parameter (δ) of the polymer was needed. In this paper we report on the solubility parameter determinations for Hypalon™ 45 carried out through theoretical calculations, equilibrium swelling measurements and turbidimetric titration. The latter made it possible the determination of the spatial components of δ: dispersive (δ_d), dipolar (δ_p) and hydrogen bonded (δ_h). The employment of these data on the characterization of irradiated Hypalon™ 45 will be the subject of a subsequent communication.

The different grades of chlorosulfonated polyethylene differ basically in chlorine content. For Hypalon™ 20 (29% Cl) and Hypalon™ 30 (43% Cl) the reported values of the solubility parameters varied according to the hydrogen bonding strength of the solvents employed, and were [3]: 8.1–9.8 $(\mathrm{cal/cm^3})^{1/2}$ and 8.4–8.8 $(\mathrm{cal/cm^3})^{1/2}$ for poor and moderately hydrogen bonded solvents (Hypalon™ 20); and 8.5–10.6 $(\mathrm{cal/cm^3})^{1/2}$ and 7.8–8.5 $(\mathrm{cal/cm^3})^{1/2}$ for poor and moderately hydrogen bonded solvents (Hypalon™ 30). No access to the methodology involved was given, and no data concerning the other Hypalon types could be found in the literature so far.

EXPERIMENTAL

Materials

Xylene, toluene, benzene, chloroform, chlorobenzene and tetrachloroethane (solvents), methanol and hexane (non solvents) were all P.A. materials from Aldrich.

Procedures

Samples of chlorosulfonated polyethylene were immersed in a series of solvents of varying δ. After 7 days at 27°C the samples were weighed. The swelling coefficient at equilibrium (Q) was determined by $Q=(m-m_0)/m_0\rho_1$ where m_0 and m stand for the mass of dry and swollen polymer respectively and ρ_1 is the solvent density.

Turbidimetric titrations were carried out at 27 °C on polymer solutions with concentrations of 0.2 g/dl. A non-solvent (methanol or hexane) was slowly added to the solution until the cloud point was reached (standard turbidity). The standard turbidity was the threshold of precipitation at which a printed page could not be read looking through the solution.

RESULTS AND DISCUSSION

The solubility parameter describes the relation between the energy of mixing and the mutual solubility of substances. In the absence of specific polymer-solvent interactions, it can be related to the polymer-solvent interaction parameter and also to the cohesive energy density which gives information about the value of intramolecular forces of a polymer in the amorphous state. The concept of solubility parameter was developed by Hildebrand and Scott [4] for solutions with regular thermodynamical behavior and consequently for the mixing of non polar substances, but later it was also applied to polar systems [5–8].

The solubility parameter δ is defined as:

$$\delta=\frac{\Delta E}{V} \tag{1}$$

where ΔE and V stand for the molar cohesive energy and molar volume respectively. For volatile substances ΔE can be measured by the energy of vaporization or other methods [9–11] but these are not applicable to high molecular weight compounds making it necessary the employment of indirect methods [12].

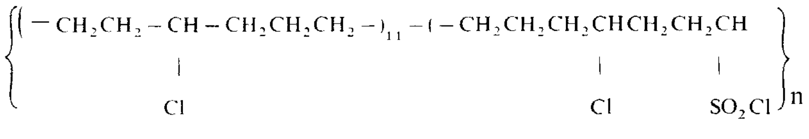
THEORETICAL CALCULATIONS OF δ

The theoretical methods for the evaluation of δ are based on the assumption that the intermolecular attractive energies (cohesive energies) are additive and compose the overall cohesive energy of the molecule as a whole. Therefore the magnitude of the intermolecular attraction of a given polymer can be calculated from the sum of the individual contribution of atoms or groups. The most used method was developed by Small [13] where the quantity from Equation 1 is obtained from the sum of the "group attractive constants" (Σf_1). According to Small

$$\delta = \rho_2 \Sigma f_1 / M \qquad (2)$$

where ρ_2 and M stand for the polymer density and molecular weight respectively. Small's method was applied to polymers by several authors and the results were compiled by Gardon [14]. Hoy and Fedors [5–7] extended the Small method to polar substances.

The theoretical prediction of δ needs the description of the repeating unit of the polymer and this is not always obvious. According to reference 2 commercial chlorosulfonated polyethylene contains a chlorine atom linked to each seventh carbon atom and a chlorosulfonyl group attached to each eighty fifth carbon atom in the chain. In the present case the repeating unit of this polymer was derived from chlorine and sulphur determinations performed by Du Pont and from published results based on NMR and thermal degradation studies, yielding the following structure [15].



$$\left\{ \left(-CH_2CH_2-\underset{Cl}{\underset{|}{CH}}-CH_2CH_2CH_2- \right)_{11} -(-CH_2CH_2CH_2\underset{Cl}{\underset{|}{CH}}CH_2CH_2\underset{SO_2Cl}{\underset{|}{CH}} \right\}_n$$

δ was calculated from Equation 2, using the density value of 1.11 g/cm^3 given by the manufacturer. The molar volume was 1544.4 cm^3/mol and the sum Σf_1 was 575940 J/mol, calculated from Table I data, giving a δ value of 19.31 (J/cm^3)$^{1/2}$ or 9.46 (cal/cm^3)$^{1/2}$.

In this method equilibrium experiments are carried out in a series of solvents which δ_1 values span over a certain range. The δ_2 value for the polymer will be the same as that of the solvent in which the maximum swelling was observed. According to Gee [16] the relationship between the degree of swelling of a polymer (Q) in a low molecular weight liquid with a solubility parameter δ_1 is expressed by a curve having Q (see Experimental) as ordinate and δ_1 as abscissa:

$$Q = Q_{\max} \exp[-V_1(\delta_1 - \delta_2)^2] \tag{3}$$

The solubility parameter of the polymer (δ_2) is equal to the δ_1 value corresponding to $Q_{\max}$. Therefore

$$\delta_2 = \delta_1 \pm \left[\frac{1}{V_1}\ln\left(\frac{Q_{\max}}{Q}\right)\right]^{1/2} \tag{4}$$

According to Equation 4 the plot of $[1/V_1 \ln(Q_{\max}/Q)]^{1/2}$ versus δ_1 is a straight line which intercepts the abcissa at $\delta_1 = \delta_2$. This method has been employed for several polymer systems [17–20]. For the swelling tests we used a sample crosslinked by a electron beam of 5 Mrad and Figure 1 shows the plot of $y = \left[\frac{1}{V_1}\ln\left(\frac{Q_{\max}}{Q}\right)\right]^{1/2}$ versus δ_1. As it can be seen from Figure 1 the intersection of the adjusted curve ($y = a + b\delta_1$,

TABLE I Cohesive energy data for chlorosulfonted polyethylene@

Group	*Number of groups/repeating unit*	*Cohesive energy (J/mol)*
$-CH_2-$	72	355680
$\rangle CH-$	13	44590
$-Cl$	12	138600
SO_2Cl	1	37070

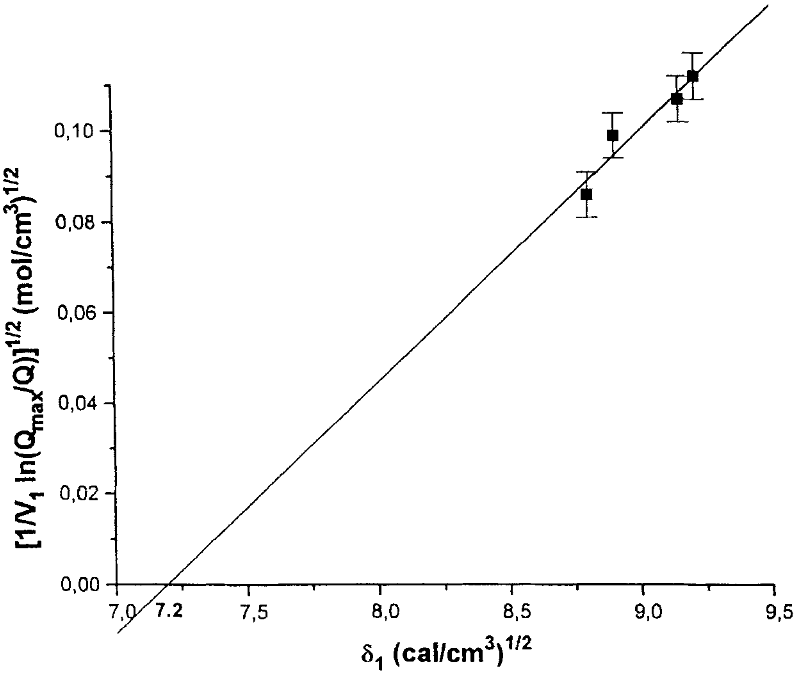


FIGURE 1 Swelling plot for Hypalon™ 45. Q = degree of swelling (see Experimental). V_1 and δ_1 are molar volume and solubility parameter of the solvent, respectively.

where $a = 0.4 \pm 0.1$ and $b = 0.06 \pm 0.01$) with the abcissa gives a value of 7.2 ± 1.9 $(\mathrm{cal/cm^3})^{1/2}$ for the solubility parameter of Hypalon™ 45.

TURBIDIMETRIC MEASUREMENTS – DETERMINATION OF THE SPATIAL COMPONENTS OF δ

The interpretation of data concerning to interaction phenomena based on the solubility parameter, in most cases related to miscibility, lead to the development of the three dimensional concept of δ. According to this theory the cohesive energy of a substance can be considered as the vectorial sum of the contributions of dispersive (δ_d), dipolar (δ_p) and hydrogen bond (δ_h) forces. The resultant solubility parameter is then.

$$\delta = (\delta_d^2 + \delta_p^2 + \delta_h^2)^{1/2} \tag{5}$$

The components are localized as vectors along the three orthogonal axis in space. The end point of the resulting vector represents the spatial δ_2 value for a polymer and the volume within a spheroid centred at δ_2 represents the solubility region of the polymer. After the initial developments of Hansen [8, 9] the subject has been explored by several authors [21–28] and has been successfully used for the determination of the spatial components of several polymers [29–37] and is based in two facts. The first is that the Flory Huggins interaction parameter χ is formed by an entropy term (χ_s) and an enthalpic term (heat of mixing χ_h) (Eq. 6). The second is that χ_h reaches a constant value at the cloud point. The relationship between χ_h, the solubility parameter of the solvent δ_1, and of the polymer δ_2, for an endothermic mixture, is given by Equation 7.

$$\chi = \chi_s + \chi_h \tag{6}$$

$$\chi_h = \frac{V_1(\delta_1 - \delta_2)^2}{RT} \tag{7}$$

The three components of δ are found by the dissolution of the polymer in a series of solvents which spatial components are known and by titrating each solution with two non-solvents, one of lower (δ_l) and one of higher (δ_h) solubility parameter. As for dilute solutions χ_h is a constant, equating the two expressions for each χ_h, Equation 8 is obtained, which can be applied for each spatial component:

$$\delta_2 = \frac{(V_{\mathrm{ml}}^{1/2} + V_{\mathrm{mh}}^{1/2}\delta_{\mathrm{mh}})}{V_{\mathrm{ml}}^{1/2} + V_{\mathrm{mh}}^{1/2}} \tag{8}$$

where δ_m is defined as the solubility parameter of the solvent/non-solvent mixtures at the cloud point and the subscripts mh and ml indicate mixtures of a solvent with a non-solvent of high and low solubility parameter, respectively. Values of δ_1 and δ_h are calculated using Scott's "single liquid" approximation:

$$\delta_m = \varphi_1\delta_1 + \varphi_3\delta_3 \tag{9}$$

$$V_m = V_1 V_3/(\varphi_1\delta_3 + \varphi_3\delta_1) \tag{10}$$

where the subscripts 1 and 3 refer to solvent and non-solvent; φ and V are volume fractions and molar volume respectively. Table II shows the experimental results from turbidimetric titrations of chlorosulfonated polyethylene Hypalon™ 45 in a series of solvents, using hexane and methanol as non solvents.

Values of δ_1 are plotted in Figures 2, 3 and 4 vs. δ_2 calculated from Equation 8 for each of the three components of the solubility parameter.

TABLE II Results of turbidimetric titrations for Hypalon™ 45 (a:

Solvents	φ_{31} *hexane*	φ_{3h} *methanol*	δ_{1d}	δ_{1p}	δ_{1h}	δ_1
Xylene	.387	.163	8.5	1.2	2.0	8.80
Toluene	.383	.151	8.67	1.0	2.0	8.90
Benzene	.185	.177	9.03	0.5	1.4	9.15
Tetrachloroethane	.392	.104	9.18	2.0	1.1	9.52
Chlorobenzene	.341	.187	9.20	1.9	2.0	9.57

a φ : volume fraction; δ_{1d}, δ_{1d}, δ_{1h} : dispersion, polar and hydrogen bond components of solubility parameter δ_1 of the solvent, values in (cal cm^3)$^{1\ 2}$ taken from references 8, 9 and 10.

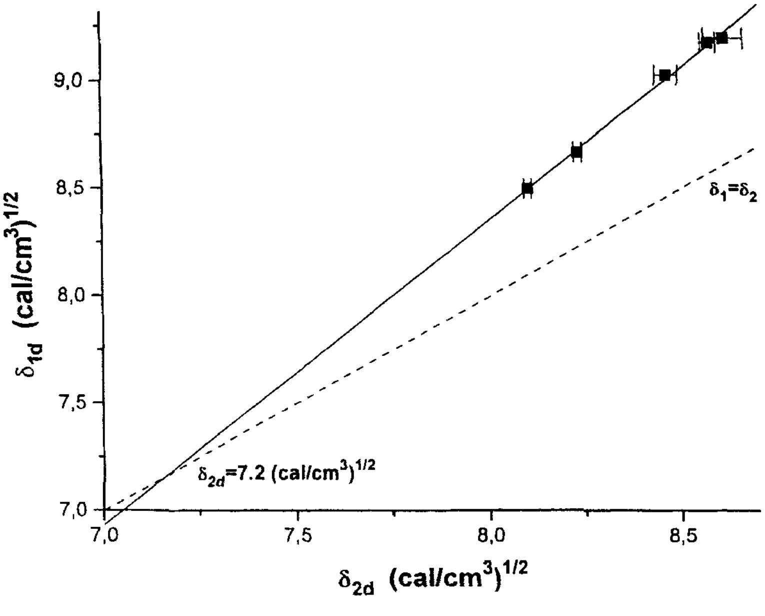


FIGURE 2 Determination of the dispersive component δ_d of the solubility parameter of Hypalon™ 45 from turbidimetric titrations.

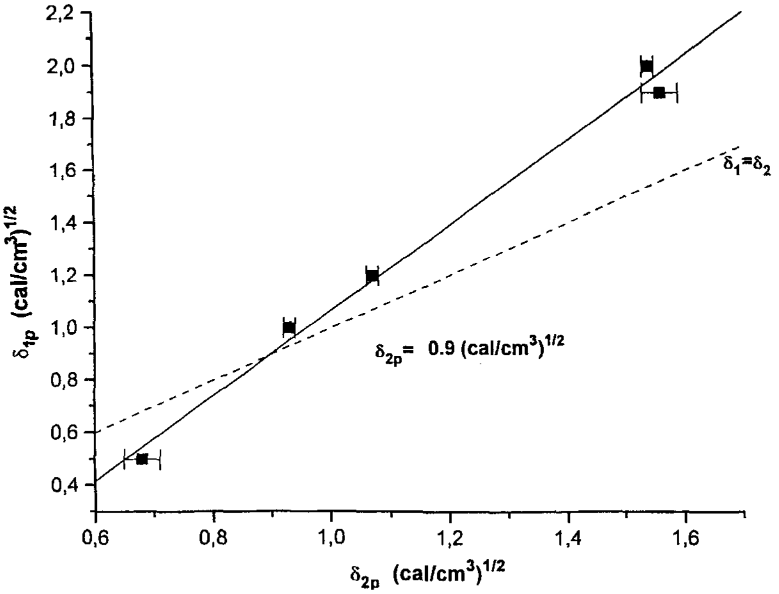


FIGURE 3 Determination of the polar component δ_p of the solubility parameter of Hypalon™ 45 from turbidimetric titrations.

The adjusted curves ($\delta_{1x} = a + b\delta_{2x}$ where x is d, p, and h) for each δ are: $\delta_d \Rightarrow a = -3.0 \pm 0.4$, $b = 1.4 \pm 0.1$; $\delta_p \Rightarrow a = -0.6 \pm 0.1$, $b = 1.6 \pm 0.1$; $\delta_h \Rightarrow a = -0.2 \pm 0.1$, $b = 1.1 \pm 0.1$. The solubility parameter was determined at zero non-solvent concentration where $\delta_1 = \delta_2$. Table III shows the spatial components of the solubility parameter. With the procedure described above the values obtained for each component of the solubility parameter of Hypalon™ 45 were:

$$\delta_d = 7.2 \pm 1.7 \quad (\text{cal/cm}^3)^{1/2}$$

$$\delta_p = 0.9 \pm 0.3 \quad (\text{cal/cm}^3)^{1/2}$$

$$\delta_h = 1.4 \pm 0.3 \quad (\text{cal/cm}^3)^{1/2}$$

These values, substituted in Equation 5 gave $\delta_2 = 7.4\,(\text{cal/cm}^3)^{1/2}$ which is in good agreement with the result obtained from swelling at equilibrium ($\delta_2 = 7.2 \pm 1.9\,(\text{cal/cm}^3)^{1/2}$). The calculated value however, was somewhat higher ($\delta_2 = 9.46\,(\text{cal/cm}^3)^{1/2}$).

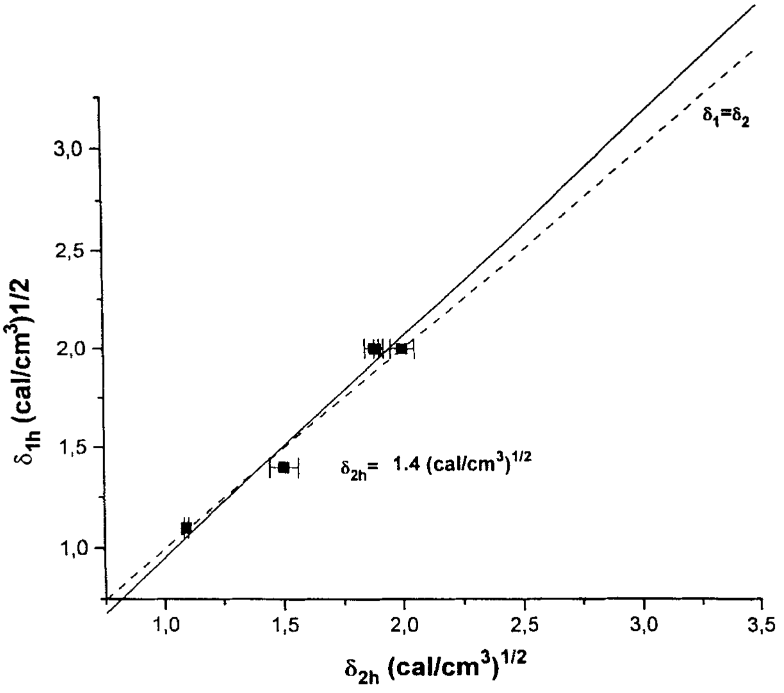


FIGURE 4 Determination of hydrogen bonding component δ_h of the solubility parameter of Hypalon™ 45 from turbidimetric titrations.

TABLE III Spatial components δ_d, δ_p and δ_h (cal cm^3)$^{1/2}$ of Hypalon 45 determined using hexane and methanol as non-solvents

Solvent	δ_{2d}	δ_{2p}	δ_{2h}
Xylene	*8.10 ± 0.01*	*1.07 ± 0.01*	*1.89 ± 0.01*
Toluene	*8.23 ± 0.01*	*0.93 ± 0.01*	*1.88 ± 0.04*
Benzene	*8.46 ± 0.03*	*0.68 ± 0.03*	*1.50 ± 0.06*
Tetrachloroethane	*8.57 ± 0.02*	*1.54 ± 0.01*	*1.09 ± 0.01*
Chlorobenzene	*8.61 ± 0.05*	*1.56 ± 0.03*	*2.00 ± 0.05*

CONCLUSIONS

To conclude we can say that among the three possibilities for the determination of the solubility parameter of chlorosulfonated polyethylene the theroetical calculation gave the nearest result to the general values reported. Despite its easiness this method requires the knowledge of the cohesive energies of the atoms or groups and the exact structure of the repeating unit, which is not always clear. The experimental methods gave δ with good agreement, and the turbidimetric measurements made it possible to determine the spatial components of the solubility parameter of the chlorosulfonated polyethylene.

Acknowledgement

The authors thank Ms. R.T. dos Santos for the experimental assistance and CNPq for the financial support.

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