

# Acoustic Behavior of Chromium Soap Solutions in Benzene–Dimethyl Formamide Mixture

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## SYNOPSIS

The critical micelle concentration and various acoustic parameters of chromium soaps (myristate, palmitate, and stearate) in a mixture of benzene and dimethyl formamide (4 : 1 v/v) have been determined by ultrasonic velocity measurements. The results showed that the ultrasonic velocity, specific acoustic impedance, molar sound velocity, and molar sound compressibility increase, while intermolecular free length, adiabatic compressibility, and available volume decrease with increasing concentration and chain length of the soap. The results show that there is a significant interaction between soap and solvent molecules in dilute solutions and the soap molecules do not aggregate appreciably in dilute solutions.

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## INTRODUCTION

The complementary use of ultrasonic measurements can provide interesting information on the specificities of ion–solvent interaction related to the structure of solute and on the reciprocal effects that arise in the solvents. However, the studies on ultrasonic measurements of the soap solutions have not drawn adequate attention, although such a study is likely to give more information on the soap–solvent and soap–soap interactions. Several workers<sup>1–10</sup> have used ultrasonic measurements for the determination of ion–solvent interactions and the solvation numbers obtained by this technique were found to be in agreement with those evaluated by other measurements. The methods of preparation and properties of chromium soaps have been reviewed by many workers.<sup>11–14</sup>

The present work dealt with the measurements of ultrasonic velocity of the solutions of chromium soaps (myristate, palmitate, and stearate) in a mixture of benzene and dimethyl formamide (4 : 1 v/v) because these soaps possess maximum solubility in the solvent mixture of this composition. The work was initiated with a view to evaluate var-

ious acoustic parameters, CMC, and soap–soap and soap–solvent interactions.

## EXPERIMENTAL

All the chemicals used were of AR grade. Chromium soaps (myristate, palmitate, and stearate) were prepared by direct metathesis of corresponding potassium soap with a slight excess of aqueous solution of chrome alum. The precipitated soaps were washed with distilled water, methanol, and acetone to remove the excess of metal ion, potassium soap, and unreacted fatty acid. The purity of soaps was checked by their melting points (myristate, 61°C; palmitate, 66°C; and stearate, 69°C), elemental analysis, and IR spectra.

The solutions of different soap concentrations were prepared in a mixture of benzene and dimethyl formamide (4 : 1 v/v) and were kept for 2 h in a thermostat. The densities of the solvent mixture and solutions of chromium soaps were measured with a dilatometer calibrated with pure benzene. A multifrequency ultrasonic interferometer M-83 (Mittal Enterprises, New Delhi) was used to measure the ultrasonic velocity in the solvent mixture and solutions at  $40 \pm 0.05^\circ\text{C}$  using a crystal of 1 MHz frequency. The relative mean error in the velocity measurements was 0.2%.

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## CALCULATIONS

The adiabatic compressibility,  $\beta$ ; specific acoustic impedance,  $Z$  (Ref. 15); intermolecular free length,  $L_f$  (Ref. 16); apparent molar compressibility,  $\phi_k$ ; apparent molar volume,  $\phi_v$  (Ref. 17); molar sound velocity,  $R$ ; available volume,  $V_a$  (Ref. 18); relative association,  $R_A$  (Ref. 19); molar sound compressibility,  $W$ ; and primary solvation number,  $S_n$  (Ref. 20) were calculated by using the relations

$$\beta = v^{-2} \rho^{-1} \quad (1)$$

$$Z = v \cdot \rho \quad (2)$$

$$L_f = (\beta/K)^{1/2} \quad (3)$$

$$\phi_k = \frac{1000}{C\rho_0} (\rho_0\beta - \beta_0\rho) + \frac{M\beta_0}{\rho_0} \quad (4)$$

$$\phi_v = \frac{1000}{C\rho_0} (\rho_0 - \rho) + \frac{M}{\rho_0} \quad (5)$$

$$R = \frac{\bar{M}}{\rho} v^{1/3} \quad (6)$$

$$\left[ \bar{M} = \frac{n_0 M_0 + nM}{n_0 + n} \right]$$

$$V_a = \bar{V} \left( 1 - \frac{v}{v_\alpha} \right) \quad (7)$$

$$R_A = \left( \frac{\rho}{\rho_0} \right) \left( \frac{v_0}{v} \right)^{1/3} \quad (8)$$

$$W = \frac{\bar{M}}{\rho} (\beta^{-1/7}) \quad (9)$$

$$S_n = \frac{n_0}{n} \left[ 1 - \frac{\bar{V}\beta}{n_0\bar{V}_0\beta_0} \right] \quad (10)$$

where  $v_0$ ,  $v$ ;  $\rho_0$ ,  $\rho$ ;  $\beta_0$ ,  $\beta$ ;  $\bar{V}_0$ ,  $\bar{V}$  are the ultrasonic velocity, density, adiabatic compressibility, and molar volume of solvent and solutions, respectively; and  $n_0$ ,  $n$  and  $M_0$ ,  $M$  are the number of moles and molecular weight of solvent and soap, respectively.  $K$  is a temperature-dependent Jacobson's constant and  $v_\alpha$  is a constant equal to  $1600 \text{ m s}^{-1}$ .

## RESULTS AND DISCUSSION

The ultrasonic velocity,  $v$ , of chromium soap solutions increases with increasing concentration and chain length of the soap (Table I). The variation of velocity,  $v$ , with concentration,  $C$ , depends on the

concentration derivative of density and adiabatic compressibility:

$$\frac{dv}{dC} = -\frac{v}{2} \left[ \frac{1}{\rho} \frac{\partial \rho}{\partial C} + \frac{1}{\beta} \frac{\partial \beta}{\partial C} \right]$$

The experimental results (Table I) indicate that the density increases while the adiabatic compressibility decreases with increasing soap concentration. Thus, the quantity  $(\partial\rho/\partial C)$  is positive, while  $(\partial\beta/\partial C)$  is negative. Since the values of  $\{(1/\beta)[(\partial\beta)/(\partial C)]\}$  are larger than  $\{(1/\rho)[(\partial\rho)/(\partial C)]\}$  for soap solutions, the concentration derivative of velocity,  $(dv)/(dC)$  is positive, which is in agreement with the results of other workers<sup>21,22</sup> reported for electrolytic solutions. The variation of ultrasonic velocity,  $v$ , with concentration,  $C$ , follows the relationship

$$v = v_0 + GC$$

where  $v_0$  is ultrasonic velocity of solvent and  $G$  is Garnsey's constant.<sup>23</sup>

The plots of ultrasonic velocity,  $v$ , vs. soap concentration,  $C$  (Fig. 1), are characterized by an intersection of two straight lines at a concentration that corresponds to the CMC of soaps (Table II). The values of intercept of the plots give the ultrasonic velocity,  $v_0$ , of the solvent mixture, which was found to be in close agreement with the calculated value of ultrasonic velocity of the solvent (Table II). It was found that the values of CMC decrease (Table II), while Garnsey's constant increases (Table III) with increasing chain length of the fatty acid constituent of the soap molecule.

The adiabatic compressibility,  $\beta$ , of soap solutions decreases with increasing soap concentration,  $C$  (Table I), which may be due to the fact that these soaps behave as simple electrolytes in solutions and are considerably ionized into simple metal cations ( $\text{Cr}^{3+}$ ) and fatty acid anions  $\text{RCOO}^-$  (where  $\text{R} = \text{C}_{13}\text{H}_{27}$ ,  $\text{C}_{15}\text{H}_{31}$ , and  $\text{C}_{17}\text{H}_{35}$  for myristate, palmitate, and stearate, respectively).

The ions in solutions are surrounded by a layer of solvent molecules firmly bound and oriented toward the ions. The orientation of solvent molecules around the ion attributed to the influence of the electrostatic field of the ion and, thus, internal pressure increase, which lowers the compressibility of solutions, i.e., the solutions become harder to compress. The decrease in adiabatic compressibility at higher soap concentrations may be explained on the basis of close packing of the ionic head groups in

**Table I Ultrasonic Measurements of Chromium Soaps in Benzene–DMF Mixture at  $40 \pm 0.05^\circ\text{C}$** 

Sample No.	Concentration, $C \times 10^3$ (mol L <sup>-1</sup> )	Density, $\rho$ (kg m <sup>-3</sup> )	Apparent Molar Volume, $\phi_v \times 10^6$ (m <sup>-3</sup> mol <sup>-1</sup> )	Ultrasonic Velocity, $v$ (m s <sup>-1</sup> )	Adiabatic Compressibility, $\beta \times 10^{10}$ (m <sup>2</sup> N <sup>-1</sup> )	Intermolecular Free length, $L_f$ (Å)	Specific Acoustic Impedance, $Z \times 10^{-5}$ (kg m <sup>-2</sup> s <sup>-1</sup> )	Solvation No., $S_n$
<b>Myristate</b>								
1	1.0	893.1	598	1152.4	8.431	35.72	10.292	27.10
2	2.0	893.3	598	1153.4	8.415	35.69	10.303	24.53
3	3.0	893.5	598	1154.6	8.395	35.65	10.305	25.50
4	4.0	893.6	626	1155.7	8.378	35.61	10.327	24.79
5	5.0	894.0	575	1157.0	8.356	35.56	10.343	26.01
6	6.0	894.2	579	1159.1	8.324	35.49	10.365	28.99
7	7.0	894.5	566	1160.5	8.301	35.44	10.381	29.36
8	8.0	894.8	556	1162.6	8.268	35.37	10.403	31.35
<b>Palmitate</b>								
1	1.0	893.2	580	1152.8	8.424	35.71	10.297	36.71
2	2.0	893.5	580	1154.2	8.401	35.66	10.313	34.14
3	3.0	893.8	580	1155.4	8.381	35.62	10.327	31.91
4	4.0	894.2	552	1157.0	8.354	35.56	10.346	33.19
5	5.0	894.6	536	1158.6	8.327	35.50	10.365	33.97
6	6.0	894.9	543	1160.3	8.300	35.44	10.383	34.48
7	7.0	895.3	532	1162.4	8.266	35.37	10.407	36.22
8	8.0	895.6	538	1167.5	8.192	35.21	10.456	44.39
<b>Stearate</b>								
1	1.0	893.3	563	1153.2	8.418	35.69	10.301	44.94
2	2.0	893.7	563	1155.3	8.383	35.62	10.325	46.49
3	3.0	894.2	525	1157.2	8.351	35.55	10.347	45.63
4	4.0	894.5	563	1159.0	8.322	35.49	10.368	44.17
5	5.0	895.0	540	1161.9	8.276	35.39	10.399	47.96
6	6.0	895.5	525	1165.1	8.226	35.28	10.433	51.41
7	7.0	896.0	515	1167.5	8.188	35.20	10.461	51.51
8	8.0	895.4	521	1169.7	8.153	35.13	10.485	51.08

the micelles, resulting in an increase in ionic repulsion and, finally, internal pressure.

The results of adiabatic compressibility,  $\beta$ , have also been explained in terms of Bachem's equation<sup>24</sup>:

$$\beta = \beta_0 + AC + BC^{3/2}$$

where  $A$  and  $B$  are constants and  $C$  is concentration (mol L<sup>-1</sup>) of the soap in solutions. Constants  $A$  and  $B$  have been determined from the intercept and slope of the plots of  $(\beta - \beta_0)/C$  vs.  $C^{1/2}$  and are recorded in Table III. The values of constants  $A$  and  $B$  decrease with increasing chain length of the fatty acid constituent of the soap molecules.

It follows from Güicker's limiting law<sup>25</sup> by using Debye–Hückel's theory<sup>26</sup> that the apparent molar compressibility,  $\phi_k$ , is related to the soap concentration,  $C$ , by the relationship

$$\phi_k = \phi_k^0 + S_k C^{1/2}$$

where  $\phi_k^0$  is the limiting apparent molar compressibility and  $S_k$  is a constant. The plots of  $\phi_k$  vs.  $C^{1/2}$  are linear for dilute soap solutions. The values of the constant  $S_k$  and the limiting molar compressibility,  $\phi_k^0$ , have been obtained from the slope and intercept of the plots of  $\phi_k$  vs.  $C^{1/2}$ . The positive values of  $S_k$  (Table III) signify a considerable soap–solvent interaction in dilute soap solutions.<sup>27</sup> The values of  $\phi_k^0$  and  $S_k$  decrease with increase in chain length of the soap molecules. The results are in agreement with the results reported in the literature.<sup>27,28</sup>

The apparent molar volume,  $\phi_v$ , is related to soap concentration by the relationship

$$\phi_v = \phi_v^0 + S_v C^{1/2}$$

where  $\phi_v^0$  is limiting apparent molar volume and  $S_v$  is a constant. The values of the apparent molar volume remain almost constant in dilute solutions, but

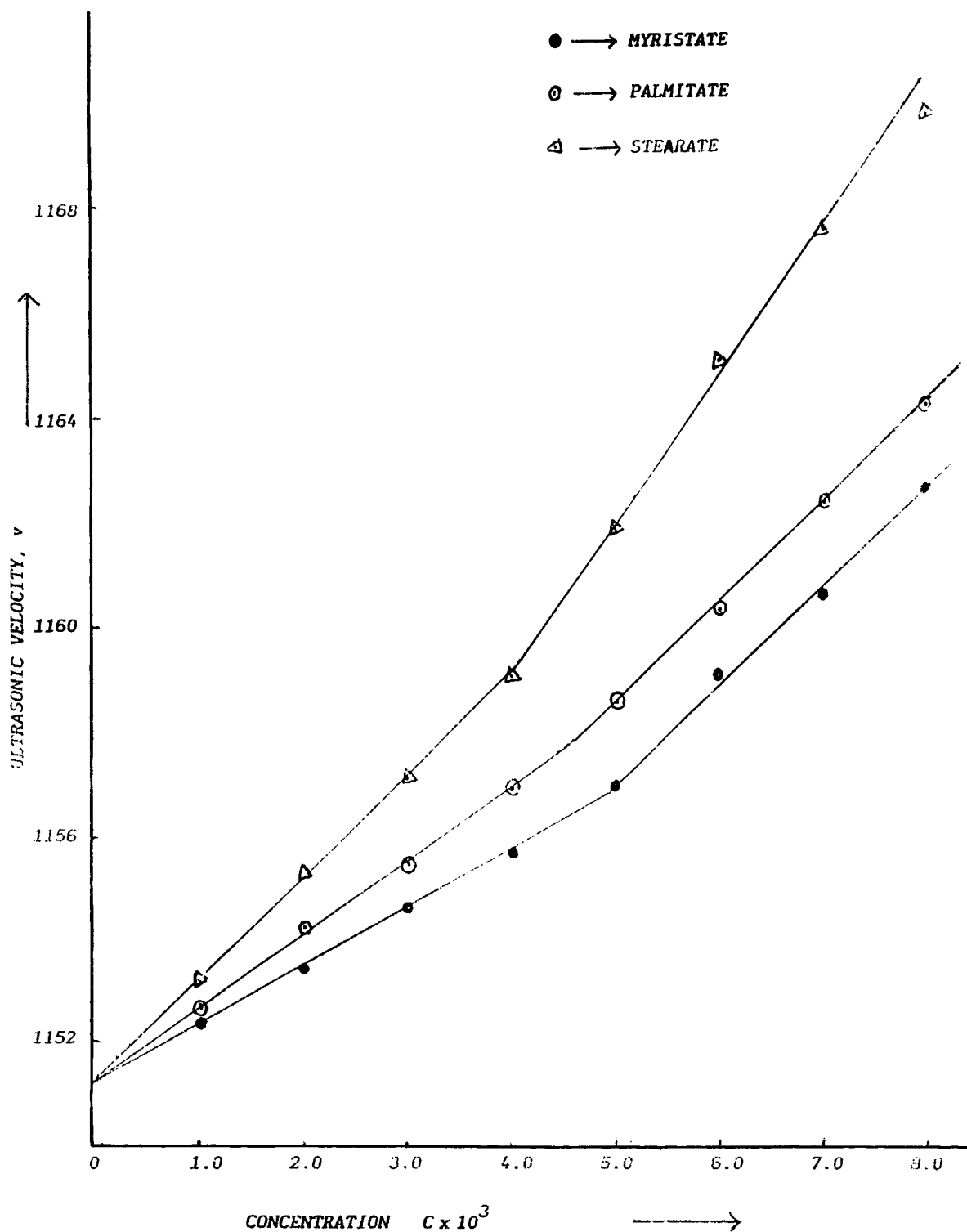


Figure 1 Ultrasonic velocity vs. soap concentration.

decrease linearly with increasing square root of soap concentration. The limiting apparent molar volume,  $\phi_v^0$ , and apparent molar compressibility,  $\phi_k^0$ , decrease

with increasing chain length of the soap. The results are in agreement with the results reported by Masson<sup>29</sup> for electrolytic solutions.

**Table II Values of CMC and Various Acoustic Parameters of Chromium Soaps in Benzene–DMF Mixture at  $40 \pm 0.05^\circ\text{C}$** 

Name of Soap	CMC $\times 10^3$ (mol L <sup>-1</sup> )	Ultrasonic Velocity, $v_0$ (m s <sup>-1</sup> ) Extrapolated	Adiabatic Compressibility, $\beta_0 \times 10^{10}$ (m <sup>2</sup> N <sup>-1</sup> ) Extrapolated	Specific Acoustic Impedance, $Z_0$ (kg m <sup>-2</sup> s <sup>-1</sup> ) Extrapolated	Intermolecular Free Length, $L_f$ (Å) Extrapolated
Myristate	5.05	1151.3	8.448	10.278	35.760
Palmitate	4.60	1151.2	8.450	10.281	35.755
Stearate	4.10	1151.3	8.450	10.279	35.765
Experimental values		$v_0 = 1151.2$	$\beta_0 = 8.451$	$Z_0 = 10.279$	$L_f = 35.764$

The decrease in the values of  $\phi_k$  and  $\phi_v$  at higher soap concentrations may be explained on the basis of the close packing of the ionic head group in the micelles, resulting in increase in ionic repulsion and, finally, internal pressure.

The decrease of intermolecular free length,  $L_f$ , and increase of specific acoustic impedance,  $Z$ , with increase in concentration and chain length of the soap (Table IV) indicates that there is significant interaction between the solute and solvent molecules, due to which the structural arrangement is considerably affected.<sup>30</sup> This can be explained on the basis of hydrophobic interaction between the soap and solvent molecules that increases with the intermolecular distance, leaving relatively wider gaps between the molecules and, thus, becoming the main cause of impediment to the propagation of ultrasound waves. Both plots ( $L_f$  vs.  $C$  and  $Z$  vs.  $C$ ) show a break at a definite soap concentration, which corresponds to the CMC of the soap.

The values of available volume,  $V_a$ , and relative association,  $R_A$ , decrease with increasing concentration and chain length of the fatty acid constituent

of the soap molecules (Table IV). The plots of  $V_a$  and  $R_A$  vs.  $C$  show a break at the CMC of the soap. The decrease in the values of relative association,  $R_A$ , is attributed to the fact that the solvation of ions decreases with increasing soap concentration. The values of molar sound velocity,  $R$ , and molar sound compressibility,  $W$ , increase with increasing concentration and chain length of the soaps.

The values of solvation number of chromium soaps at first decrease in dilute solutions and then show an increase with increasing soap concentration (Table I). The solvation number increases with the increasing chain length of the fatty acid constituent of the soap molecule.

It is concluded that the chromium soaps in the benzene–dimethyl formamide (4 : 1 v/v) mixture behave as simple electrolytes. The results confirm that there is a significant interaction between the soap and solvent molecules in dilute solutions. The values of the CMC obtained from different plots are in agreement and found to decrease with increasing chain length of the fatty acid constituent of the soap molecule.

**Table III Acoustic Parameters of Chromium Soaps**

Soaps	Garnsey Constant (G)	Bachem's Equations		Limiting Apparent Molar Volume $\phi_v^0$	Limiting Apparent Molar Compressibility $-\phi_k^0 \times 10^8$	$S_k \times 10^7$
		$-A \times 10^{10}$	$B \times 10^{10}$			
Myristate	1137.2	26.1	138	598	26.1	145
Palmitate	1428.6	30.9	131	580	33.9	137
Stearate	1937.5	38.1	93	563	41.8	89

Table IV Ultrasonic Measurements of Chromium Soaps in Benzene-DMF Mixture at  $40 \pm 0.05^\circ\text{C}$ 

Sample No.	Concentration, $C \times 10^3$ (mol L <sup>-1</sup> )	Molar Sound Velocity, $R \times 10^4$ [m <sup>3</sup> /mol (N/m <sup>2</sup> ) <sup>1/3</sup> ]	Molar Sound Compressibility, $W \times 10^4$ [m <sup>3</sup> /mol (N/m <sup>2</sup> ) <sup>1/7</sup> ]	Available Volume, $V_a \times 10^6$ (m <sup>3</sup> )	Relative Association, $R_A \times 10^2$	Apparent Molar Compressibility, $-\phi_k \times 10^7$ (m <sup>5</sup> N <sup>-1</sup> kg <sup>-1</sup> mol <sup>-1</sup> )
<u>Myristate</u>						
1	1.0	8.834	17.118	24.134	99.988	21.59
2	2.0	8.841	17.131	24.092	99.982	19.77
3	3.0	8.848	17.146	24.040	99.970	20.48
4	4.0	8.857	17.161	23.995	99.950	17.50
5	5.0	8.863	17.173	23.932	99.957	18.77
6	6.0	8.873	17.191	23.830	99.920	23.18
7	7.0	8.880	17.205	23.766	99.913	23.56
8	8.0	8.889	17.221	23.660	99.888	25.09
<u>Palmitate</u>						
1	1.0	8.835	17.120	24.116	99.988	29.59
2	2.0	8.843	17.135	24.048	99.981	27.72
3	3.0	8.851	17.149	23.995	99.980	26.09
4	4.0	8.858	17.163	23.918	99.980	27.26
5	5.0	8.865	17.178	23.840	99.980	27.97
6	6.0	8.874	17.195	23.760	99.964	28.28
7	7.0	8.883	17.211	23.656	99.949	29.64
8	8.0	8.900	17.241	23.391	99.838	35.54
<u>Stearate</u>						
1	1.0	8.836	17.121	24.090	99.987	36.54
2	2.0	8.846	17.139	23.990	99.972	37.66
3	3.0	8.854	17.155	23.894	99.974	37.35
4	4.0	8.863	17.174	23.811	99.956	35.97
5	5.0	8.874	17.194	23.665	99.930	38.93
6	6.0	8.885	17.215	23.498	99.895	41.56
7	7.0	8.894	17.232	23.377	99.883	41.73
8	8.0	8.904	17.251	23.269	99.865	41.36

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