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CRITICAL COALESCENCE CONCENTRATION (CCC) OF VARIOUS SURFACTANTS USED AS FLOTATION REAGENTS IN MINERAL

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Abstract: The role of flotation frothing agents in the flotation process is generally known, especially due to the size of bubbles and the stability of the foam formed. In recent years, a number of new reagents have been introduced. The purpose of this article is to present a comprehensive database containing the characteristics of surfactant families discussed using the parameter of the so called the Critical Coalescence Concentration (CCC). This article presents an analysis of the experimental data set by the author and the experimental data published in the literature.

Keywords: *flotation, frothers, bubble size, critical coalescence concentration (CCC), hydrophile-lipophile balance (HLB)*

1. INTRODUCTION

Frothers play a key role in the flotation process of minerals. The effect of frothers on the size of bubbles and the flotation was studied by many authors (Zang et al. 2021; Cho and Laskowski 2006; Grau and Laskowski 2006; Grupa et al. 2007; Finch and Nesset 2008). Frothers reduce the size of bubbles, prevent their coalescence (CCC) and stabilize the foam. The surfactants used as flotation frothers are characterized by a number of parameters, but the most useful one seems to be the so called critical coalescence concentration (CCC). This parameter was proposed by Laskowski and his colleagues in 2002 (Cho and Laskowski 2002b; 2006; Laskowski 2003, Laskowski

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et al. 2003). The authors demonstrated that an increase in concentration of a particular frothers increases the size of air bubbles, which prevents fusion of the bubbles, that is, coalescence. Further increase in the concentration of frother above the CCC value does not affect the size of air bubbles (Fig. 1).

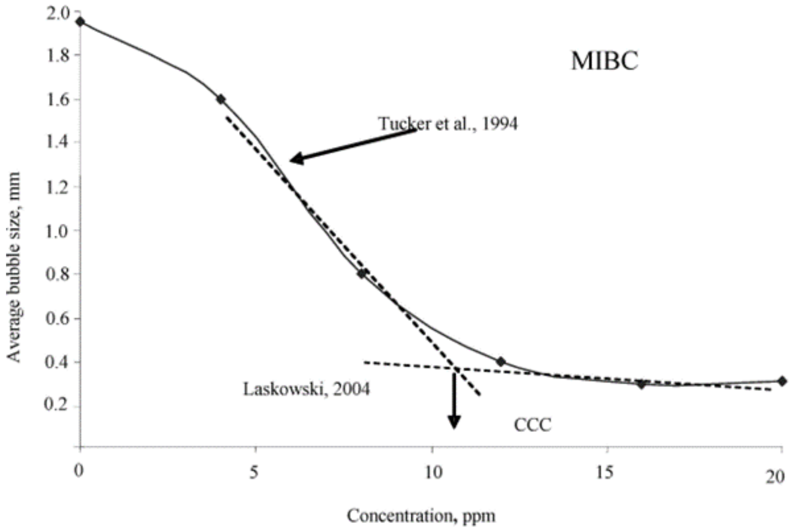

Fig. 1. The impact of the concentration of frother on the properties of gas–water system for methyl isobutyl carbinol (MIBC), and CCC evaluation (Laskowski 2004; Tucker et al. 1994; Drzymala 2007)

In many studies, correlation was found between a critical coalescence concentration (CCC), hydrophilic-lipophilic balance (HLB) balance and molecular weight (MW) for different flotation frothers on the basis of experimental data published in the literature (Laskowski et al. 2003; Szyszka, Glapiak, and Drzymala 2008a; Finch and Zhang 2014; Kowalczuk 2013; Szyszka 2013; Szyszka 2018; Drzymala and Kowalczuk 2018; Szyszka et al. 2006).

2. MATERIALS AND METHODS

CCC measurement tests in this study were carried out in a flotation cell with a capacity of 89 cm^3. The formation process of air bubbles was photographed. A digital camera NICON D5000 with a matrix of 12.5 million of pixels with the lens NIKKOR AF-S and a resolution of 2144 × 1424 (JPEG) was used during the tests. Best quality pictures were chosen to perform an analysis of images and measure the diameters of air bubbles in the tested concentration. A diagram of the experimental set-up is shown in the study authored by Szyszka et al. (2006) (Fig. 2).

The air was pressed through two thin capillaries rigidly fixed on a metal plate by means of peristaltic pump in the quantity of 5 dm^3/min. Measurements were taken after establishing equilibrium in the analysed system.

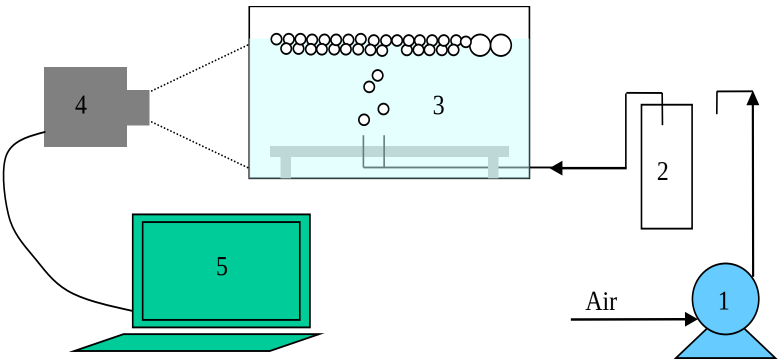

Fig. 2. Experimental set-up for CCC measurements: 1) peristaltic pumps, 2) equalizing tank, 3) cell, 4) digital camera, 5) computer (Szyszka et al. 2006)

On the basis of documentation obtained, the measurements of mean diameters of air bubbles were taken using Meazure software, and the values obtained were used to plot curves of the dependence of Sauter mean diameter (1) (Pacek, Man, and Nienow 1998; Drzymala 2017) on the concentration of surfactant analysed.

$$d_{śrS} = \frac{\Sigma d^3}{\Sigma d^2}, \tag{1}$$

where:

d – air bubble diameter, mm

$d_{śrS}$ – Sauter mean diameter, mm.

Bubble size measurement technique has been presented in detail in the study authored by Szyszka (2018). In case of bubbles with elliptical shape, the horizontal (d_h) and vertical (d_v) diameter was measured to obtain total diameter of bubble using the following formula (2)

$$d = \sqrt[3]{d_h^2 d_v}, \tag{2}$$

where:

d – air bubble diameter, mm

d_h – height of air bubble, mm

d_v – width of air bubble, mm.

3. RESULTS

Based on review of literature and the authors own research, HLB and CCC values determined using different methods for the selected frothers families were calculated and listed in Table 4.

Table 4. List of CCC values obtained in this study and literature values determined by different methods for selected frothers families

No.	Frother family	Name	Formula	MW [g/mol]	HLB Davies	CCC [$mmol/dm^3$]
1	aliphatic alcohols	1-propanol	C_3H_7OH	60	7.48	3.933[1] (CCC95)
2		2-propanol	C_3H_7OH	60	7.48	5.117[1] (CCC95)
3		1-butanol	C_4H_9OH	74	7,00	0.851[1] (CCC95)
4		2-butanol	C_4H_9OH	74	7.00	1.041[1] (CCC95)
5		t-butanol	C_4H_9OH	74.12	7.00	
6		1-pentanol (amyl alcohol)	$C_5H_{11}OH$	88.15	6.53	0.284[1] (CCC95) 0.153 [9]
7		2-pentanol	$C_5H_{11}OH$	88.15	6.53	0.341[1] (CCC95)
8		3-pentanol	$C_5H_{11}OH$	88.15	6.53	0.466[1] (CCC95)
9		1-hexsanol	$C_6H_{13}OH$	102.17	6.05	0.108[1] (CCC95)
10		2-hexsanol	$C_6H_{13}OH$	102.17	6.05	0.108[1] (CCC95)
11		3-hexsanol	$C_6H_{13}OH$	102.17	6.05	0.127[1] (CCC95)
12		1-heptanol	$C_7H_{15}OH$	116.2	5.58	0.069[1] (CCC95)
13		2-heptanol	$C_7H_{15}OH$	116.2	5.58	0.078[1] (CCC95)
14		4-heptanol	$C_7H_{15}OH$	116.23	5.58	
15		1-octanol	$C_8H_{17}OH$	130.23	5.10	0.062 [1] (CCC95) 0,042 [11]
16		2-octanol	$C_8H_{17}OH$	130.23	5.10	0.062 [1] (CCC95)
17		1-hexadecanol- (acetyl alcohol)	$C_{16}H_{33}OH$	242.44	1.30	
18		diacetone alcohol	$C_6H_{11}O_2$	116.16	7.35	
19		methyl isobutyl carbinol (MIBC)	$C_6H_{13}OH$	102.17	6.05	0.111 [9](CCC95) 0.051 [9] (CCC75) 0.110 [3] 0.370 [4] 0,108 [10] 0.372 [11]
20		TEXANOL (2,2,4-trimethyl-pentanediol 1,3-monoisobutyrate)	$C_{12}H_{24}O_3$	216.32	5.80	
21	cyclic alcohols	alphfa-terpineol	$C_{10}H_{18}O$	154	5.4 4.15	0.160 [4] 0.052[8] 0,080[11]

Table 4 continued

22	polyethylene glycol alkyl ethers		tricoseneethylene-glycol 1-hexa-decanoic ether	$C_{16}H_{33}O(C_2H_4O)_{23}$ $C_{16}E_{23}$	1253	9.35		
			ethyl ether of diethylene glycol	$C_6H_{14}O_3$ C_2E_2	134.17		0.580 [11]	
23		Corflot 2.3	Diethylene glycol butyl ether	$C_8H_{18}O_3$ C_4E_2	162.23	7.70	0,840 [7]	0.33 [11]
24			triethylene glycol monoethyl ether	$C_8H_{18}O_3C_2E_3$	178.23	9,00		
25		Nasfroth245B	triethylene glycol butyl ether	$C_{10}H_{22}O_4$ C_4E_3	206.28	8.05	0.540 [7]	0,115 [11]
26			ethylene glycol butyl ether	$C_6H_{14}O_2$ C_4E_1	118.17	7.35	1,190 [7]	
27			diethylene glycol butyl ether	$C_8H_{18}O_3$ C_4E_2	162.23	7.70	0,840 [7] 0.839 [11]	
28			1,1,3-triethoxy butane (TEB)	$H_9C_4(OC_2H_4)_3H$ C_4E_3	176.26	6.6 7		
29			polyethyleneglycol hexadecyl ether Brij 58P	$C_{16}H_{33}O(C_2H_4O)_{20}$ $C_{16}E_{20}$	1121		0,027 [11]	
30	polypro-pylene glycol alkyl ethers		propylene glycol methyl ether,	$H_3C(OC_3H_6)OH$ C_1P_1OH	90	8.28	0.489[1](CCC95) 0.520 [5]	
31			propylene glycol propyl ether	$H_7C_3OC_3H_6OH$ C_3P_1OH	118	7.33	0.246[1](CCC95)	
32			propylene glycol butyl ether	$H_9C_4OC_3H_6OH$ C_4P_1OH	132	6.85	0.159[1](CCC95)	
33			dipropylene glycol methyl ether	$H_3C(OC_3H_6)OH$ C_1P_2OH	148	8.13	0.176[1](CCC95) 0,170 [5]	
34			dipropylene glycol propylene ether	$H_7C_3OC_3H_6OH$ C_3P_2OH	176	7.18	0.091[1](CCC95)	
35			dipropylene glycol butyl ether	$H_9C_4OC_3H_6OH$ C_4P_2OH	190	6.70	0.063[1](CCC95)	
36			tripropylene glycol methyl ether	$H_3C(OC_3H_6)OH$ C_1P_3OH	206	7.98	0.073[1](CCC95)	
37			tripropylene glycol propyl ether	$H_7C_3OC_3H_6OH$ C_3P_3OH	234	7.03	0.047[1](CCC95)	
38			tripropylene glycol butyl ether	$H_9C_4OC_3H_6OH$ C_4P_3OH	248	6.55	0.028[1](CCC95)	
	methyl poly-alkylene ethers glycol		DF-1012	$CH_3(C_3H_6O)_{6.3}OH$ $C_1P_{6.3}$	397.95	7.48	0.014[1](CCC95) 0,016 [8]	

Table 4 continued

39		DF-200	$CH_3(OC_3H_6)_3OH$ C_1P_3	206.29	7.98	0,085 [5]
40		DF-250	$CH_3(OC_3H_6)_4OH$ C_1P_4	264.37	7.83	0.038 [1](CCC95) 0.039 [9](CCC95) 0,033 [5] 0,018 [9] (CCC75)
41		DF-1263	$CH_3(OC_3H_6)_4OH$ (C_4H_6O) $C_1P_4B_1$	336.53	7.70	
42	poly(propylene) glycols	DF-400	$H(OC_3H_6)_{6.5}OH$	395.61	9.83	
43		DF-1400	$H(OC_3H_6)_6OH$	366.56	9.90	
44		dipropylene glycol	$HOC_3H_6OC_3H_6OH$	134	9.23	0.396[1](CCC95)
45		PPG-192 dripropylene glycol	$H(OC_3H_6)_3OH$	192	10.4 [2] 9.12 [1] 9.08	0.172[1](CCC95)
46		tetrapropylene glycol	$HOC_3H_6OC_3H_6OH$	250	9.00 [1] 8.78	0.088[1](CCC95)
47		PPG-400	$H(OC_3H_6)_{6.5}OH$	420	9.83	
48		polypropylene glycol 425	$HOC_3H_6OC_3H_6OH$	425	8.62 [1] 8.47	0.014[1](CCC95)
49		PPG-725 polypropylene glycol 725	$H(OC_3H_6)_{12.8}OH$	762 [2] 725 [1]	9.2 [2] 8.88 8.00 [1] 7.70	0.010[1](CCC95)
50		PPG-1000 polypropylene glycol 1000	$H(OC_3H_6)_{16.5}OH$	950 [2] 1000 [1]	8.4 [2] 7.38 [1] 8.33	0.008[1](CCC95)
51		PPG-2000	$H(OC_3H_6)_{34}OH$	1940	5.6 [2] 5.70	
	commercial frothers	FX120-01		102	6.05 [1]	0.108[1](CCC95)
52		FX160-05		207	7.11 [1]	0.072[1](CCC95)
53		FX160-01		251	7.86 [1]	0.048[1](CCC95)
54		F150		425	8.62 [1]	0.014[1](CCC95) 0.010[9](CCC95) 0.005[9](CCC95)
55		F160		217	6.63 [1]	0.037[1](CCC95)
56	quaternary ammonium compounds	DMM-11 N-[3-(dodecanyl-oxycarboxy) prophyl]-N,N, N-(trimethyl-ammonium) bromide	$C_{17}H_{36}BrNO_2$	366	10.93	0.051 [4]
57		DMGM-12 N- [2-(dodecyoxycarboxy) ethyl] -N, N, N- (tri-methylammonium) bromide	$C_{17}H_{36}O_2$	366	10.93	0.102 [6]

Table 4 continued

58		DMALM-12 N- [2-(dodecyoxycarboxy) ethyl] -N, N, N- (tri-methylammonium) bromide	$C_{18}H_{38}O_2BrN$	368	10.45	0.125 [6]
59		DMPM-11 N (do-decyloxycarboxy methyl) -N, N, N-(trimethylammo-nium) bromide	$C_{18}H_{38}O_2BrN$	368	10.45	0.115 [6]
60	aromatic amines	bromide N-hex-sadecylopyrydine N-Hexadecylpyri-dinium bromide	$C_{21}H_{38}BrN$	383.9	6.4	
61		pyridine	C_5H_5N	79.1	14.0	12.000 [11]
62		N-dodecyl--2-aminopropionic acid	$C_{12}H_{25}NH2COOH$	230	12.8	
63	acetals	ethyl acetal	$C_2H_5O(C_2H_5O)_2$	132	6.3	184.7 [11]
64	phthalates	dibutyl phthalate	$C_6H_4O(C_4H_9O)_2$	278.34	14.0	0.015 [11]
65	phenols	cresol	C_7H_8O	108.14		8.51 [11]
66	fatty acids	oleic acid	$CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$	282.47	1.025	0.152 [10]
67	alkyl sulfates RO-SO_4 H	dodecylsulfate	$C_{12}H_{25}SO_4H$	266.38	40	
68	Alkyl sulfonates R-SO_3 H	dodecylsulfonate	$C_{12}H_{25}SO_3H$	250.39	12.3	
69	salts of alkyl sulfonates R-SO_3Na	sodium dodecylsulfonate	$C_{12}H_{25}SO_4H$	288.37		0.24 [11]
70	salts of fatty acids	sodium palmitate	$C_{16}H_{33}COONa$	292	18.5	
71		sodium stearate	$C_{18}H_{37}COONa$	320	17.5	
72		sodium oleate	$C_{17}H_{33}COONa$	304.44	18.0	0.108 [10]
73		sodium laurate	$C_{12}H_{25}COONa$	236	20.4	
74	alkyl sulfate salts RO-SO_4 Na	Sodium dodecylsulphate	$C_{12}H_{25}SO_4On$	288.38	40	
75	salts of alkyl sulfonates R-SO_3 On	sodium dodecylsulfonate	$C_{12}H_{25}SO_3Na$	272.39	12.3	
76	sulphur hydrocarbons,	sulfolane	$C_4H_80_2S$	120.17		13.37 [11]
77	mesityl oxide in the mixture with diacetone alcohol ADTM	ADTM	$C_6H_{12}O_2$ $C_6H_{10}O$	114.36		0.79 [11]

where:

[1] Zhang et al. 2012
[2] Tan et al. 2005
[3] Melo and Laskowski 2006
[4] Szyszka et al. 2006
[5] Szyszka 2016
[6] Szyszka 2013
[7] Szyszka 2014
[8] Gupta et al. 2007
[9] Kracht and Finch 2009
[10] Atrafi et al. 2012
[11] Szyszka 2014; 2016

4. DISCUSSION

Results obtained for the tested frothers including polyglycols indicate that with increasing number of groups (ethoxy, propoxy groups) in homologous series molecules of frothers tested, the size of air bubbles decreases (Szyszka 2018). These results show correlation between the CCC value and the Molecular Weight of the frothers tested, and thus the content of ethoxy groups in the molecule tested (Figs. 3–5). As the number of groups (ethoxy, propoxy) in the polyglycol molecules increases, the CCC value decreases. Figures 4 and 5 illustrate this relationship.

Figure 6 shows the relationship between CCC and HLB/MW for the family of ether polyglycols. This figure shows correlation between the Critical Coalescence Concentration and HLB value index designated as the Hydrophilic-Lipophilic Balance in a weight ratio to the Molecular Weight for surfactants, which are the frothers. The relationship between the Critical Coalescence Concentration (CCC), the Hydrophilic-Lipophilic Balance (HLB) and the Molecular Weight (MW) for different frothers was studied and described by several authors (Laskowski at al. 2003; Finch and Zhang 2014; Kowalczuk 2013). This relationship as regards ether polyglycols was also found in research conducted by Szyszka et al. (2008b).

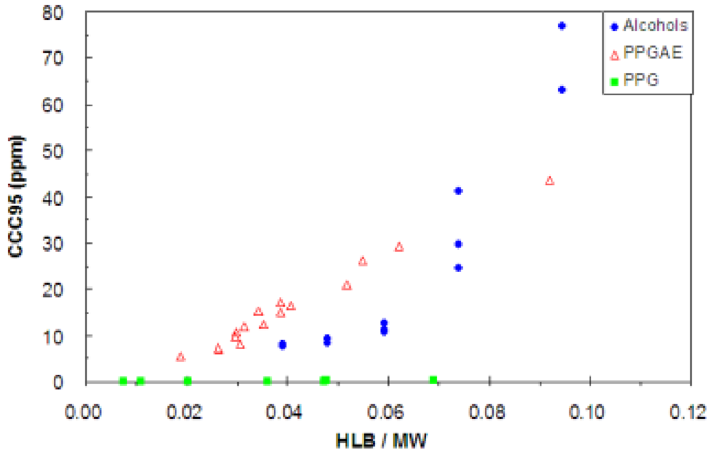

Fig. 3. Correlation between CCC95 and HLB/MW (Molecular Weight) for 36 frothers (Finch and Zhang 2014)

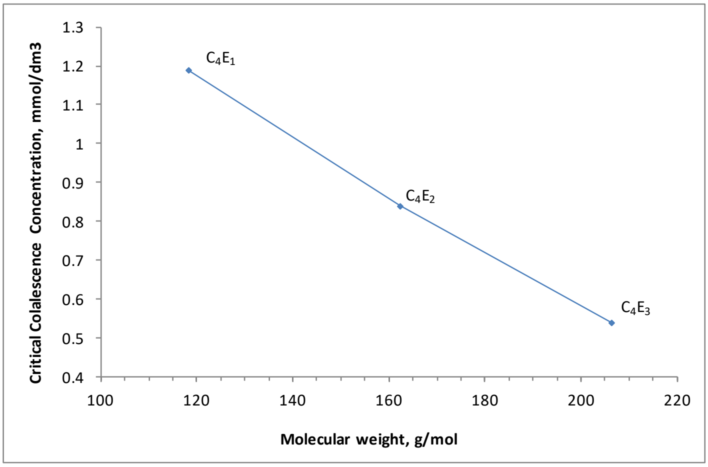

Fig. 4. Correlation between CCC and molecular weight (MW)
for C4E1, C4E2 and C4E3
(Szyszka 2018)

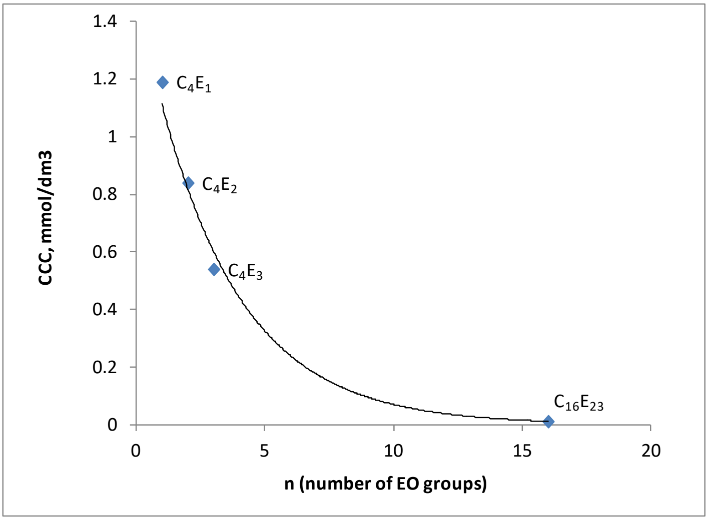

Fig. 5. Effect of the number of (EO) groups in the molecule
on CCC values for polyglycol frothers
(Szyszka 2018)

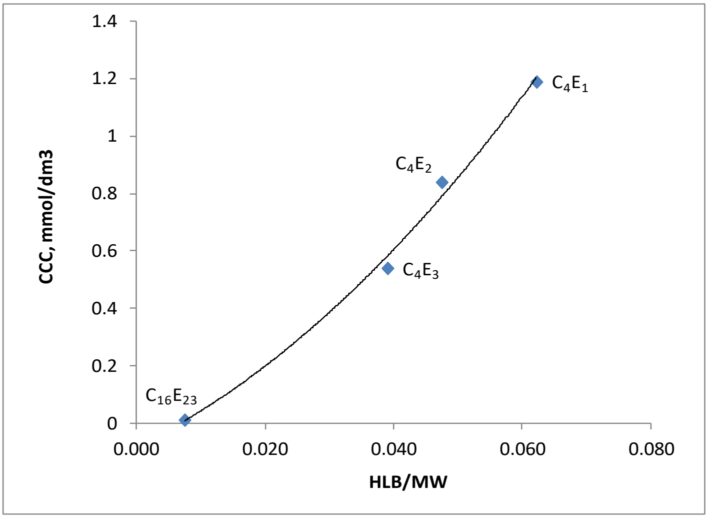

Fig. 6. Effect of HLB/MW on CCC values for the polyglycol frothers (Szyszka 2018)

5. CONCLUSIONS

Based on the analysis of experimental data set out in this study and the experimental data reported in literature for surfactants used as flotation frothers, the following conclusions can be drawn.

The most important group of frothers used in the flotation of metal ores are special aliphatic alcohols and ethers.

It seems that the most useful way of characterizing flotation frothers is by the molecular weight (MW), the Hydrophile-Lipophile Balance (HLB), the Dynamic Foam Index (DFI) and the Critical Coalescence Concentration (CCC).

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