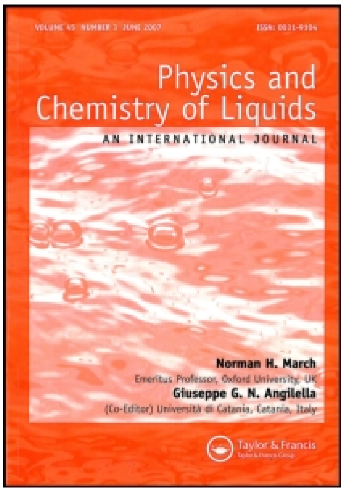

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Solubility of SO_2, CO_2 in desulfuration solution from 293.15 to 313.15 K

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The solubility of dilute SO_2, CO_2 gas mixture in desulfuration solution has been determined from 293.15 to 313.15 K, along with the partial pressures of SO_2 from 0.15 to 3.0 kPa, and of CO_2 from 5 to 18 kPa. The measured solubility data are useful in the process design of SO_2 removal from flue gas.

Keywords: Solubility; Desulfuration solution; Sulfur dioxide; Carbon dioxide

1. Introduction

Selective removal of SO_2 and CO_2 from flue gas by liquid absorption has received considerable attention in the recent past. The new developed desulfuration solution [1–8] can effectively solve this problem. Such a method possesses not only a strong desulfurizing efficiency, but also a good selectivity for SO_2 and CO_2 when they coexist in flue gas. In order to further research the absorption effect by this sort $b_{SO_2,P}$ of desulfuration absorbent, we determine the solubility of dilute SO_2 and CO_2 mixture gas in desulfuration solution to research their absorption capacity and selectivity for SO_2 and CO_2 from flue gas.

2. Experimental section

2.1. *Materials and analysis method*

Desulfuration solution: DMSO + $MnSO_4$ mixture solvent. Dimethyl sulfoxide and $MnSO_4$ were AR grade and their purity was greater than 99%. Water was purified by vacuum distillation and deionization. Mixture solvents were obtained by mixing 0.96546 mol L^{-1} $MnSO_4$ solution in DMSO, which were mixed in the ratio 0.03 : 1 by volume. They were degassed under vacuum. The dilute SO_2, CO_2 mixture gas was

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prepared by mixing sulfur dioxide, carbon dioxide, oxygen and nitrogen. The sulfur dioxide, carbon dioxide, oxygen and nitrogen had a purity x (SO_2) > 0.999, x (CO_2) > 0.99, x (O_2) > 0.999 and x (N_2) > 0.99999, respectively. A flue gas analyzer with SO_2 and O_2 sensor (type NTS 100, Nanjing, China) was used for SO_2 ($\leq 0.5\%$ SO_2) and O_2 analysis of the gas phase. The uncertainty of the SO_2 analyzer was ±10 ppm; O_2 was ±1%. The SO_2 in the liquid was analyzed by $KMnO_4$ titration. Sulfate ions were determined by barium chromate spectrophotometry (thermal method), CO_2 concentration was analyzed by CO_2 analyzer RD-7AG (type RD-7AG, Nanjing, China), the uncertainty of the CO_2 analyzer was $\pm 3\% \mathrm{F} \cdot \mathrm{S} \pm 1$.

2.2. *Reaction mechanism*

DMSO is a polar organic solvent with a rather large dipole matrix, SO_2 is also a polar gas molecule, while CO_2 is a nonpolar gas molecule. According to the principle 'like dissolves like', DMSO has a strong solubility for SO_2 and less solubility for CO_2. The absorption model of SO_2 in DMSO and chemical reaction equation have been described in a previous study [1].

After adding Mn^{2+} to DMSO, SO_2 is oxidized to H_2SO_4 catalyzed by $MnSO_4$ [1]. Therefore the mixed absorbent has a rather large solubility for SO_2 and less solubility for CO_2.

2.3. *Solubility measurement*

The schematic diagram of the experimental apparatus is the same as in our previous paper [1]. The principle for this method and the procedure for making a solubility measurement is also the same as in that study [1].

The only difference from our previous study [1] is when gas–liquid equilibrium was reached, the absorption flask was taken out from experimental apparatus, and the liquid in the absorption flask was aspirated by injector and weighed which gave approx. mass and injected into 10 mL volumetric flask. After bringing volume to 10 mL with distilled water, 2 mL solution of that was aspirated and was used to determine sulfate ions concentration with barium chromate spectrophotometry. The residual 8 mL solution was titrated by $0.011568\,\mathrm{mol\,L^{-1}}$ $KMnO_4$ solution to analyze SO_2 physical absorption solubility.

In other words, the concentration of SO_2 physical absorption in solution was analyzed by $KMnO_4$ titration. The chemical reaction SO_2 concentration, i.e., sulfate ions, was determined by barium chromate spectrophotometry.

Total S solubility = physical SO_2 solubility + chemical reaction SO_2 solubility. The concentration of CO_2 physical absorption in solution was calculated by material equilibrium.

2.4. *Data reduction*

There are two phases in the system: (1) the gas phase which includes SO_2, CO_2, O_2, N_2 and solvent vapor; (2) the liquid phase which includes DMSO, Mn^{2+}, the dissolved SO_2, CO_2 and SO_4^{2-}.

The measured volume change was equal to the volume of the gas absorbed minus the volume of liquid sample. The volume of the gas absorbed includes the volume of SO_2, CO_2 (physical absorbed SO_2, CO_2 and chemical reacted SO_2) and the reacted O_2 volume.

The solubility calculation is as follows:

(1) The concentration of SO_2 physical absorption $b_{SO_2,P}$ (mmol) in the liquid whose quantity is m_l (g) aspirated by injector from the absorption flask, was analyzed by $KMnO_4$ titration; the sulfate ions was determined by barium chromate spectrophotometry, it includes the chemical reaction SO_2 concentration, $b_{SO_2,C}$ (mmol), as well as SO_4^{2-} concentration from $MnSO_4$ solution.

$$b_{SO_2,P} = \frac{5 \times 0.011568 \times V_{KMnO_4}}{1.6} \tag{1}$$

$$b_{SO_2,C+MnSO_4} = \frac{A + 0.005272}{0.11645 \times 96 \times 0.2} \tag{2}$$

in which, V_{KMnO_4} (mL) represents the titration volume of $KMnO_4$, and A represents absorbency.

The concentration of SO_2 physical absorption in solution $bt_{SO_2,P}$ (mmol) and the chemical reaction SO_2 concentration $bt_{SO_2,C}$ (mmol) can be calculated with mass ratio and shown in equations (3) and (4), then they can be as initial value of iterative computation,

$$bt_{SO_2,P} = b_{SO_2,P} \times \frac{m_t}{m_l} \tag{3}$$

$$bt_{SO_2,C} = \left(b_{SO_2,C+MnSO_4} \times \frac{m_t}{m_l} - n_{MnSO_4} \right). \tag{4}$$

In which, m_t (g) represents injected mass of the desulfuration solution sample; n_{MnSO_4} (mmol) represents the mole number of $SO_4^{2-}$from mixture solvents (DMSO + $MnSO_4$).

The reacted O_2 mole number (bt_{O_2}/mmol) can be obtained from equation (5):

$$bt_{O_2} = \frac{bt_{SO_2,C}}{2}. \tag{5}$$

The measured volume change was equal to the volume of the gas absorbed minus the volume of liquid sample, the volume of the gas absorbed includes physical SO_2 solubility + chemical reaction SO_2 solubility as well as O_2 reacted number and CO_2 physical absorption solubility, so CO_2 physical dissolved volume can be obtained from equation (6)

$$\mathrm{d}V_{CO_2} = \left(\mathrm{d}V + V - \frac{(bt_{SO_2,P} + bt_{SO_2,C}) \times 64}{\rho_{SO_2}} - \frac{bt_{O_2} \times 32}{\rho_{O_2}} \right) \mathrm{mL} \tag{6}$$

where dV represents the change in the volume of the gas in the absorption flask (cm^3); V represents the volume injected desulfuration solution (mL); ρ_{SO_2}, ρ_{O_2} represents the density of SO_2 and O_2 ($mg\,cm^{-3}$), respectively.

The CO_2 physical solubility is:

$$bt_{CO_2} = \frac{dV_{CO_2} \times \rho_{CO_2}}{44}\ \text{mmol} \tag{7}$$

while the mass of desulfuration solution m in m_l equals m_l minus dissolved gas number in m_l.

$$m = \left(m_l - \frac{(b_{SO_2,P} + b_{SO_2,C+MnSO_4} - dn_{MnSO_4}) \times 64}{1000} - \frac{b_{O_2} \times 32}{1000} - \frac{b_{CO_2} \times 44}{100} \right) \text{g}. \tag{8}$$

In which, dn_{MnSO_4} represents the mole number of SO_4^{2-} from $MnSO_4$ in m_l (mmol).

The SO_2 physical absorption solubility and the chemical reaction SO_2 solubility can be calculated as follows. According to the aforementioned analysis, the total SO_2 physical absorption solubility, $rt_{SO_2,P}$ and the total chemical reaction SO_2 solubility, $rt_{SO_2,C}$ can be calculated from equations (9) and (10):

$$rt_{SO_2,C} = b_{SO_2,C} \times \frac{m_t}{m}\text{mmol} \tag{9}$$

$$rt_{SO_2,P} = b_{SO_2,P} \times \frac{m_t}{m}\text{mmol.} \tag{10}$$

Put these as initial value of $bt_{SO_2,P}, bt_{SO_2,C}$ and iterate repeatedly, till $|rt_{SO_2,P} - bt_{SO_2,P}| \leq e$, and $|rt_{SO_2,C} - bt_{SO_2,C}| \leq e$, in which e represents precision, in this program, $e = 0.000000001$. Then, let $bt_{SO_2,P} = rt_{SO_2,P}$ $bt_{SO_2,C} = rt_{SO_2,C}$. The physical SO_2 solubility is $r_{SO_2,P} = rt_{SO_2,P}/m_t$. The chemical reaction SO_2 solubility is $r_{SO_2,C} = rt_{SO_2,C}/m_t$. Total S solubility = physical SO_2 solubility + chemical reaction SO_2 solubility, i.e., $r_{SO_2} = r_{SO_2,P} + r_{SO_2,C}$. The physical CO_2 solubility is $r_{CO_2} = bt_{CO_2}/m_t$.

(2) After calculating the solubility of SO_2 and CO_2, the corresponding equilibrium partial pressure of SO_2 and CO_2 can be calculated as in the previous paper [1].

2.5. *Test of apparatus*

In order to ensure proper operation of the apparatus, the solubility of SO_2 in water was measured and compared with the values reported in the literature [9]. The experimental measurements agreed with the reported values with a mean relative deviation of 2.22% [1].

3. The experiment result and discussion

The measured solubilities of dilute SO_2 and CO_2 in DMSO + Mn^{2+} mixture solvent are shown in tables 1–5 and figures 1–3, respectively.

The SO_2 physical solubilities are listed in table 1 and figure 1. From table 1 and figure 1, we can find that the physical absorption SO_2 solubilities decrease with the temperature, and increase with the SO_2 partial pressure.

The chemical reacted SO_2 solubilities are listed in table 2. From table 2, we can find that the chemical reacted SO_2 solubilities increase with the temperature too; and the reacted SO_2 solubilities increase with the SO_2 partial pressure.

Table 1. Physical SO_2 solubility from 293.15 to 313.15 K.

	SO_2 physical solubility, $r_{SO_2,P}$ (mol kg^{-1})					
T (K)	2.40% SO_2	2.20% SO_2	2.00% SO_2	1.40% SO_2	0.760% SO_2	0.470% SO_2
293.15	1.40	1.29	1.17	0.819	0.445	0.275
298.15	1.32	1.21	1.10	0.770	0.418	0.259
303.15	1.24	1.13	1.03	0.721	0.391	0.242
308.15	1.10	1.01	0.920	0.644	0.350	0.216
313.15	0.901	0.826	0.751	0.526	0.285	0.176

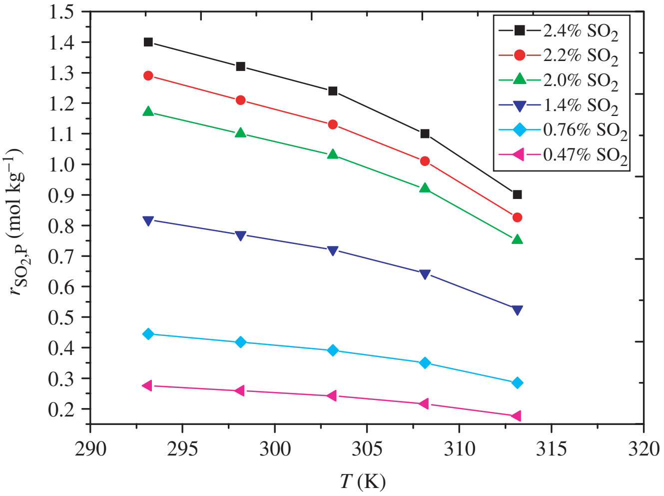

Figure 1. The relation of physical SO_2 solubility with temperature at different SO_2, CO_2 mixture gas.

Table 2. Chemical reacted SO_2 solubility at different percentages of SO_2 and CO_2 mixture gas from 293.15 to 313.15 K.

	$r_{SO_2,C}$ (mol kg^{-1})					
T (K)	2.40% SO_2	2.20% SO_2	2.00% SO_2	1.40% SO_2	0.760% SO_2	0.470% SO_2
293.15	1.58	1.50	1.37	1.10	0.639	0.456
298.15	1.85	1.78	1.62	1.37	0.691	0.519
303.15	1.99	1.94	1.75	1.52	0.770	0.621
308.15	2.42	2.37	2.16	1.73	0.896	0.68
313.15	2.77	2.71	2.47	2.04	1.08	0.790

The total S solubilities are listed in table 3 and figure 2. From table 3 and figure 2, we can find that the total S solubilities increase with the temperature, and at the same temperature, the total S solubilities increase with the SO_2 partial pressure.

CO_2 physical solubilities with equilibrium partial pressure are listed in table 4 and figure 3. From table 4 and figure 3, we can find that CO_2 solubilities decrease with the temperature, CO_2 solubilities increase with the CO_2 partial pressure.

Table 3. The total S solubility at different percentages of dilute SO_2 and CO_2 mixture gas.

	Total solubility S (mol kg^{-1})					
T (K)	2.40% SO_2	2.20% SO_2	2.00% SO_2	1.40% SO_2	0.760% SO_2	0.470% SO_2
293.15	2.99	2.79	2.54	1.92	1.08	0.731
298.15	3.17	2.99	2.72	2.15	1.11	0.778
303.15	3.22	3.07	2.78	2.24	1.16	0.863
308.15	3.53	3.38	3.08	2.37	1.25	0.897
313.15	3.67	3.54	3.22	2.56	1.36	0.966

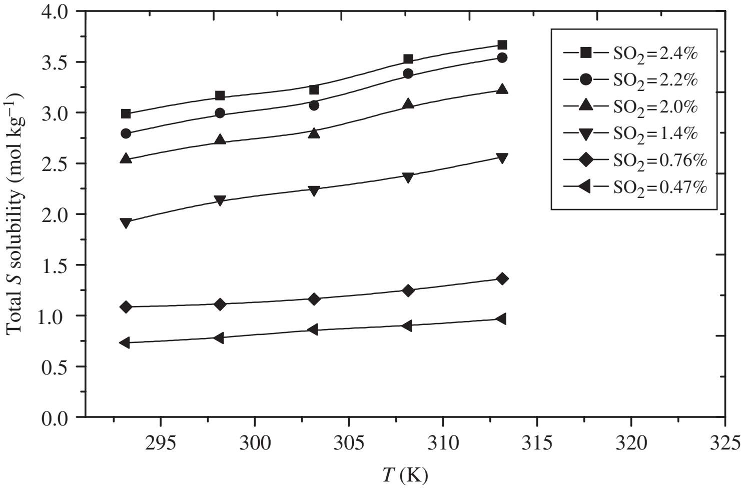

Figure 2. The relation of total solubility S with temperature at different SO_2 and CO_2 mixture gas.

Table 4. The relation of CO_2 solubility with equilibrium partial pressure.

293.15 K		298.15 K		303.15 K		308.15 K		313.15 K	
r_{CO_2}	P_{CO_2}	r_{CO_2}	P_{CO_2}	r_{CO_2}	P_{CO_2}	r_{CO_2}	P_{CO_2}	r_{CO_2}	P_{CO_2}
0.0166	13.3	0.0159	13.3	0.0153	13.3	0.0101	13.3	0.00893	13.3
0.0235	18.8	0.0224	18.8	0.0216	18.8	0.0142	18.8	0.0126	18.8
0.0151	12.1	0.0144	12.1	0.0138	12.1	0.00909	12.0	0.00808	12.0
0.0114	9.14	0.0109	9.13	0.0105	9.12	0.00688	9.11	0.00610	9.10
0.00836	6.69	0.00794	6.68	0.00764	6.67	0.00502	6.65	0.00446	6.65
0.0143	11.4	0.0136	11.4	0.0131	11.4	0.00860	11.4	0.00763	11.4

Solubility unit, mol kg^{-1}; equilibrium partial pressure unit, kPa.

The SO_2 and CO_2 solubilities and the equilibrium composition are listed in table 5. From table 5, we can find that at the same temperature and partial pressure, SO_2 solubilities is much more than CO_2 solubilities, which shows that the selected desulfuration solution have good selectivity for SO_2 and CO_2.

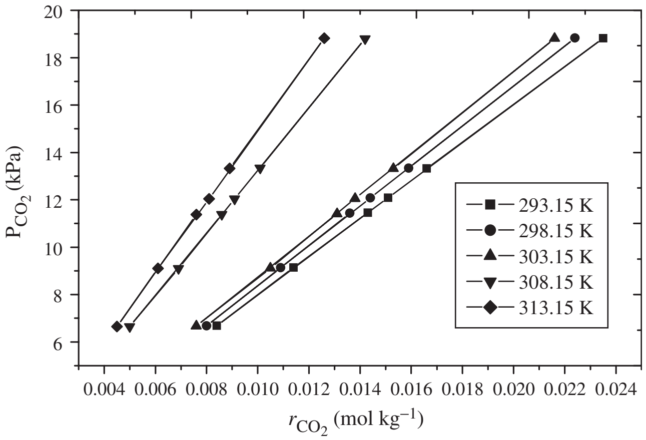

Figure 3. The relation of CO_2 solubility with equilibrium partial pressure at different temperature.

Table 5. The SO_2 and CO_2 solubilities in desulfuration solution and the equilibrium composition.

T (K)	P_{SO_2} (kPa)	P_{CO_2} (kPa)	y_{SO_2}	y_{CO_2}	y_{O_2}	y_{DMSO}	y_{N_2}
293.15	1.68	13.32	0.0168	0.133	0.120	0.00184	0.729
293.15	1.56	18.81	0.0156	0.188	0.0828	0.00181	0.712
293.15	1.39	12.08	0.0139	0.121	0.0801	0.00183	0.784
293.15	0.925	9.14	0.00924	0.0913	0.0609	0.00182	0.837
293.15	0.571	6.69	0.00571	0.0670	0.0382	0.00183	0.887
293.15	0.336	11.46	0.00338	0.115	0.0225	0.00183	0.857
298.15	1.57	13.34	0.0157	0.133	0.119	0.00259	0.729
298.15	1.47	18.83	0.0147	0.188	0.0824	0.0026	0.712
298.15	1.34	12.07	0.0134	0.121	0.0798	0.0026	0.784
298.15	0.877	9.13	0.00877	0.0913	0.0605	0.00260	0.837
298.15	0.481	6.68	0.00483	0.0670	0.0380	0.00260	0.888
298.15	0.319	11.43	0.00321	0.115	0.0225	0.0026	0.857
303.15	1.56	13.31	0.0155	0.133	0.119	0.00366	0.729
303.15	1.38	18.81	0.0138	0.188	0.0820	0.00361	0.712
303.15	1.30	12.05	0.0130	0.121	0.0795	0.00365	0.783
303.15	0.811	9.12	0.00813	0.0913	0.0602	0.00365	0.837
303.15	0.480	6.67	0.00482	0.0670	0.0379	0.00365	0.887
303.15	0.315	11.41	0.00317	0.115	0.0224	0.00366	0.856
308.15	1.50	13.34	0.0150	0.133	0.118	0.00506	0.729
308.15	1.41	18.80	0.0141	0.188	0.0807	0.00507	0.712
308.15	1.22	12.04	0.0122	0.121	0.0790	0.00507	0.783
308.15	0.807	9.11	0.00808	0.0912	0.0600	0.00507	0.836
308.15	0.446	6.65	0.00448	0.0669	0.0376	0.00507	0.886
308.15	0.294	11.39	0.00296	0.115	0.0223	0.00507	0.855
313.15	1.49	13.32	0.0149	0.133	0.118	0.00694	0.727
313.15	1.35	18.82	0.0134	0.188	0.0811	0.00702	0.71
313.15	1.22	12.04	0.0122	0.121	0.0786	0.00694	0.782
313.15	0.778	9.10	0.00777	0.0911	0.0596	0.00695	0.835
313.15	0.434	6.65	0.00437	0.0668	0.0374	0.00695	0.884
313.15	0.279	11.38	0.00281	0.115	0.0221	0.00695	0.854

(*Continued*)

Table 5. Continued.

T (K)	x_{DMSO}	$x_{\mathrm{SO_4^{2-}}}$	$x_{\mathrm{H^+}}$	$x_{\mathrm{Mn^{2+}}}$	$x_{\mathrm{SO_2}}$	$x_{\mathrm{CO_2}}$
293.15	0.809	0.102	0.200	0.00167	0.0887	0.00105
293.15	0.818	0.0979	0.192	0.00169	0.0823	0.00150
293.15	0.832	0.0907	0.178	0.00172	0.0761	0.000982
293.15	0.867	0.0765	0.150	0.00179	0.0555	0.000774
293.15	0.920	0.0478	0.0918	0.00190	0.0320	0.000601
293.15	0.943	0.0356	0.0672	0.00195	0.0203	0.000948
298.15	0.800	0.117	0.231	0.00165	0.0825	0.000991
298.15	0.808	0.114	0.225	0.00167	0.0764	0.00141
298.15	0.822	0.106	0.208	0.00170	0.0707	0.000923
298.15	0.854	0.0936	0.184	0.00177	0.0514	0.000725
298.15	0.918	0.0515	0.0991	0.00190	0.0300	0.000570
298.15	0.940	0.0401	0.0763	0.00194	0.0190	0.000892
303.15	0.797	0.125	0.247	0.00165	0.0769	0.000950
303.15	0.804	0.123	0.243	0.00166	0.0711	0.00135
303.15	0.819	0.114	0.224	0.00169	0.0659	0.000885
303.15	0.849	0.103	0.202	0.00176	0.0478	0.000693
303.15	0.915	0.0569	0.110	0.00189	0.0280	0.000546
303.15	0.934	0.0472	0.0906	0.00193	0.0177	0.000854
308.15	0.782	0.150	0.296	0.00162	0.0675	0.000615
308.15	0.789	0.148	0.292	0.00163	0.0624	0.000875
308.15	0.804	0.137	0.271	0.00166	0.0578	0.000571
308.15	0.842	0.115	0.227	0.00174	0.0424	0.000452
308.15	0.909	0.0655	0.127	0.00188	0.0248	0.000357
308.15	0.932	0.0515	0.0992	0.00193	0.0157	0.000554
313.15	0.776	0.169	0.335	0.00160	0.0546	0.000541
313.15	0.781	0.167	0.331	0.00162	0.0504	0.000771
313.15	0.797	0.155	0.307	0.00165	0.0468	0.000503
313.15	0.831	0.134	0.265	0.00172	0.0341	0.000396
313.15	0.902	0.0778	0.152	0.00186	0.0201	0.000314
313.15	0.928	0.0592	0.114	0.00192	0.0128	0.000487

4. Conclusions

(1) According to the practical engineering need of removal of sulfur dioxide selectively from flue gas with solvent method, the solubility of dilute SO_2 and CO_2 in DMSO + Mn^{2+} mixture solvent has been determined from 293.15 to 313.15 K and partial pressure of SO_2 from 0.15 to 3.0 kPa, CO_2 from 5 to 18 kPa.

(2) From the determined solubility data, we can find the developed desulfuration solution has a rather large solubility for SO_2 and less solubility for CO_2 and has a good selectivity for SO_2 and CO_2.

(3) The measured solubility data can be used as essential data to serve the process design of removal of SO_2 from flue gas.

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