

Article

The Thermodynamic and Kinetic Effects of Sodium Lignin Sulfonate on Ethylene Hydrate Formation

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S1. The interfacial tension between ethylene gas and SLS solution

Table S1. The interfacial tensions ($\text{mN}\cdot\text{m}^{-1}$) between ethylene gas and different liquids at different temperatures under 0.5 MPa.

T(K)	0.05 mass%		0.10 mass%		0.20 mass%		0.50 mass%		Pure water	
	\overline{Data}	$Data_{\sigma}$ (\pm)								
276.15	64.5	0.5	62.1	0.5	62.6	0.5	63.4	0.6	75.2	0.5
277.15	64.0	0.4	61.5	0.5	61.9	0.3	62.9	0.4	-	-
278.15	63.3	0.5	60.9	0.4	61.2	0.4	62.4	0.6	74.8	0.5
279.15	62.9	0.5	60.2	0.6	60.6	0.6	61.8	0.5	-	-
280.15	62.2	0.5	59.8	0.3	60.1	0.5	61.3	0.4	74.4	0.4
281.15	61.7	0.5	59.5	0.6	59.8	0.4	60.9	0.5	-	-
282.15	61.1	0.6	59.3	0.5	59.6	0.6	60.5	0.5	74.2	0.5
283.15	60.8	0.5	58.7	0.5	59.2	0.3	60.0	0.5	-	-
284.15	60.3	0.6	58.5	0.6	58.9	0.5	59.6	0.6	74.0	0.5
285.15	60.0	0.5	58.2	0.5	58.6	0.6	59.2	0.5	-	-
286.15	59.6	0.3	58.0	0.4	58.4	0.5	58.6	0.4	73.9	0.5

Table S2. The interfacial tensions ($\text{mN}\cdot\text{m}^{-1}$) between ethylene gas and different liquids under different pressures at 286.15 K.

w(mass%)	0.5 MPa		1.0 MPa		1.5 MPa		2.0 MPa	
	\overline{Data}	$Data_u(\pm)$	\overline{Data}	$Data_u(\pm)$	\overline{Data}	$Data_u(\pm)$	\overline{Data}	$Data_u(\pm)$
0	73.9	0.5	72.8	0.5	72.0	0.5	71.2	0.4
0.05	59.6	0.3	58.4	0.6	57.5	0.4	56.8	0.5
0.10	58.0	0.4	56.8	0.4	55.9	0.5	55.2	0.4
0.20	58.4	0.5	57.2	0.5	56.3	0.4	55.6	0.5
0.50	58.6	0.4	57.4	0.5	56.4	0.4	55.7	0.4

S2. The uncertainties caused by the uncertainties of the measurements in each individual experiment

As shown in Section 2.5, the amount of the ethylene in hydrate slurry ($N_{d,t,jjj}$, mol) at the time t in an individual experiment is calculated by Equation (1). The uncertainties in the volume of the crystallizer (± 0.05 ml), temperature ($\pm 0.05\text{K}$) and pressure (± 0.005 MPa) are considered while calculating the uncertainty in $N_{d,t,jjj}$. The maximum ($N_{d,t,max,jjj}$) and minimum ($N_{d,t,min,jjj}$) values of $N_{d,t,jjj}$ in each individual experiment due to the uncertainties of measurements are calculated by Equations (S1) and (S2). The uncertainty of $N_{d,t,jjj}$ caused by uncertainties of measurements in each individual experiment ($N_{d,t,u,jjj}$) is calculated by Equation (S3):

$$N_{d,t,max,jjj} = \frac{P_f + 0.005\text{MPa}}{Z \cdot R \cdot (T_f - 0.05\text{K})} \cdot [(V_{cr,0} + 0.05 \text{ ml}) - (V_{cr,t} - 0.05 \text{ ml})] \quad (\text{S1})$$

$$N_{d,t,min,jjj} = \frac{P_f - 0.005\text{MPa}}{Z \cdot R \cdot (T_f + 0.05\text{K})} \cdot [(V_{cr,0} - 0.05 \text{ ml}) - (V_{cr,t} + 0.05 \text{ ml})] \quad (\text{S2})$$

$$N_{d,t,u,jjj} = \max\{|N_{d,t,max,jjj} - N_{d,t,jjj}|, |N_{d,t,jjj} - N_{d,t,min,jjj}|\} \quad (\text{S3})$$

where jjj is the sequence number for the repeated experiments under the same experimental condition. The uncertainties of $G\text{SCHS}$, $R_{\text{WH,end}}$ and $w_{\text{p,end}}$ caused by the uncertainties of measurements in each individual experiment are calculated by Equations (S4) to (S10):

$$R_{\text{WH,end,max},jjj} = N_{d,t,max,jjj}/\lambda_2 / [(m_0 - m_{\text{SLS}})/M_w] \times 100\% \quad (\text{S4})$$

$$R_{\text{WH,end,min},jjj} = N_{d,t,min,jjj}/\lambda_2 / [(m_0 - m_{\text{SLS}})/M_w] \times 100\% \quad (\text{S5})$$

$$R_{\text{WH,end,u},jjj} = \max\{|R_{\text{WH,end,max},jjj} - R_{\text{WH,end},jjj}|, |R_{\text{WH,end},jjj} - R_{\text{WH,end,min},jjj}|\} \quad (\text{S6})$$

$$w_{\text{p,end,max},jjj} = m_{\text{SLS}}/(m_0 - M_w \cdot N_{d,end,max,jjj}/\lambda_2) \times 100\% \quad (\text{S7})$$

$$w_{p,end,min,jjj} = m_{SLS}/(m_0 - M_w \cdot N_{d,end,min,jjj}/\lambda_2) \times 100\% \quad (S8)$$

$$w_{p,end,u,jjj} = \max\{|w_{p,end,max,jjj} - w_{p,end,jjj}|, |w_{p,end,jjj} - w_{p,end,min,jjj}|\} \quad (S9)$$

$$GSCHS_{u,jjj} = \left| \frac{Z_{st,jjj} \cdot N_{d,end,u,jjj} \cdot R \cdot T_{st}}{P_{st} \cdot V_{sol}} \right| \quad (S10)$$

The experimental data of each individual experiment and the uncertainties caused by uncertainties of measurements in each individual experiment are shown in Table S3. It can be seen from Table S3 that the uncertainties caused by the uncertainties of the measurements in each individual experiment are much smaller than the uncertainties caused by the repeated experiments in Tables 2 and 3. For this reason, the uncertainties caused by the repeated experiments are used to describe the uncertainties of the experiments under each experimental condition.

Table S3. The effect of SLS on hydrate formation.

No.	$w_{p,0}$ (mass%)	T (K)	P (MPa)	$GSCHS$ (NL/L)	$GSCHS_u$ (NL/L)	$P_{eq,0}$ (MPa)	DRS_0 (%)	$P_{eq,end}$ (MPa)	DRS_{end} (%)	$R_{WH,end}$ (%)	$R_{WH,end,u}$ (%)	$w_{p,end}$ (mass%)	$w_{p,end,u}$ (mass%)
1	0.10	278.15	1.12	107.7	0.53	0.964	16.2	0.966	15.9	66.9	0.33	0.30	0.00
2	0.10	278.15	1.12	110.1	0.54	0.964	16.2	0.966	15.9	68.4	0.34	0.32	0.00
3	0.10	278.15	1.12	112.4	0.56	0.964	16.2	0.966	15.9	69.8	0.35	0.33	0.00
4	0.10	278.15	1.24	120.6	0.54	0.964	28.6	0.967	28.2	74.9	0.34	0.40	0.01
5	0.10	278.15	1.24	125.0	0.56	0.964	28.6	0.967	28.2	77.7	0.35	0.45	0.01
6	0.10	278.15	1.24	126.3	0.57	0.964	28.6	0.967	28.2	78.5	0.35	0.46	0.01
7	0.10	278.15	1.49	124.8	0.48	0.964	54.6	0.967	54.1	77.6	0.30	0.44	0.01
8	0.10	278.15	1.49	130.7	0.51	0.964	54.6	0.968	53.9	81.2	0.32	0.53	0.01
9	0.10	278.15	1.49	128.9	0.50	0.964	54.6	0.967	54.1	80.1	0.31	0.50	0.01
10	0.10	278.15	2.00	121.7	0.39	0.964	107.5	0.967	106.8	75.6	0.24	0.41	0.00
11	0.10	278.15	2.00	125.3	0.40	0.964	107.5	0.967	106.8	77.9	0.25	0.45	0.00
12	0.10	278.15	2.00	120.2	0.39	0.964	107.5	0.967	106.8	74.7	0.24	0.39	0.00
13	0.00	278.15	1.24	92.6	0.43	0.963	28.8	0.963	28.8	57.5	0.27	0.00	0.00
14	0.00	278.15	1.24	90.2	0.42	0.963	28.8	0.963	28.8	56.0	0.26	0.00	0.00
15	0.00	278.15	1.24	95.4	0.45	0.963	28.8	0.963	28.8	59.2	0.28	0.00	0.00
16	0.05	278.15	1.24	114.1	0.52	0.964	28.6	0.965	28.5	70.9	0.32	0.17	0.00
17	0.05	278.15	1.24	109.4	0.50	0.964	28.6	0.965	28.5	68.0	0.31	0.16	0.00
18	0.05	278.15	1.24	115.2	0.52	0.964	28.6	0.965	28.5	71.5	0.32	0.18	0.00
19	0.10	278.15	1.24	120.6	0.54	0.964	28.6	0.967	28.2	74.9	0.34	0.40	0.01
20	0.10	278.15	1.24	125.0	0.56	0.964	28.6	0.967	28.2	77.7	0.35	0.45	0.01
21	0.10	278.15	1.24	126.3	0.57	0.964	28.6	0.967	28.2	78.5	0.35	0.46	0.01
22	0.20	278.15	1.24	119.1	0.54	0.965	28.5	0.970	27.8	74.1	0.34	0.77	0.01
23	0.20	278.15	1.24	124.0	0.56	0.965	28.5	0.971	27.7	77.1	0.35	0.87	0.01
24	0.20	278.15	1.24	121.7	0.55	0.965	28.5	0.970	27.8	75.7	0.34	0.82	0.01
25	0.50	278.15	1.24	117.4	0.53	0.967	28.2	0.979	26.7	73.3	0.33	1.84	0.02
26	0.50	278.15	1.24	115.3	0.53	0.967	28.2	0.978	26.8	71.9	0.33	1.76	0.02
27	0.50	278.15	1.24	119.5	0.54	0.967	28.2	0.980	26.5	74.5	0.34	1.94	0.03

S3. The calculation of $f_{C_2H_4}^0$

$f_{C_2H_4}^0$ in Equation (12) can be calculated as follows and the corresponding parameters are listed in Table S4 [27, 39]:

$$f_{C_2H_4}^0 = f_T^0(T) \cdot \exp\left(\frac{\beta P}{T}\right) \cdot \alpha_w^{-1/\lambda_2} \quad (S11)$$

where $f_T^0(T)$ is a function of temperature, β is a parameter which depends on the structure of the hydrate. α_w is the activity of the water in the liquid phase. In this work, $f_T^0(T)$ is correlated as a function of temperature through the following Antoine-type equation [27,39]:

$$f_T^0(T) = A' \exp [B'/(T - C')] \quad (S12)$$

Table 4. The parameters for the calculation of f^0 .

Structure I	A`bar	B`/K	C`/K	β /(K/bar)	λ_1	λ_2
C ₂ H ₄	4.8418×10 ¹¹	-5597.59	51.8	0.4242	1/23	3/23

SLS solution is a kind of electrolyte solution, the thermodynamic properties of the liquid phase are calculated by the Modified Patel-Teja equation of state (MPT EOS) [45]. α_w in Equation (S11) can be calculated by Equation (S13) [27]:

$$\alpha_w = f_w/f_{w,0} \quad (S13)$$

where f_w is the fugacity of the water in the solution and $f_{w,0}$ is the fugacity of pure water. Since the contribution to the complex nature of the phase equilibria of the electrolyte system is mainly from the liquid phase, it is assumed that no ion is in the gas phase [45,50]. The fugacity coefficient of component j in liquid phase is composed of two terms: an equation of state term (short-range interactions) and a Debye-Huckel electrostatic term (long-range interionic forces) [45,50]:

$$\ln\varphi_j = \ln\varphi_{j,EOS} + \ln\varphi_{j,DH} \quad (S14)$$

where $\varphi_{j,EOS}$ is the fugacity coefficient expression derived from PT EOS [45, 50]. For ionic species, the parameter a in PT EOS is calculated by following equation [45,50]:

$$a = 15.42072\pi \cdot \varepsilon \cdot N_a^2 \cdot \psi^3 \times 10^{-13} \quad (S15)$$

where N_a is Avogadro number. ψ is ionic diameter (Na⁺: 1.92Å [27,50]). The ionic energy parameter (ε) is calculated by using the dispersion theory [45,50]:

$$\varepsilon/k = 2.2789 \times 10^{-8} \eta^{0.5} \cdot a_0^{1.5} \cdot \psi^{-6} \quad (S16)$$

where η and a_0 stand for the number of electrons in an ion and the polarizability (Na⁺: 0.18Å³ [45,50]) of an ion, respectively. k is Boltzmann constant (1.38066×10⁻¹⁶erg·K⁻¹ [45,50]). The parameters b and c can be calculated as [45,50]:

$$b = 2/3\pi \cdot N_a \cdot \psi^3 \times 10^{-6} \quad (S17)$$

$$c = b \quad (S18)$$

The $\ln\varphi_{j,DH}$ in Equation (S14) is a Debye-Huckel expression using fully dissociated salt as standard state [45,50]:

$$\ln\varphi_{j,DH} = -A'' \left[\frac{2Z_i^2}{B''} \ln \left(\frac{1 + B'' \cdot I^{0.5}}{1 + B''/\sqrt{2}} \right) + \frac{I^{0.5}Z_i^2 - 2I^{1.5}}{1 + B'' \cdot I^{0.5}} \right] \quad (S19)$$

$$I = 0.5 \sum_j x_j Z_i^2 \quad (S20)$$

$$A'' = \frac{1}{3} (2\pi \cdot N_a \cdot d_0/M_w)^{0.5} \cdot (e^2/DkT)^{1.5} \quad (S21)$$

$$B'' = 2150(d_0/DT)^{0.5} \quad (S22)$$

$$D = 78.54 \times (1 - 4.579 \times 10^{-3}tt + 1.19 \times 10^{-5}tt^2 - 2.8 \times 10^{-8}tt^3) \quad (S23)$$

$$tt = T - 298.15 \quad (S24)$$

where D stands for the dielectric constant, e stands for electronic charge (4.80656×10^{-10} esu [26, 50]), M_w is the molecular weight of water, d_0 is the density of water (g/cm^3), and Z_i is the electronic charge. It should be pointed out that the Debye-Huckel term is neglected for the gas phase. The polarizability and ionic diameter of the anion of SLS (a_0 of LS: 35.92 \AA ; ψ of LS: 23.87 \AA) were fitted using the experimental data in Section 4.1 by trial-and-error method[15] and the fitting process is shown in Section S4.

S4. Determination of the a_0 and ψ in the model by fitting experimental data

a_0 and ψ were fitted as:

1. The initial values of a_0 and ψ were set at 0.18 \AA^3 and 1.92 \AA , which are same with the values of Na^+ .
2. The method shown in Figure. 2 was used to calculate the hydrate equilibrium formation pressures of ethylene gas + SLS solution systems under the operating conditions in Table 1.
3. If most of the calculated data of the ethylene gas + SLS solution systems were higher than the experimental data, then ψ was decreased or a_0 was increased, and then the fitting process went to step 2. If most of the calculated data of the ethylene gas + SLS solution systems were lower than the experimental data, then ψ was increased or a_0 was decreased, and then the fitting process went to step 2. In the other situations, the fitting process went to step 4.
4. The *ARD*, *MRD* and *GF* were calculated. For all the data in Table 1, if *ARD* <4%, *MRD* < 5% and *GF*>0.99, then ψ and a_0 were recorded; if not, then ψ and a_0 were adjusted to further optimize the parameters, and then the fitting process went to step 2.

After above fitting process, a_0 and ψ were achieved (a_0 of LS: 35.92 \AA^3 ; ψ of LS: 23.87 \AA). The *ARD* and *MRD* of all data in Table 1 are 1.6 % and 4.7 %, respectively. The *GF* is higher than 0.994 for all the curves (3 curves) of the thermodynamic equilibrium hydrate formation pressure vs temperature in Table 1.