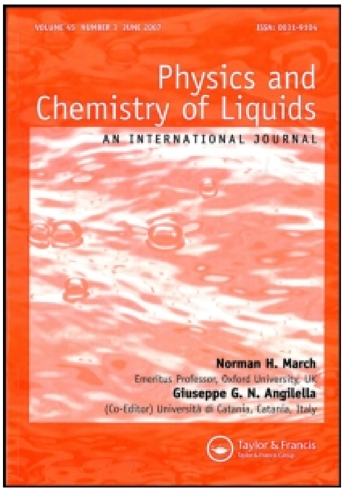

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Measurement of surface tension of desulfurization solution and thermodynamic model-(I)

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According to the need of industrial design and application of new desulfurization technique, we determine surface tension of dilute SO_2 mixture gas in DMSO and DMSO + Mn^{2+} mixture absorbents, and establish their thermodynamic model based on experimental data, and the surface tension calculated by the model shows good agreement with experimental data.

Keywords: Desulfurization solution; Surface tension; Group theory; Model

1. Introduction

With the development of economy, the problem of environment pollution has become more and more serious, in which SO_2, NO_x, and CO_2 are primary pollution sources from flue gas, and they not only break ecological balance, but also directly do great damage to people's health. It is necessary to remove SO_2 and NO_x from flue gas for protecting environment. In order to find effective method of removal of SO_2 from flue gas, various desulfurization technique [1–4] are all utilized. Compared with these methods, a liquid organic absorbent (DMSO) is selected in laboratory and will be used to remove SO_2 from flue gas to solve industrial problem for flue gas purification [5,6]. DMSO has not only strong desulfurizing efficiency, but also high regeneration efficiency and good selectivity for SO_2 NO_x, and CO_2. By adding Mn^{2+} to DMSO, the purification efficiency of the mixed absorbent has been much improved. Meanwhile, the surface tension of solution is an important physical property during the process of removal of SO_2, and their values are important in industrial design and application for flue gas removal. The change of absorbent's surface tension during the course of removal of SO_2 is one of the fundamental data in engineering design. The data available in literature were only the surface tension of pure substance. Very few experimental data for this system can be found and no suitable correlation

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model for this system can be proposed. So with the need of industrial design, in this article, we determine surface tension of dilute SO_2 mixture gas in dimethyl sulfoxide and $DMSO + Mn^{2+}$ mixture absorbents, and establish their thermodynamic model based on experimental data.

2. The measurement of surface tension

2.1. *The experimental instrument and materials*

2.1.1. The instrument. The automatic surface tension meter (JYW-200A-type, Chengde, China).

The relative error of show value of instrument is less than ±1%.
Distinguishability of instrument is $0.1\,\mathrm{mN\,m^{-1}}$.
In this instrument, the formula for calculating the correction factor F is as follows:

$$F = 0.7250 + \sqrt{0.0004040P - 0.0073979}$$

in which, P is the show value of instrument, $\mathrm{mN\,m^{-1}}$.
Actual surface tension of solution, $\sigma = P^*F$.

2.1.2. Materials. Dimethyl sulfoxide and $MnSO_4$ were of AR grade and their purity values were greater than 99%. Water was purified by vacuum distillation and deionization. The dilute SO_2 mixture was prepared by mixing sulfur dioxide, oxygen, and nitrogen. The sulfur dioxide and nitrogen had a purity $x\ (SO_2) > 0.999$, $x\ (O_2) > 0.999$, 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 the SO_2 and O_2 analysis ($\leq 0.5\%\ SO_2$) of the gas phase. The uncertainty of the SO_2 analyzer was ±10 ppm; O_2 was ±1%. More than 0.5% SO_2 concentration was analyzed by iodometry. The two methods were calibrated before measuring SO_2 concentration.

2.2. *Test of apparatus*

In order to ensure proper operation of the instrument, the surface tension of acetone was measured and compared with the values reported in the literature [7]. The experimental measurements agreed with the reported values with a mean relative deviation of 0.75%. The measured values are listed in table 1.

Table 1. Comparison of experiment data for acetone and literature data [10].

T/K	$\sigma/(\mathrm{mN\,m^{-1}})$	$\sigma(\mathrm{lit.})^7/(\mathrm{mN\,m^{-1}})$	$100(\sigma(\mathrm{lit.}) - \sigma)/\sigma(\mathrm{lit.})$
293.15	24.05	24.49	1.80
283.15	25.17	25.14	0.12
273.15	27.16	27.25	0.33

2.3. *The surface tension measurement during the process of DMSO absorbing SO_2*

A known amount of degassed absorbent is sucked into the absorption tube, and SO_2 passed through the absorption tube at a rate of 25 mL min^{-1} at different temperatures till its saturation. The uncertainty of mass was ±0.00001 g. The surface tension of the absorption solution was determined by JYW-200A-type automatic surface tension meter. The uncertainty of surface tension is ±1%. The SO_2 in the liquid was analyzed by iodometry.

The measurement results are listed in table 2 and plotted in figure 1.

2.4. *The molecule thermodynamic model of solubilities and surface tension of SO_2 in DMSO*

Based on molecule structure theory of solution derived by references [8,9], the solution property lies on interaction between molecules. Such effect is not simple plus between homogeneity molecules or heterogeneity molecules, but is a sort of complex

Table 2. The solubilities x_{SO_2} and surface tension σ of SO_2 in DMSO at 25°C.

		σ (mN m^{-1})		
x_{SO_2}	P (mN m^{-1})	Experimental value	Calculated value	RD (%)
0.01373	50.50	42.3713	42.4297	0.14
0.01915	50.60	42.4642	42.5491	0.20
0.02430	50.80	42.6499	42.6153	−0.08
0.03461	51.10	42.9288	42.6730	−0.60
0.04280	50.90	42.7429	42.6772	−0.15
0.06221	50.65	42.5106	42.6086	0.23
0.07554	50.55	42.4177	42.5235	0.25
0.09204	50.40	42.2785	42.3921	0.27
0.1186	50.25	42.1392	42.1416	0.00572
0.1376	50.15	42.0465	41.9424	−0.25

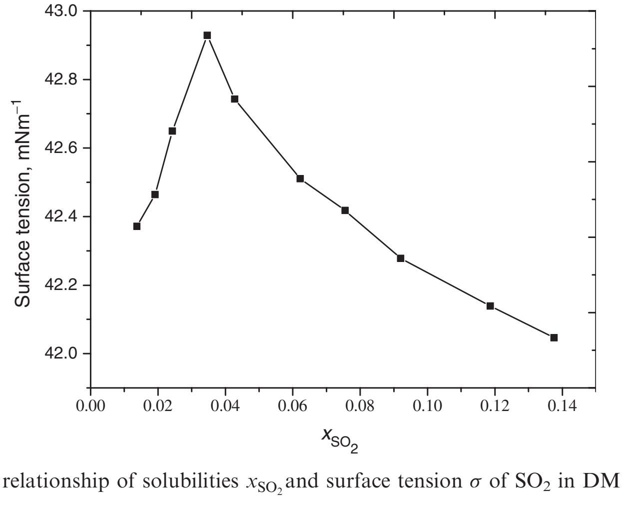

Figure 1. The relationship of solubilities x_{SO_2} and surface tension σ of SO_2 in DMSO at 25°C.

coordination behavior in integer. Compared with the pure liquid, the composition and property of solution is so unusual, in that the special group statistical systems were formed among molecules. The binary solution can be looked upon the group statistical systems formed by quantity ‘group’. Every ‘group’ is made up of some of the first sort molecule (group center) and the second kind molecule (gathered molecule). It is fundamental composition unit of solution. The degree of its composition and group gathered reflect the macroscopic property of the solution.

In the solution of unit volume, we assume

k_{ij} – interaction energy between molecules;
V – the volume held of grouped molecule (solute molecule);
V_m – the volume held of grouped molecule when single molecule thronged; and
χ – mole fraction of solution.

Then, according to group statistics theory, based on the method of Lagrange undetermined multiplier and quasi-chemical reaction mechanism, the molecular thermodynamic equation for binary solution was taken to be as follows,

$$V = V_\mathrm{m}\frac{k_{12}x(k_{21}+k_{22}x)}{k_{21}(k_{12}x+k_{11})} \tag{1}$$

The prediction model about dielectric constant, coefficient of thermal conductivity, and excess enthalpy of binary solution had been successfully established on the basis of equation (1). In this article we extended it to the calculation of surface tension of DMSO absorbing SO_2 and x_{SO_2} is the independent variable.

According to the deduction of Zhou [10], combining with Gibbs isothermal equation of adsorption, we can obtain:

$$\frac{d\sigma}{dx} = \frac{jV_\mathrm{m}k_{12}(k_{21}+k_{22}x)}{k_{21}(k_{12}x+k_{11})} \tag{2}$$

Integration of equation (2) under constant temperature and constant pressure leads to the result:

$$\sigma-\sigma_0 = \frac{jV_\mathrm{m}k_{22}}{k_{21}}x + jV_\mathrm{m}\left(1-\frac{k_{11}k_{22}}{k_{21}k_{22}}\right)\ln\left(1+\frac{k_{12}}{k_{11}}x\right) \tag{3}$$

at definite temperature and pressure:

$$a = \frac{jV_\mathrm{m}k_{22}}{k_{21}} \tag{4}$$

$$b = jV_\mathrm{m}\left(1-\frac{k_{11}k_{22}}{k_{21}k_{12}}\right) \tag{5}$$

$$c = \frac{k_{12}}{k_{11}} \tag{6}$$

The group statistical theory model of surface tension for binary solution:

$$\sigma = \sigma_0 + ax + b\ln(1 + cx) \tag{7}$$

where x is the solution composition, in this article x being explicitly the solubility of SO_2 in DMSO (mole fraction), σ is surface tension of solution, σ_0 is surface tension of pure DMSO (the measurement value of pure DMSO is $\sigma_0 = 0.03748\,\mathrm{N\,m^{-1}}$ at 25°C).

In equation (7), the adjustable parameters a, b, c, have been obtained from simplex optimization. With $F = \min\sum\left|(\sigma_{\mathrm{cal}} - \sigma_{\mathrm{exp}})/\sigma_{\mathrm{cal}}\right|^2$, the results are $a = -0.0152285$, $b = 0.000607076$, $c = 357105$. The calculated result is shown in table 2 based on these a, b, c parameters. The average relative deviation is ARD = 0.22%, the max. relative error is less than 0.60%, the surface tensions calculated by the model show good agreement with the experimental data. Obviously, the molecule thermodynamic model of solubilities and surface tension of SO_2 in DMSO established in this article is quite successful.

2.5. *The surface tension measurement of DMSO + Mn^{2+} mixture absorbent absorbing SO_2*

A known amount of DMSO + Mn^{2+} mixture solvents are sucked into the absorption tube, mixture solvents were dimethyl sulfoxide and $0.96546\,\mathrm{mol\,L^{-1}}$ $MnSO_4$ solution, which were mixed in ratio 1 : 0.03 by volume. and mixture gas containing SO_2 and O_2 go through the absorption tube at a rate of $25\,\mathrm{mL\,min^{-1}}$ at different temperatures till its saturation. The uncertainty of mass was ±0.00001 g. The whole apparatus was kept at a constant temperature inside a temperature-controlled bath. The uncertainty of temperature is ±0.05 K. The surface tension of absorption solution was determined by JYW-200A-type automatic surface tension meter. The uncertainty of surface tension is ±1%. The SO_2 in the liquid was analyzed by iodometry. The concentration of sulfate ions in the liquid were determined by barium chromate spectrophotometry (UNICO ultraviolet visible spectrophotometer).

The measurements of surface tension are presented in table 3 and figure 2.

Table 3. The total solubilities x_T and surface tension σ of SO_2 in DMSO + Mn^{2+} mixture absorbent at 25°C.

						σ ($\mathrm{mN\,m^{-1}}$)		
C_{SO_2} ($\mathrm{mol\,kg^{-1}}$)	$C_{SO_4^{2-}}$ ($\mathrm{mol\,kg^{-1}}$)	x_{SO_2}	$x_{SO_4^{2-}}$	x_T	P ($\mathrm{mN\,m^{-1}}$)	Experimental data	Calculated value	RD%
0.1117	0.2072	0.008497	0.01576	0.02426	51.6	43.3939	43.4214	0.063
0.1553	0.3592	0.01164	0.02692	0.03857	51.8	43.5801	43.8147	0.54
0.2371	0.4621	0.01753	0.03416	0.05169	52.3	44.0460	43.9355	−0.25
0.2725	0.4788	0.02007	0.03526	0.05533	52.6	44.3258	43.9449	−0.87
0.3815	0.5161	0.02780	0.03761	0.06540	52.3	44.0460	43.9321	−0.26
0.6431	0.5534	0.04586	0.03946	0.08532	51.8	43.5801	43.7871	0.47
0.8121	0.6141	0.05698	0.04309	0.1001	51.6	43.3939	43.6100	0.50
1.0273	0.6239	0.07096	0.04309	0.1141	51.5	43.3009	43.4043	0.24
1.4988	0.6876	0.09983	0.04580	0.1456	51.2	43.0218	42.8468	−0.41

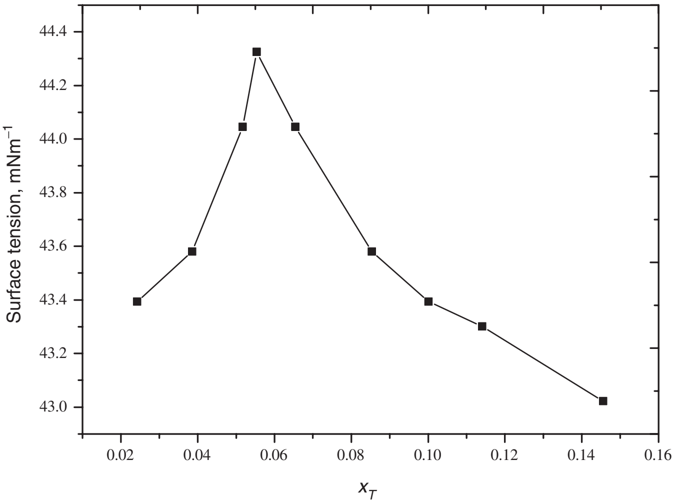

Figure 2. The relation of surface tension and SO_2 solubility x_T in the process of mixture absorbents absorbing SO_2.

2.6. *The molecule thermodynamic model of solubilities and surface tension of SO_2 in DMSO + Mn^{2+} mixture absorbent SO_2*

The essential component developed mixture absorption by this article is DMSO, small quantity is $MnSO_4$ solution. The desulfurated gas is dilute SO_2 mixture gas containing O_2 with N_2 as dilution agent. It can generate H_2SO_4 in the desulfuration process, i.e., the desulfurated solution is the complicated system made of DMSO, Mn^{2+}, SO_4^{2-}, H^+, H_2O, etc. Considering the engineering goal (in this article) is removal of SO_2, for convenience research, we assume the total solubility x_T (i.e., the sum of physical solubility x_{SO_2} and chemical reaction solubility $x_{SO_4^{2-}}$) as an independent variable. The mixture absorbent is a fictitious solute, therefore the above-mentioned molecule group model of surface tension about binary solution can extend this fictitious binary system. Writing

$$\sigma = \sigma_0 + ax + b\ln(1 + cx) \tag{8}$$

where in equation (8), x denotes the total solubility of SO_2 in mixture absorbents, σ is surface tension corresponding to x, σ_0 is surface tension at $x = 0$, i.e., absorbents unabsorbed SO_2 ($\sigma_0 = 0.03748\,\mathrm{N\,m^{-1}}$ determined by experiment at 25°C). In equation (8), the adjustable parameters a, b, c can be obtained from simplex optimization.

The object function

$$F = \min \sum \left|\sigma_{\mathrm{cal}} - \sigma_{\mathrm{exp}}\right|^2$$

the result being $a = -0.0322055$, $b = 0.0018851$, $c = 1417.29$. The calculated results are shown in table 3. The average relative deviation ARD is 0.36%, the maximum relative deviation is less than 0.87%, the surface tensions calculated by the model show good agreement with the experimental data. Certainly we can also predict SO_2 solubility with the experimental value of surface tension according equation (8). Obviously, the molecule thermodynamic model of solubilities and surface tension of SO_2 in mixture absorbents established in this article is successful.

3. Conclusion

The surface tensions of absorbent for DMSO and $DMSO + Mn^{2+}$ were measured at different SO_2 partial pressure according to the need of industrial design.

The model of surface tension with solubility was proposed according to the group statistical theory, and the surface tensions calculated by the model show good agreement with the experimental data.

The surface tension and correlation model in this work can be used to serve the process design of removal of SO_2 from flue gas.

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