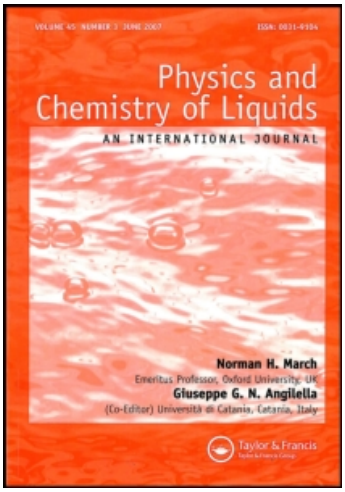

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Surface tension of desulfurization solution and thermodynamic model (II)

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According to the need of industrial design and application of a new desulfurization technique, we determined surface tension of dimethyl sulfoxide and Mn^{2+} absorbents, and established their thermodynamic model based on experimental data; the surface tension calculated by the model had good agreement with experimental data.

Keywords: Desulfurization absorbents; Surface tension; Group theory

1. Introduction

Removal of SO_2, CO_2 and other acidic gases from flue gas is one of the very important research projects in the world. In order to find an effective method for the removal of SO_2 from flue gas, various desulfurization techniques [1–6] are utilized. Compared with these methods, a liquid organic absorbent dimethyl sulfoxide (DMSO) and $MnSO_4$ solution were respectively selected in laboratory. DMSO has not only strong desulfurizing efficiency, but also high regeneration efficiency and good selectivity for SO_2 NOx and CO_2. $MnSO_4$ solution has also good desulfurizing efficiency. The surface tension of desulfurization solution is an important physical property during the process of removal of SO_2, and quantitative values are needed in industrial design and application for flue gas removal. The change of the absorbent's surface tension during the process of removal of SO_2 is one of the fundamental data in engineering design. The data available in the literature were only the surface tension of pure substance; very few experimental data for this system can be found and no suitable correlation model for this system has been proposed. Therefore with the needs of industrial design, we have determined the surface tension of DMSO and $MnSO_4$ solution, and have established a model of group theory based on the experimental data.

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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 accuracy of the instrument is less than ±1%, the sensitivity of instrument is 0.1 mN m^{-1}.

$$\sigma = P * F$$

in which, σ – actual surface tension of solution, P – the show value of instrument (mN m^{-1}) and F – correction factor. In this instrument, the calculated formula of correction factor F is as follows,

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

2.1.2. Materials. Dimethyl sulfoxide and $MnSO_4$ were AR grade and their purity were greater than 99%. Water was purified by vacuum distillation and deionization.

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 1.19%. The measured values are listed in table 1.

2.3. *The surface tension measurement of $MnSO_4$ solution*

The different concentration of $MnSO_4$ solution was prepared by adding 1 M $MnSO_4$ standard solution and suitable water. The surface tension of absorption solution was determined using JYW-200A-type automatic surface tension meter. The uncertainty of surface tension was ±1%. The measurement result of surface tension is listed in table 2 and figure 1.

2.4. *The molecule thermodynamic model of surface tension of $MnSO_4$ solution*

Based on the 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 molecule or heterogeneity molecule, but is a sort of complex coordination behavior in integer. Compared with the pure liquid, the composition

Table 1. Comparison of experiment data for acetone and literature data [7].

T (K)	σ (mN m^{-1})	σ (lit.) (mN m^{-1})	[100(σ(lit.)−σ)/σ(lit.)]
298.15	23.15	23.46	1.32
308.15	22.27	22.34	0.31
313.15	21.36	21.78	1.93

Table 2. The mole concentration of $MnSO_4$ solution x_{MnSO_4} and surface tension σ at 25°C.

C_{MnSO_4} (mol kg^{-1})	x_{MnSO_4}	P (mN m^{-1})	σ (mN m^{-1})		RD%
			Experimental data	Calculated data	
0.060	0.001079	81.40	72.0104	73.8239	2.46
0.070	0.001258	81.20	71.8129	73.4816	2.27
0.080	0.001438	80.90	71.5168	73.1395	2.22
0.085	0.001528	80.80	71.4181	72.9695	2.13
0.090	0.001617	81.00	71.6155	72.7975	1.62
0.095	0.001707	81.40	72.0104	72.6265	0.85
0.100	0.001797	82.10	72.7022	72.4556	−0.34
0.110	0.001976	82.60	73.1968	72.1138	−1.50
0.120	0.002155	82.80	73.3948	71.7722	−2.26
0.130	0.002335	82.85	73.4443	71.4307	−2.82

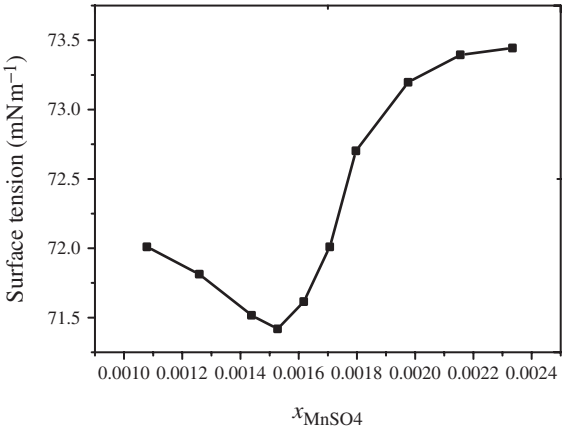

Figure 1. The relationship of x_{MnSO_4} and surface tension σ at 25°C.

and property of solution is so unusual, in that the special group statistical systems were formed among molecule. The binary solution can be looked upon as the group statistical systems formed by quantity "group". Every "group" is made up of some of the first sort molecules (group center) and the second kind molecules (gathered molecule). It is fundamental composition unit of solution. The degree of its composition and group gathered reflects the macroscopic property of solution.

In the solution of unit volume, if we assume

k_{ij} – interaction energy between molecules, J;
V – the volume held by grouped molecule (solute molecule);
V_m – the volume held by grouped molecule when single molecule is 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:

$$V = \frac{V_m[k_{12}x(k_{21} + k_{22}x)]}{[k_{21}(k_{12}x + k_{11})]}. \quad (1)$$

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 $MnSO_4$ solution. x_{MnSO_4} is an independent variable.

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

$$\frac{d\sigma}{dx} = \frac{jV_m k_{12}(k_{21} + k_{22}x)}{[k_{21}(k_{12}x + k_{11})]}. \tag{2}$$

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

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

at definite temperature and pressure:

$$a = \frac{jV_m k_{22}}{k_{21}} \tag{4}$$

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

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

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 Mn^{2+} mole fraction, σ is surface tension of solution, σ_0 is surface tension of pure water (the measurement value of pure water is $\sigma_0 = 0.07588\ N\ m^{-1}$ at 25°C).

In equation (7), the adjustable parameters a, b, c, have been obtained from simplex optimization.

With $F = \min\sum|(\sigma_{cal} - \sigma_{exp})/\sigma_{cal}|^2$, the results are $a = -1.90576$, $b = 0.0777165$, $c = -0.00151999$. The calculated result is shown in table 2 based on these a, b, c parameters. The average relative deviation (ARD) is 1.85%, the maximal relative error is less than 2.82%, and the surface tension calculated by the model show good agreement with the experimental data. Obviously, the molecule thermodynamic model of concentration and surface tension established in this article is quite successful.

2.5. *The surface tension measurement of DMSO solution*

A different concentration DMSO solution are prepared by adding pure DMSO and water. The measurements of surface tension are presented in table 3 and figure 2.

Table 3. The mole concentration of DMSO x_{DMSO} and surface tension σ at 25°C.

Volume percent of DMSO	x_{DMSO}	P (mN m^{-1})	σ (mN m^{-1})		RD%
			Experimental data	Calculated data	
1.0	1	50.20	42.0928	41.9260	−0.40
0.9	0.6956	47.50	39.5956	38.5018	−2.84
0.8	0.5039	43.50	35.9256	36.8775	2.58
0.7	0.3720	42.35	34.8772	36.2236	3.72
0.6	0.2758	43.00	35.4694	36.1881	1.99
0.5	0.2025	44.80	37.1144	36.6204	−1.35
0.4	0.1448	45.95	38.1692	37.4839	−1.83
0.3	0.09813	48.10	40.1492	38.8483	−3.35
0.2	0.05968	49.70	41.6292	40.9738	−1.60
0.1	0.02744	51.30	43.1148	44.7921	3.74

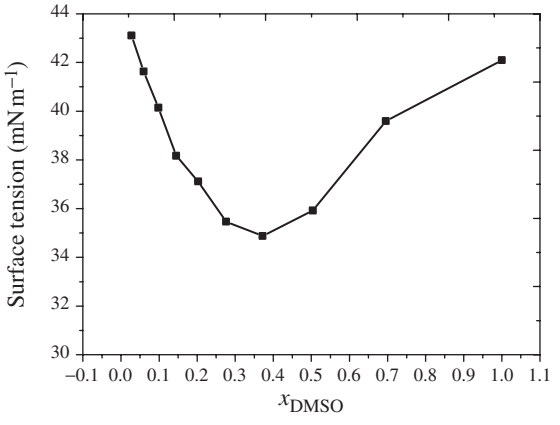

Figure 2. The relation of surface tension σ and x_{DMSO} at 25°C.

2.6. *The molecule thermodynamic model of surface tension of DMSO solution*

Writing

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

where in equation (8), x denotes the concentration of DMSO, σ is surface tension corresponding to x, σ_0 is surface tension at $x = 0$, i.e., pure water $\sigma_0 = 0.07588$ 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

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

the result being $a = -1.90576$, $b = 0.0777165$, $c = -0.00151999$. The calculated results are shown in table 3. The ARD is 2.34%, the maximum relative deviation

is less than 3.74% and the surface tensions calculated by the model show good agreement with the experimental data.

3. Conclusion

The surface tension of absorbent for different concentration of DMSO and $MnSO_4$ were measured at 25°C, in this study, according to the need of industrial design.

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

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