

EXPERIMENTAL STUDY ON CONTACT ANGLE OF ETHANOL AND N-PROPANOL AQUEOUS SOLUTIONS ON METAL SURFACES

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Abstract

Experimental studies on the contact angles of aqueous solution of ethanol and that of n-propanol on copper, aluminum and stainless steel surfaces are reported in this paper. The contact angles were measured under atmospheric condition, and then under vapor-liquid equilibrium conditions at different temperatures. The results showed the variations of the contact angles with concentrations of aqueous solutions on different metal material surfaces with different roughness. Some unstable behaviours of the wetting ability around the azeotropic point of a binary solution are reported. The influences of concentration, kind of materials and the surface roughness on the wetting ability are discussed.

Keywords: contact angle, alcohol aqueous solution, metal surface, wetting ability

1. Introduction

Wetting ability of liquid on packing surface is of great importance for gas-liquid contactors, such as distillation and absorption columns, especially for the cases where alcohol aqueous solution is involved. Contact angle of liquid on solid surface, which is the result of balance of the interfacial tensions of the three phases, is one of the key parameters reflecting the wettabilities. Methods and apparatus for studying contact angle have been well established^{1, 2} since Young Equation was proposed. Contact angles can be measured by sessile drop method³, pendent bubble method⁴, Wilhelmy method and specular reflection method^{3, 4} and parallel light beam method¹. With extensive applications of computers, Neumann et al² developed an Axisymmetric Drop Shape Analysis-Profile (ADSA-P) measurement system, which is reported to be able to improve measurement precision⁵⁻¹⁰. The hysteresis produced by solid surface roughness and heterogeneous has been examined^{11, 12}, and the theoretical understanding of the relationship between the contact angle and the dimensions of liquid drop was greatly advanced¹³⁻¹⁵. Most of these works have been mainly for contact angle of pure liquid under atmosphere condition. However, in real chemical process operations, the wetting of liquid on solid surface are usually under vapor liquid equilibrium or saturated conditions, and studies on contact angle under such a condition have been rarely reported because of the difficulties in the experimental measurement. In the present paper, contact angle of ethanol and n-propanol aqueous solutions on metal surfaces under vapor liquid equilibrium conditions were measured based on ADSA method. The alcohol aqueous were selected since their wettabilities vary greatly with composition and play an important role in mass transfer behavior. The relationships between contact angle and mixture composition as well as metal surface roughness are also presented.

2. Experimental material and method

2.1 Material and Apparatus

Metal materials used in the experiments are copper, stainless steel and aluminum sheets with a thickness of 0.15mm. Stainless steel was supplied by Tianda Beiyang Chemical Equipment Co., Ltd and the aluminum sheets used are signed as AL_1 (Specification: EN485 1050A H12; Supplier: CORUS Aluminum) and AL_2 (Specification: EN485 1050 H22; Supplier: Pechiney Rhenalu). Copper was supplied by Metelec Ltd and its specification is BS2870 C101. Ethanol and n-propanol used in experiments are analytically pure (more than 99.7% and 99.8% of weight fraction for ethanol and n-propanol respectively).

The experimental apparatus include a contact angle measurement cell under vapor-liquid equilibrium condition and a data collecting system as shown in Figure 1. The measurement cell in which the vapor-liquid equilibrium condition is provided is a total reflux distillation apparatus. It consists of a

quadruple mouth bottle and a glass chamber with sample platform in it. Three mouths are used for thermometer, reflux and feeding respectively. There are two optical windows in the both sides of the chamber. Through the windows light was supplied and pictures were taken by CCD. The testing metal sheet was conglutinated on a glass flat that is put on the sample platform. The liquid drop was fed onto the metal sheet surface through the mouth just over the sample platform in the upper part of the chamber. There is a liquid reservoir near and on the same level of the sample platform. Liquid sample was taken out of system from the reservoir for composition analysis by gas chromatography HP4890D at the same time of contact angle measurement. The flask was heated by oil bath, the chamber was wrapped by heater band and asbestos. The heating was controlled to keep an isothermal condition. Up-flowing vapor was condensed by ball condenser to reflux to the bottle. There are two thermometers, whose precisions are 0.1°C , fixed in the bottle and in the chamber to monitor the equilibrium conditions, which was considered as to be achieved when the temperature difference was within 1°C . Liquid samples used in experiments were weighed by Mettler AE163 electronic balance and their compositions were measured by gas chromatography HP4890D. Data collecting system includes a CCD (MTV-1881EX supplied by MINTRON corporation) supported by a high speed picture collecting card (OK-M10A supplied by Beijing Jointhope Image Tech Ltd) installed in a PC. Pictures taken by the system for contact angle measurement can be seen in figure 5.

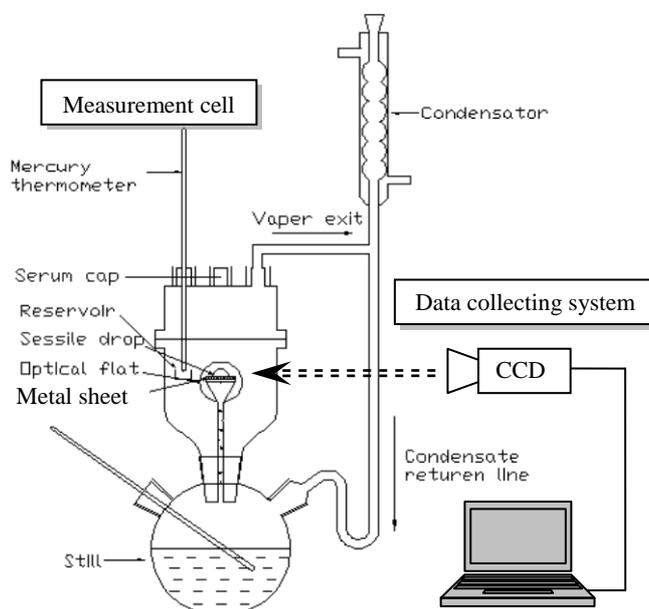


Figure 1. Contact angle measurement cell under vapor liquid equilibrium condition

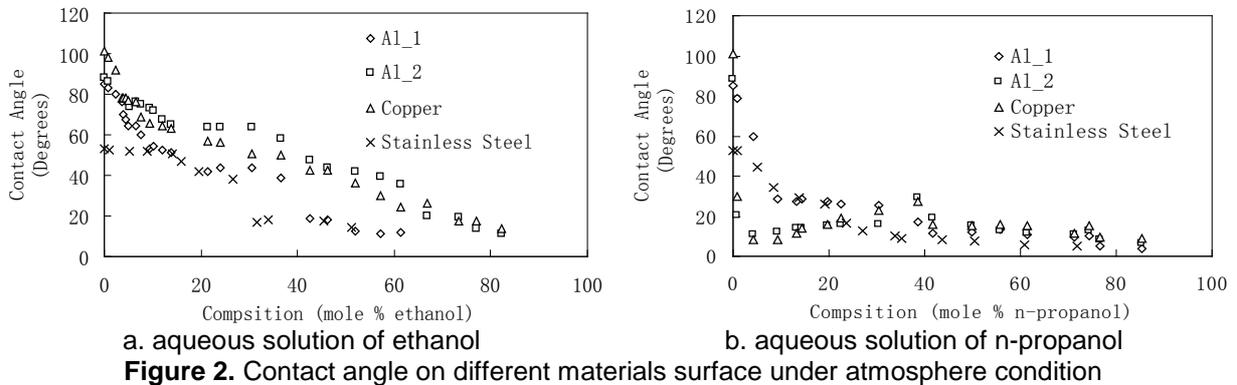
2.2 Experimental process

For the contact angle measurements in atmospheric condition, a goniometer was used. Liquid drop of $5\ \mu\text{l}$ in volume with a given concentration of ethanol was dispatched onto the metal sheet surface on the testing platform of JY-82 goniometer by sample syringe. Three contact angle measurements were taken by the goniometer eyepiece for the same concentration. The presented contact angle corresponding to each concentration aqueous is the average value of the three measurements. The same procedure was used to measure the contact angle of n-propanol. For the measurements in vapour-liquid equilibrium condition, the apparatus in figure 1 was applied. After putting the testing metal sheet on sample platform and filling quadruple mouth bottle with 500 ml ethanol solution, the system was heated to a desired temperature. When the temperature difference between the upper thermometer and that in quadruple mouth bottle was within 1°C (about 2 hours needed), then liquid drop was dipped on the metal surface, and at the same time, pictures were collected. In the experiments, the concentration of mixture was changed by adding ethanol in the still gradually. The same method was used to measure contact angles for n-propanol. Two metal surface roughness were fabricated by using 500# sand cloth and 2# sand paper scraping 30 times respectively, along one direction and then perpendicularly for another 30 times, they are then washed with water, then dunking in acetone for twenty minutes and washing again with water.

3. Experimental results and discussion

3.1 Contact angles under atmosphere condition

The measurement results of contact angles of ethanol and n-propanol aqueous solutions with various mole fractions on smooth metal surfaces under atmosphere are shown in figure 2 a and b.



It can be seen from figure 2a that contact angle decreases with the increase of ethanol concentration and the liquid totally spreads finally on all the metal surfaces. At a same concentration, stainless steel gives the least contact angle and seem to be most conducive to liquid spread compared with the other tested materials. Comparing with ethanol, Figure 2b shows that with the increase of its concentration, contact angles of n-propanol aqueous on all the material surfaces decrease faster at lower concentrations and then keeps low after 10% of n-propanol mole fraction. This indicates a better wettability of n-propanol aqueous than that of ethanol on the tested materials. As noted in figure 2a and b, the two aluminum surfaces conduct differently in wettability for ether of the two solutions

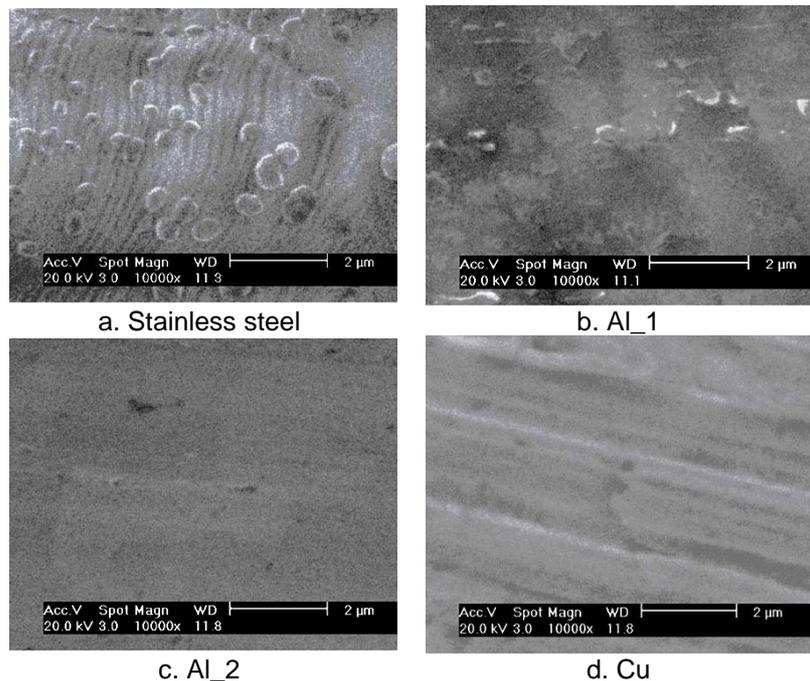
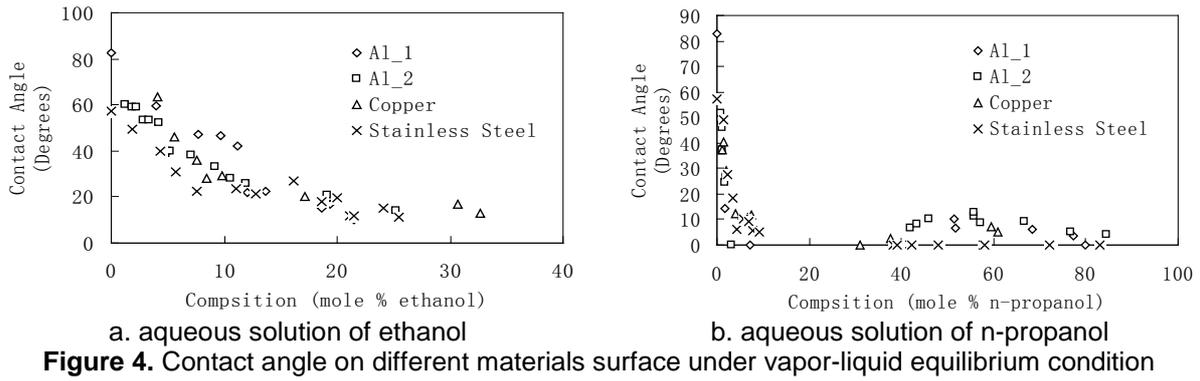
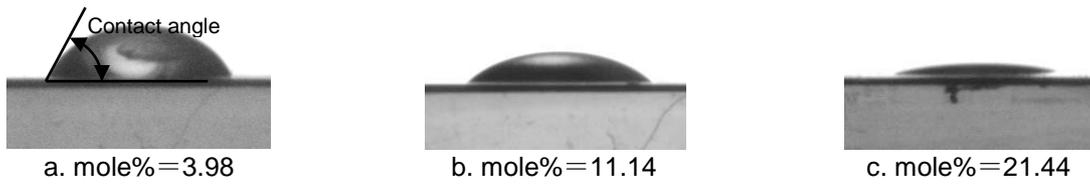


Figure 3. Texture of different metal surfaces scanned by electronic microscope

The surface tensions, which determine contact angles, of both the ethanol and n-propanol are smaller than that of water, so the surface tensions of the aqueous solutions decrease with the increase in the alcohol concentrations. This explains the behaviors of the variations of the contact angles with the increase of alcohol concentrations as demonstrated in fig.2. Figure 3 shows the surface configurations of the four experimental metal surfaces, taken by electron microscopic autoradiography magnifying 10000 times of actual dimension. Comparing (b) with (c) in figure 3, it can be seen that the difference of the two aluminum surface structure is significant, and Al₂ is smoother than Al₁. With the measurement results in fig. 2, this indicates that surface structure of a material may affect its wetting ability.



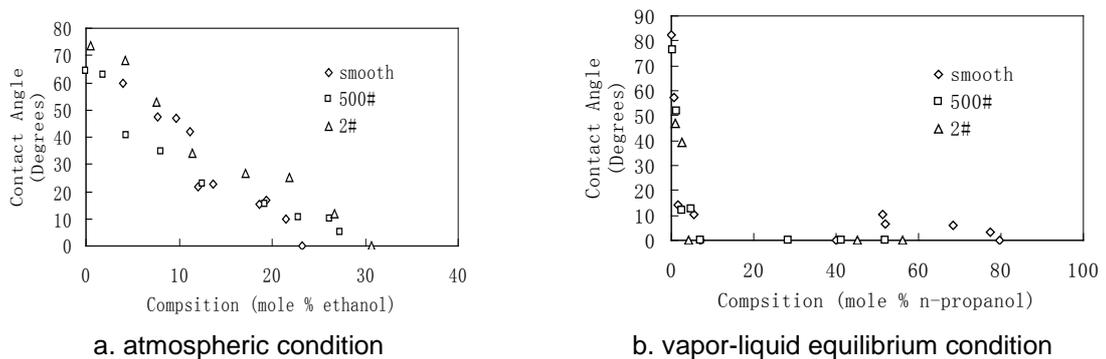
a. aqueous solution of ethanol
b. aqueous solution of n-propanol
Figure 4. Contact angle on different materials surface under vapor-liquid equilibrium condition



a. mole%=3.98
b. mole%=11.14
c. mole%=21.44
Figure 5. Variation of contact angles with different ethanol concentrations on Al_1 surface

3.2 Contact angle varies with concentration under vapor-liquid equilibrium conditions

Contact angles of ethanol and n-propanol aqueous solutions on smooth metal surfaces under vapor liquid equilibrium condition are measured and the variations of the contact angle with ethanol and n-propanol mole fractions are given in figure 4. Some images demonstrating the variation of contact angles with different ethanol concentrations on Al_1 surface are given in figure 5. It can be seen from figure 4a that the variation on the contact angle vs ethanol concentration exhibit the same trend with those under atmospheric condition in figure 2a, but with much lower value magnitude. This indicates that the wetting ability of the tested metal surfaces under vapor liquid equilibrium condition is higher than that under the atmospheric condition. As noted in figure 4b, with the increase of n-propanol mole fraction, the contact angle of n-propanol aqueous on the metal surfaces decreases rapidly at lower concentration, then becomes constant and close to zero as n-propanol mole fraction is over 10%. However, when the concentration passes 40%, the contact angle variations undergo a gurgitation within the concentration interval of 40-62% for copper, 40-80% for Al_1 and 40-85% for Al_2. Actually, in the experiments it was found that for an n-propanol mole fraction around these intervals, the wetted boundary on the metal surface appeared to be unstable and the droplet moved back and forth on the metal surface. But these phenomena have not happened on the surfaces of stainless steel.



a. atmospheric condition
b. vapor-liquid equilibrium condition
Figure 7. Contact angle of ethanol aqueous on Al_1 surface with different roughness

Surface tension of pure liquid decreases with increase of temperature and so does the contact angle. For binary systems, the mixture with a volatile component having lower surface tension is termed as “positive system”. But for a azeotropic mixture, there may be a transition between “positive” and “negative” as the concentration comes across a azeotropic point. Near the turning point, contact angle changes acutely and wetted boundary of liquid on metal surface appears to be unstable because Marangoni convection, a phenomenon for a positive system and may favor liquid spreading,

disappears. In mass transfer apparatus, this phenomenon may destroy liquid film on metal surface and in some cases results in a strong effect on mass transfer.

3.3 Effect of metal surface roughness on contact angle

Selected results of contact angle of ethanol and n-propanol aqueous on treated metal surfaces are shown in Figure 7. It can be seen from the figures that the improvement of wetting ability on a metal surface by changing its roughness through mechanical treating is ineffective. Lin et al¹⁴ presented that contact angle changes only when the three-phase line is on mechanical dentations or indentations. Our results revealed that mechanical treating in our experiments was not enough to produce a mechanical dentations and indentations inducing three-phase line changes. Thus, any difference between the results shown in figure 7 and those without treatment can be known as stochastic effects from the experiments.

3.4 Modeling of contact angle

Modeling for the contact angle is made by data fitting with Young Equation. This equation is written as $\gamma^L \cos(\theta) = \gamma^S - \gamma^{SL}$ where γ^L , γ^S and γ^{SL} are interfacial tension of liquid, solid and solid-liquid respectively, and θ is the contact angle. An exponential function is used for the data fitting with the alcohol concentration. For the liquid surface tension, we use

$$\gamma^L = C_A \exp(C_B x) + C_C \exp(C_D x) \quad (1)$$

Where x is the mole fraction of the alcohol in the aqueous solution. And for the contact angle we use

$$\gamma^L \cos(\theta) = \gamma^S - \gamma^{SL} = a_1 \exp(a_2 x) + a_3 \exp(a_4 x) \quad (2)$$

In equation (1) and (2) C_A through C_D and a_1 through a_4 are the constants to be determined by fitting the experimental data. The contact angle of an alcoholic solution in its saturated condition should be related to the vapor-liquid interfacial tension, which is not available for the authors. For modeling purpose, we assume that the interfacial tension in a saturated condition is only a function of temperature, and the interfacial tension and temperature dependence law $\gamma^L = \Gamma(1-T/T_C)^n$ could be applied, where Γ is a constant, T_C is the critical temperature of the mixture and $n=1.21$. So the liquid surface tension at a boiling temperature (saturated condition) can be determined as

$$\gamma_s^L = \gamma^L \left(\left(1 - \frac{T}{T_C} \right) / \left(1 - \frac{25 + 273}{T_C} \right) \right)^n \quad (3)$$

For data fitting, equation (2) is used again, with γ^L is replaced by γ_s^L . The results of the constants obtained by data fitting and the corresponding errors are summarized in table 1. The predictions of the contact angle in various conditions for the two alcoholic aqueous solutions are shown in figure 8. It can be seen from fig. 8 and table 1 that the predictions are pretty good for ethanol aqueous for both conditions. The predictions for n-propanol lose accuracy due to the wetting behaviors around the azeotropic point.

4. Conclusions

Under atmosphere as well as vapor-liquid equilibrium conditions contact angles of the aqueous solutions on different metal surfaces were experimentally studied and found to decrease with the increase of alcohol mole fraction. The wetting ability of the aluminum surfaces of different type showed some moderate variations. Stainless steel surface seems to be most conducive to liquid spread compared with other studied materials. Under vapor liquid equilibrium mass transfer condition, contact angles decrease with the increase of ethanol mole fraction, and are smaller than those under atmosphere at the same concentration. Contact angle decreases rapidly with n-propanol mole fraction increasing at very low concentration and increases at the azeotropic concentration. This is expected from a surface tension positive system. As approaching azeotropic conditions, the wetted boundary of n-propanol aqueous on metal surface appears to be unstable due to lack of Marangoni mass transfer driving force. At higher n-propanol concentration, "surface tension negative system", a moderate increase in the contact angle was observed, the liquid surface tend to contract and discourage spreading. The industrial application of this detailed study is immense and points at particular care in optimum design of the packed column, such as structured packing to avoid "pitfalls" of surface tension.

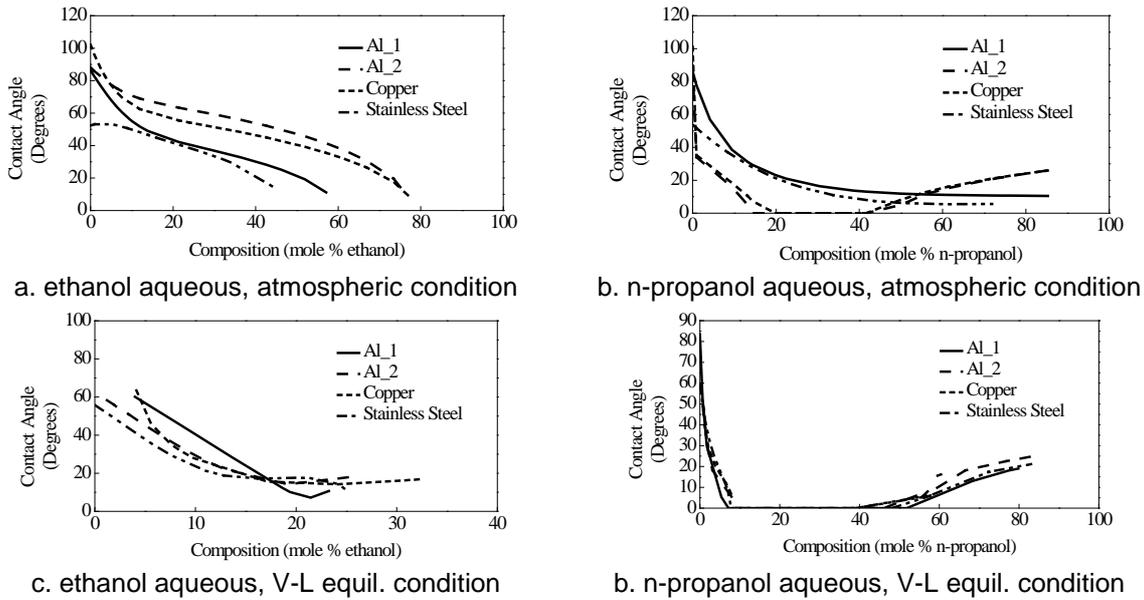


Figure 8. Model predictions for contact angles

Table 1. Values of model constant by data fitting

Condition	Material	C _A	C _B	C _C	C _D	a ₁	a ₂	a ₃	a ₄	Avg. Err	Mean Abs. Err
Ethanol aqueous solution											
Atmosphere	Al_1					20.95	0.28	-16.40	-26.54	2.9195	8.5362
	Al_2					11.00	0.94	-8.77	-32.91	-0.846	8.0334
	Copper					15.23	0.51	-30.06	-33.99	-2.007	8.6162
	Stls Steel					22.91	-26.28	20.2	0.5338	2.5674	13.7987
Vapor-liquid equilibrium	Al_1	38.05	-21.26	32.58	-0.46	-29.38	6.28	46.05	5.06	0.1239	31.5591
	Al_2					-42.96	2.29	67.59	1.49	-1.152	9.8601
	Copper					26.83	-0.76	-530.60	-97.57	-1.388	9.1071
	Stls Steel					0.002	28.24	29.66	-1.44	-1.529	15.9869
n- propanol aqueous solution											
Atmosphere	Al_1					49.91	-0.15	-45.04	-28.14	2.714	18.8994
	Al_2					59.12	-0.45	-56.58	-2601.0	-1.811	64.0089
	Copper					58.22	-0.43	-72.27	-3003.0	9.9448	43.357
	Stls Steel					51.07	-0.16	-7.90	-13.60	-0.162	9.1378
Vapor-liquid equilibrium	Al_1	22.04	-9.88	50.95	-0.15	49.08	-0.67	-43.09	-136.50	27.2527	34.9931
	Al_2					49.81	-0.73	-32.56	-99.25	4.5046	42.7994
	Copper					47.51	-0.68	-37.53	-128.50	12.7901	22.4101
	Stls Steel					47.91	-0.65	-20.85	-63.62	52.3788	55.4327

*Err=100(Calculated θ - Experiment θ)/(Experiment θ)
 Avg. Err = (Σ%Err)/number of data points
 Mean Abs. Err = (Σ|%Err|)/number of data points

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