Surface Tension of HFC Refrigerant Mixtures [1]

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1 Paper presented at the Thirteenth Symposium on Thermophysical Properties, June 22-27, 1997, Boulder, Colorado, U.S.A.

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ABSTRACT

The surface tension of refrigerant mixtures, i.e., R-410A (50mass% R-32 / 50mass% R-125), R-410B (45mass% R-32 / 55mass% R-125), R-407C (23mass% R-32 / 25mass% R-125 / 52mass% R-134a), R-404A (44mass% R-125 / 52mass% R-143a / 4mass% R-134a) and R-507 (50mass% R-125 / 50mass% R-143a), has been measured and correlated in the present study. Although the first three mixtures are very important as promising replacements for R-22 in air-conditioners and heat-pumps and the last two are promising replacements for R-502, the surface tension data of these mixtures were not available. The measurements were conducted under conditions of coexistence of the sample liquid and its saturated vapor in equilibrium. The differential capillary rise method (DCRM) was utilized using two glass capillaries with inner radii of 0.3034 ± 0.0002 mm and 0.5717 ± 0.0002 mm, respectively. The temperature range covered was from 273 K to 323 K and accuracy of measurements for surface tensions and temperatures is estimated to be at most ±0.2 mN/m and ±20 mK, respectively. A mixing rule was discussed for representing the temperature dependence of the resultant data. These data were successfully represented by a mixing rule using mass fraction based on the van der Waals' correlation.

KEY WORDS: differential capillary-rise method; mixtures; R-410A; R-410B; R-407C; R-404A; R-507; refrigerants; surface tension.

1. INTRODUCTION

As the phasing out of hydrochlorofluorocarbons (HCFC) has started because of its ozone depletion potential, the mixtures of hydrofluorocarbons (HFC) are supposed to be the most promising alternatives to the R-22 and R-502, which are the most widely used refrigerants at the present. Surface tension is a basic thermophysical property with respect to a vapor-liquid interface and is required to analyze the heat transfer during boiling and condensation in refrigeration and heat pump systems. This paper presents the surface tension measurements for five refrigerant mixtures, i.e., R-410A (50mass% R-32 / 50mass% R-125), R-410B (45mass% R-32 / 55mass% R-125), R-407C (23mass% R-32 / 25mass% R-125 / 52mass% R-134a), R-404A (44mass% R-125 / 52mass% R-143a / 4mass% R-134a) and R-507 (50mass% R-125 / 50mass% R-143a). The first three mixtures are very important as promising replacements for R-22 in air-conditioners and heat-pumps and the last two are promising replacements for R-502. In addition, a mixing rule is discussed for representing the temperature dependence of the resultant data.

2. EXPERIMENTS

The experimental technique employed in obtaining surface tension data was based on the differential capillary-rise method, which is known to be one of the most accurate methods. We have reported the measurements of surface tension for the alternative refrigerants for chlorofluorocarbons (CFC) by the differential capillary-rise method [1, 2, 3] and the same apparatus and procedure which was explained in these previous works are also used in the present study.

In this method, two different capillaries with larger and smaller radii r_1 and r_2 were used. The measured difference in the heights between the menisci in two capillaries was corrected for the amount of material held above the meniscus. This was

accomplished using Rayleigh's correction [4]. Then, surface tension σ was determined using the corrected difference in the heights (h_1 - h_2) by the following relation.

$$\sigma = \frac{g(\rho' - \rho'')(h_1 - h_2)}{2(1/r_1 - 1/r_2)\cos\theta} \qquad (1)$$

where θ denotes the contact angle of the liquid-vapor meniscus at the inner surface of capillary, g is the local gravitational acceleration at Iwaki, Japan (= 9.8002 m•s^{-2}), and ρ' and ρ'' are the saturated vapor and liquid densities, respectively.

Two Pyrex glass capillaries were placed vertically in a pressure vessel composed of a thick-walled Pyrex glass tube (17 mm in inner diameter and 25 mm in outer diameter). The inner radii of two capillaries are 0.3034 ± 0.0002 and 0.5717 ± 0.0002 mm, respectively. These radii were determined by means of a mercury thread. The pressure vessel was installed in the thermostated bath. The temperature in the bath was maintained constant to within ±5 mK and measured based on ITS-90.

The difference in rise heights in the capillaries was determined by the measurement of the location of meniscus in each capillary. The location of the bottom of meniscus was measured through the window of the thermostated bath by a traveling microscope with an uncertainty of ± 0.02 mm. The contact angle θ is assumed to be zero, since the inner walls of the capillaries were carefully washed and the capillary-rise height measurements were performed under the condition of a receding contact angle. The saturated liquid density values of R-410A and R-410B are calculated from the correlation by Widiatmo [5]. For other cases, the saturated vapor and liquid density values of mixtures are calculated from REFPROP ver.5.10 [6].

Asahi Glass Co. Ltd. furnished and analyzed the sample mixtures. The reported compositions are given below:

R-410A (49.6mass% R-32 / 50.4mass% R-125)

R-410B (44.3mass% R-32 / 55.7mass% R-125)

R-407C (22.5mass% R-32 / 25.1mass% R-125 / 52.4mass% R-134a)

R-404A (44.1mass% R-125 / 51.8mass% R-143a / 4.1mass% R-134a)

R-507 (49.9mass% R-125 / 50.1mass% R-143a).

As a precaution, the sample compositions of liquid phase were checked before and after the experiments using gas chromatography. The measured compositions agreed with the reports compositions within the experimental uncertainty of the measurements.

All of the measurements were carried out under equilibrium conditions between the liquid and its saturated vapor. Through the total error analysis, it is concluded that the accuracy of the measurements for surface tensions and temperatures is estimated to be within ±0.2mN•m^{-1} and ±20 mK, respectively.

3. RESULTS AND DISCUSSION

The experiment was repeated three times by refilling the cell with a fresh sample and repeating the measurements. This was done to verify the repeatability of the measurements. The experimental results that are listed in Table I are the mean value of repeated measurements at the same temperature. The capillary constant a^2 is also listed in Table I as well as the surface tension, because it is not affected by the uncertainty of density values. The relation between the surface tension and the capillary constant is

$$a^2 = \frac{(h_1 - h_2)}{(1/r_1 - 1/r_2)\cos\theta} \cdot \frac{g}{g_n} = \frac{2\sigma}{g_n(\rho' - \rho'')} \qquad (2)$$

where g_n denotes the normal gravitational acceleration of 9.80665 m•s^{-2}.

These results in Table I show that the surface tension of mixtures decreases with

increasing temperature and becomes zero at the critical point. This is the same behavior observed when studying pure fluids. The following simple expression by van der Waals is known to represent the temperature dependence of surface tension, σ, of pure fluids:

$$\sigma = \sigma_0 (1 - T/T_c)^n \tag{3}$$

where T and T_c denote the temperature (K) and the critical temperature (K), respectively. The σ_0 and n are numerical constants which depend on the substance. For mixtures, a similar expression was used:

$$\sigma_m = \sigma_{0m} (1 - T/T_{cm})^{n_m} \tag{4}$$

where T_{cm} denotes the critical temperature (K) of mixture. The σ_{0m} and n_m are numerical constants which are determined by a mixing rule. The following three types of mixing rules were tested:

$$\sigma_{0m} = \sum_i \sigma_{0i} w_i \; ; \qquad n_m = \sum_i n_i w_i \tag{4a}$$

$$\sigma_{0m} = \sum_i \sigma_{0i} x_i \; ; \qquad n_m = \sum_i n_i x_i \tag{4b}$$

$$\sigma_{0m} = \sum_i \sigma_{0i} \theta_i \; ; \qquad n_m = \sum_i n_i \theta_i \tag{4c}$$

where σ_{0i} and n_i are the constants for each component, and i indicates which component. The values for the pure components were determined from the measured data in the previous work [2, 3]. The w_i denotes the mass fraction, x_i denotes the mole fraction and

θ_i denotes the surface fraction of each component i. And the surface fraction, θ_i, are defined by the following relation:

$$\theta_i = \frac{x_i V_{ci}^{2/3}}{\sum_j x_j V_{cj}^{2/3}} \tag{5}$$

where V_{ci} and V_{cj} denote the critical molar volume of each component.

These three types of mixing rule were compared using the present results. The results showed that equation (4a), which uses the mass fraction, produced the best agreement between the fit and the data for every mixture. Therefore, the coefficients, σ_0, σ_{0m}, n and n_m, used in the equation (4a), the cited critical temperature T_c and T_{cm}, and the literature sources [7-11] for these substances, are listed in Table II.

The deviation plots from equation (4a) for five mixtures are illustrated in Figs. 1-5. In these Figs., each symbol shows the present experimental result and the error bar shows the standard deviation of repeated measurements. The error bar shows that the repeatability is within the estimated accuracy of ± 0.2 mN·m^{-1} in most cases. Experimental data of other investigators are not available, thus not plotted on these Figs. The deviation plots also show that equation (4a) represents most experimental surface-tension data for five mixtures. This means the mixing rule by mass fraction is appropriate for these mixtures.

4. CONCLUSION

The surface tensions of five refrigerant mixtures were measured over a wide temperature range using the differential capillary-rise method. The experimental results of this study are accurately represented by van der Waals' expression based on the mixing rule by mass fraction.

ACKNOWLEDGMENTS

We are grateful to Messrs. N. Azuma and H. Ito, students at the Department of Mechanical Engineering, Iwaki Meisei University, for their valuable assistance in carrying out many of the experiments. We are also indebted to Asahi Glass Co. Ltd. for furnishing the samples and analyzing the purity of the sample.

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Table I. Experimental Results of the Surface Tension σ and Capillary Constant a^2 at Temperature T_{90}.

T_{90} (K)	a^2 (mm^2)	σ ($mN \cdot m^{-1}$)
	R-410A	
273.33	1.562	8.73
278.89	1.456	7.94
283.14	1.351	7.21
287.87	1.257	6.55
293.41	1.140	5.75
289.32	1.040	5.08
303.22	0.940	4.43
307.90	0.835	3.79
313.31	0.727	3.13
	R-410B	
273.33	1.523	8.62
278.53	1.397	7.71
283.27	1.309	7.09
288.10	1.206	6.34
293.32	1.101	5.62
298.18	1.016	4.96
303.18	0.901	4.30
308.15	0.804	3.68
312.86	0.704	3.08
	R-407C	
273.32	1.716	10.26
276.88	1.650	9.74
278.41	1.592	9.34
283.11	1.529	8.81
286.48	1.464	8.32
288.43	1.397	7.87
293.51	1.324	7.29
298.16	1.242	6.68
302.92	1.145	6.00
308.15	1.056	5.37
313.06	0.981	4.83
318.41	0.862	4.08
323.02	0.760	3.46
	R-404A	
273.33	1.395	7.64
278.27	1.285	6.88
283.27	1.224	6.40
287.83	1.137	5.80
293.28	1.012	5.00
298.23	0.949	4.53
303.21	0.817	3.76
308.28	0.750	3.31

Table I. continued.

T_{90} (K)	a^2 (mm^2)	σ (mN·m^{-1})
	R-507	
273.32	1.343	7.39
278.24	1.234	6.64
283.31	1.181	6.19
288.27	1.069	5.45
293.25	0.981	4.85
298.26	0.887	4.24
303.09	0.811	3.74

Table II. Numerical Constants in Eq. (3) and (4a).

Refrigerants	σ_{0i} or σ_{0m} (mN·m^{-1})	n_i or n_m	T_{ci} or T_{cm} (K)
R-32	72.16[2]	1.252[2]	351.26[7]
R-125	52.60[2]	1.240[2]	339.17[7]
R-134a	55.81[3]	1.213[3]	374.11[7]
R-143a	54.27[3]	1.259[3]	345.88[8]
R-410A	62.38	1.246	344.56[9]
R-410B	61.40	1.245	343.89[9]
R-407C	58.77	1.229	359.23[10]
R-404A	53.60	1.249	345.18[11]
R-507	53.44	1.250	343.76[10]

FIGURE CAPTIONS

Fig.1. Deviations of the surface tension values σ (⊥● : experimental result; ——— : by Eq. (4b); -----: by Eq.(4c)) of R-410A from the calculated values σ_{cal} by Eq.(4a).

Fig.2. Deviations of the surface tension values σ (⊥● : experimental result; ——— : by Eq. (4b); -----: by Eq.(4c)) of R-410B from the calculated values σ_{cal} by Eq.(4a).

Fig.3. Deviations of the surface tension values σ (⊥● : experimental result; ——— : by Eq. (4b); -----: by Eq.(4c)) of R-407C from the calculated values σ_{cal} by Eq.(4a).

Fig.4. Deviations of the surface tension values σ (⊥● : experimental result; ——— : by Eq. (4b); -----: by Eq.(4c)) of R-404A from the calculated values σ_{cal} by Eq.(4a).

Fig.5. Deviations of the surface tension values σ (⊥● : experimental result; ——— : by Eq. (4b); -----: by Eq.(4c)) of R-507 from the calculated values σ_{cal} by Eq.(4a).

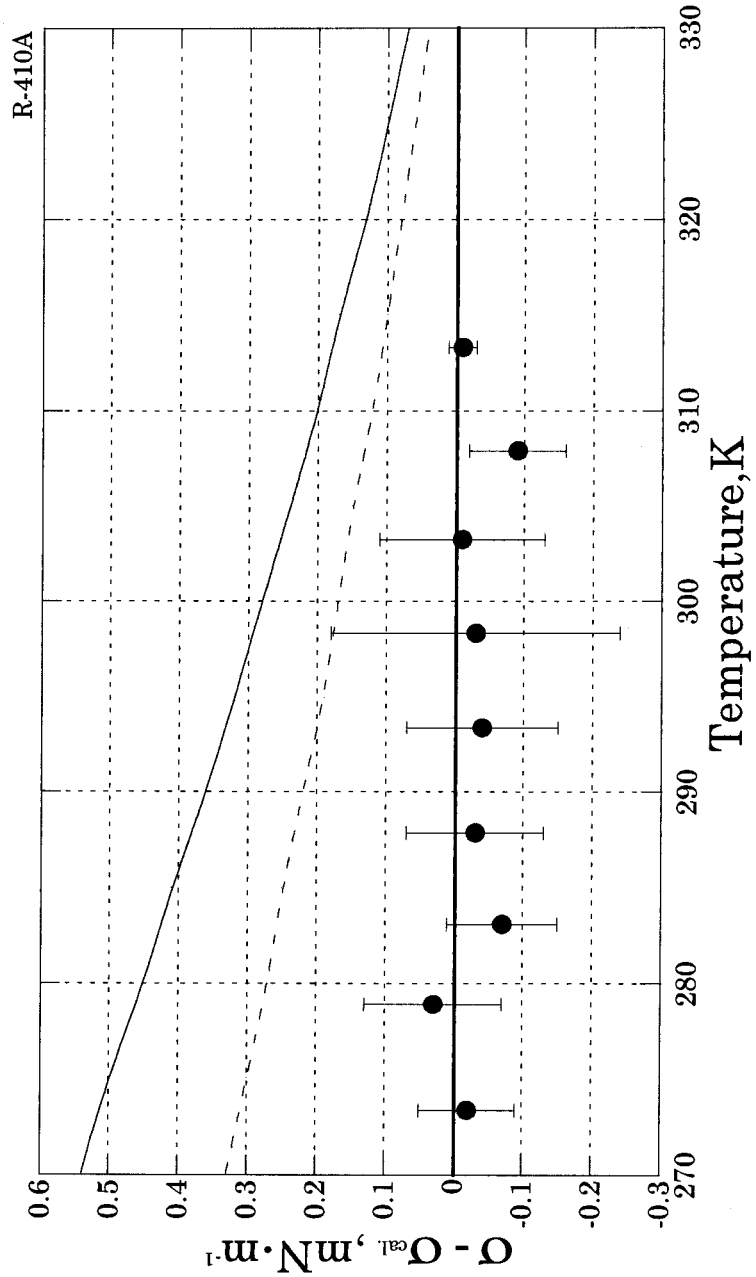
R-410A
σ - σcal, mN·m-1
0.6
0.5
0.4
0.3
0.2
0.1
0
-0.1
-0.2
-0.3
270
280
290
300
310
320
330
Temperature,K

Fig.1.

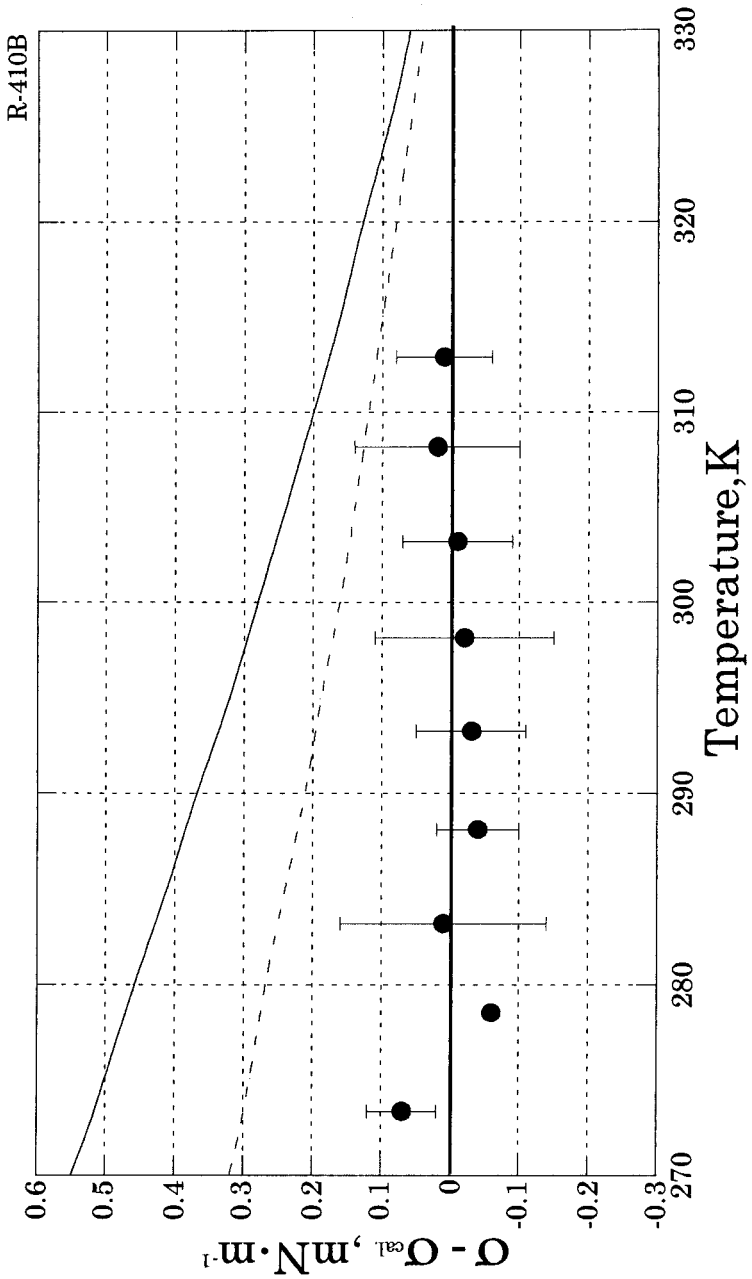
R-410B
σ - σcal, mN·m-1
0.6
0.5
0.4
0.3
0.2
0.1
0
-0.1
-0.2
-0.3
270
280
290
300
310
320
330
Temperature,K

Fig.2.

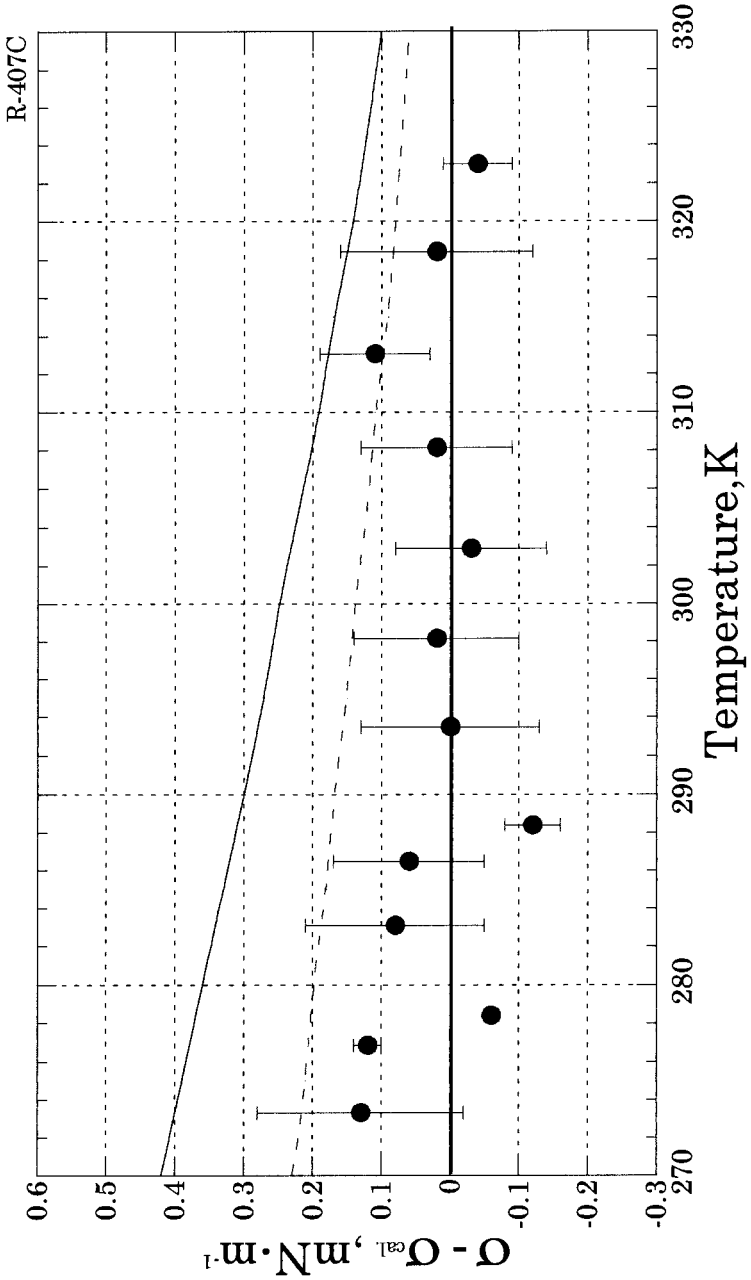
R-407C
σ - σcal , mN·m-1
0.6
0.5
0.4
0.3
0.2
0.1
0
-0.1
-0.2
-0.3
270
280
290
300
310
320
330
Temperature,K

Fig.3.

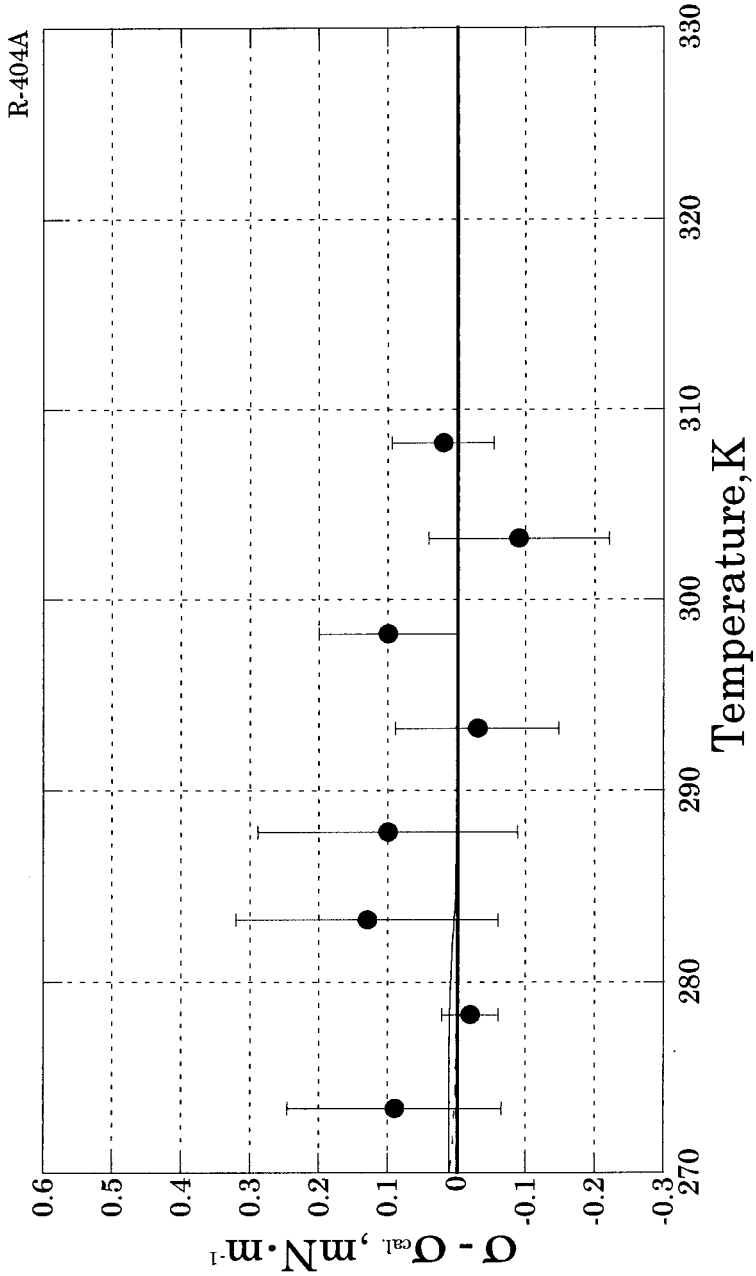
R-404A
0.6
0.5
0.4
0.3
0.2
0.1
0
-0.1
-0.2
-0.3
σ - σcal ,mN·m-1
270
280
290
300
310
320
330
Temperature,K

Fig.4.

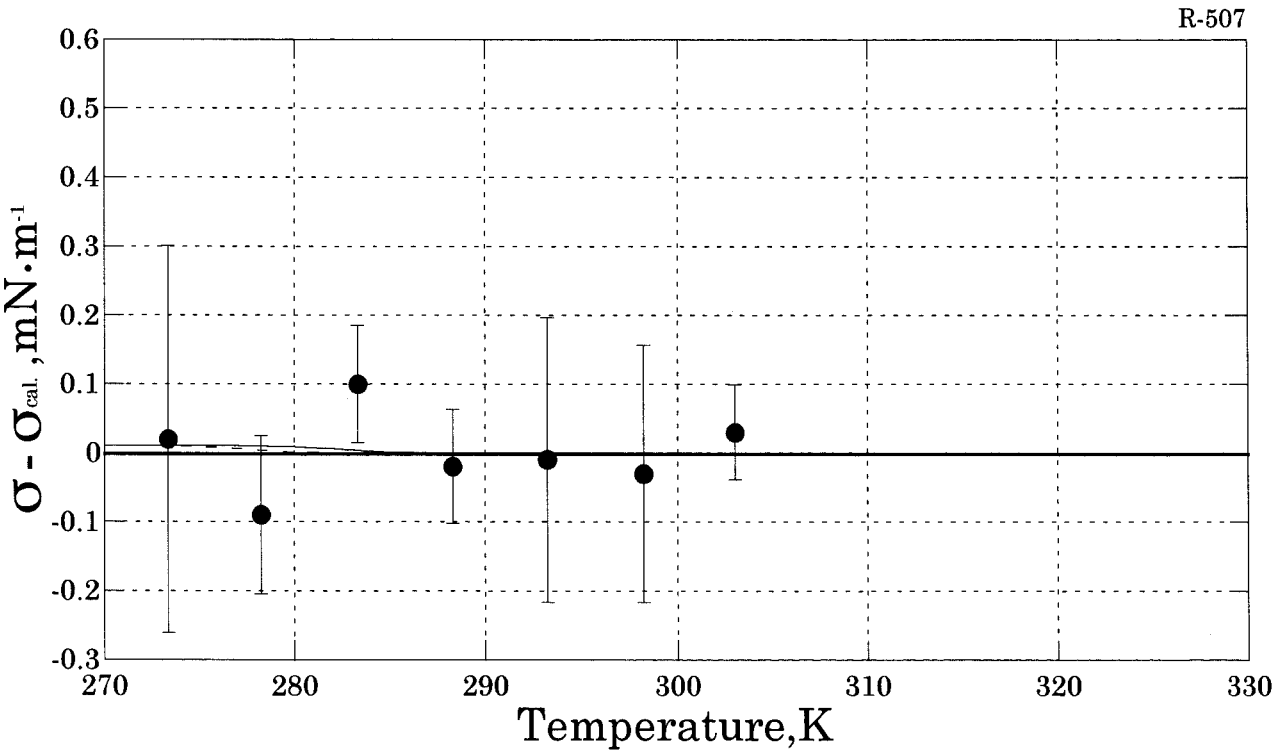
R-507
0.6
0.5
0.4
0.3
0.2
0.1
0
-0.1
-0.2
-0.3
σ - σcal. ,mN·m-1
270
280
290
300
310
320
330
Temperature,K

Fig.5.