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Global Representation of Interfacial Tension in the System $(Ar + Kr)$[1]

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Experimentally measured interfacial tension in the system $(Ar + Kr)$ is shown to obey a law of corresponding states for temperatures above 120 K if a suitable "field variable" is used in the scaling law form. A brief description of the experimental method is given, followed by a comparison of corresponding states fits made using (1) the liquid mole fraction and (2) the fugacity fraction, a field variable in the Griffiths–Wheeler sense. The latter gives significantly better results. A formula for the scaling amplitude of the interfacial tension at constant fugacity fraction recently proposed by Moldover and Rainwater has been tested.

KEY WORDS: argon; corresponding states; fugacity fraction; interfacial tension; krypton.

1. INTRODUCTION

Interfacial tension between liquid and vapor is an important property of mixtures, playing an important role in droplet and bubble formation, adsorption, wetting, and related phenomena. However, interfacial tension of mixtures has rarely been measured at pressures far above ambient [1]. Thus there is a particular need for a method for correlating and predicting interfacial tension of mixtures which does not require extensive experimental data as input. This paper shows that a corresponding-states principle based on a power-law representation of the variation of tension with reduced temperature, which gives good results for pure fluids, can be extended to mixtures provided that the composition variable for the

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mixture is chosen to be a thermodynamic "field" variable, taken here to be fugacity fraction.

The differential capillary rise method has been used to collect interfacial tension data for the (argon + krypton) system. These measurements were made over the entire composition range, at temperatures from 120 to 200 K and at pressures up to 6 MPa. They cover all of the liquid–vapor coexistence region above 120 K. A detailed description of the experimental apparatus and tables of the interfacial tension results have been reported elsewhere [2, 3].

Two forms of the corresponding-states theory have been tested against the mixture data. The first, more traditional, method involves using interfacial tension versus temperature data along lines of a constant liquid composition. The second method represents the interfacial tension versus temperature data along lines of a constant fugacity fraction.

2. INTERFACIAL TENSION DATA

2.1. Experimental Methods

Measurements of interfacial tension were performed in a sapphire pressure vessel which was immersed in a stirred cryostat bath which could be controlled to ±0.02 K. Four carefully selected borosilicate glass capillaries with diameters between 0.267 and 1.05 mm were held between two Teflon disks. The capillary assembly could be manipulated from outside the apparatus. With the assembly near the top of the vessel, argon and krypton of minimum purity 99.995% were condensed in the cell and brought to liquid–vapor equilibrium using a solenoid-operated vapor recirculation pump for mixing. Samples of liquid and vapor were taken through stainless steel capillaries; their composition was determined by measurement of their thermal conductivity at 0°C and ambient pressure. A diagram of the pressure vessel is shown in Fig. 1. Pressure in the vessel was measured using a Ruska DDR 6000 direct reading quartz spiral gauge with an accuracy of 0.004 MPa. Temperature was measured with a platinum resistance temperature detector having a precision of 0.001 K. Experiments were not performed at temperatures below 120 K because the bath fluid, which was a mixture of hexanes, became too viscous to be stirred effectively.

After phase equilibrium was achieved, the capillary assembly was completely submerged in the liquid to drive out vapor bubbles and to wet the capillary walls. The assembly was then partially withdrawn from the liquid so that the readings of meniscus height were recorded for receding menisci. The height of each meniscus was measured using a cathetometer. The

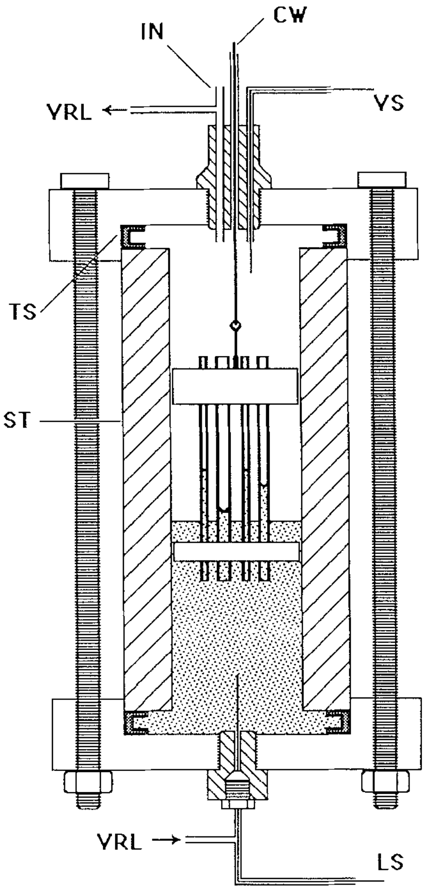

Fig. 1. Sapphire pressure cell and capillary assembly. VRL, vapor recirculation loop; IN, inlet; CW, capillary holding wire; VS, sample line for vapor; LS, sample line for liquid; ST, sapphire tube; TS, spring-loaded Teflon seal.

capillary constant, $a^2 = 2\gamma/\Delta\rho\ g$, where γ is the interfacial tension, $\Delta\rho$ is the density difference between liquid and vapor, and g is the acceleration of gravity, was calculated from the observed meniscus heights, h, by the formula

$$a^2 = \frac{h_i - h_j}{1/b_j - 1/b_i} \tag{1}$$

where b_i and b_j are the radii of curvature at the bottoms of the menisci, calculated according to the method of Lane [4]. In every case, the heights could be measured for at least three capillaries, so there were two independent determinations of a^2 at each state point. In addition, each height measurement was replicated four times and averaged.

2.2. Interfacial Tension Calculations from Experimental Data

The interfacial tension values were derived from the capillary constant data through use of the local value of g, 9.803 m · s^{-2}, and values for $\Delta\rho$ which were calculated by treating the argon + krypton mixture as a conformal fluid. The reference equation of state was the Twu equation for argon, which is of the Strobridge form [5]. A conformal fluid is characterized by a length scale σ_x and an energy scale ε_x which define a reduced temperature $T^* \equiv kT/\varepsilon$ and a reduced density $\rho^* \equiv \rho\sigma^3$. These parameters are related to the pure fluid parameters by the van der Waals mixing rules,

$$\sigma_x^3 = \sum_{\alpha\beta} x_\alpha x_\beta \sigma_{\alpha\beta}^3 \tag{2}$$

and

$$\varepsilon_x \sigma_x^3 = \sum_{\alpha\beta} x_\alpha x_\beta \varepsilon_{\alpha\beta} \sigma_{\alpha\beta}^3 \tag{3}$$

where x_α and x_β are the mole fractions of components α and β. The pure-component parameters used were $\sigma = 0.3405$ nm and $\varepsilon/k = 119.8$ K for argon and $\sigma = 0.3638$ nm and $\varepsilon/k = 166.7$ K for krypton. The cross interaction parameters, $\sigma_{\alpha\beta}$ and $\varepsilon_{\alpha\beta}$, were computed using the modified arithmetic and geometric mean combining rules,

$$\sigma_{\alpha\beta} = \eta \frac{(\sigma_{\alpha\alpha} + \sigma_{\beta\beta})}{2} \tag{4}$$

and

$$\varepsilon_{\alpha\beta} = \xi(\varepsilon_{\alpha\alpha}\varepsilon_{\beta\beta})^{1/2} \tag{5}$$

The correction factors, η and ξ, were chosen to make the equation of state fit the density data of Barreiros *et al.* [6] for argon + krypton mixtures at pressures up to 6 MPa. Their experimental densities were reproduced with an average absolute deviation of 0.18% by using the values $\eta = 1.00296$ and $\xi = 0.9970064$.

Two types of experiments were performed. The first were pure fluid experiments in which interfacial tension was measured as a function of temperature on a single charge of material. The second type of experiments was performed on mixtures with data recorded along isotherms. After each measurement, the capillaries were completely removed from the liquid, the composition was adjusted to a new value, and vapor–liquid equilibrium was reestablished before the capillaries were again submerged in the liquid.

3. CORRESPONDING-STATES CALCULATIONS OF INTERFACIAL TENSION

Any fluid obeying the corresponding-states principle (CSP) has a reduced interfacial tension equal to that of a reference fluid at the same reduced temperature. Here, the reference fluid is chosen to be one whose interfacial tension is described by the power-law equation

$$\gamma/\gamma_0 = (1 - T/T_c)^\mu \tag{6}$$

where γ_0 is the interfacial tension amplitude, T_c is the critical temperature, and μ is the critical exponent for interfacial tension. This equation accurately represents the interfacial tension of many pure fluids, including argon and krypton. For fluids of monatomic or small, nonpolar molecules, the critical exponent has been experimentally determined to be $\mu = 1.28 \pm 0.05$ [7].

3.1. Liquid Mole Fraction as Composition Variable

The assumption that the interfacial tension of a constant-composition liquid mixture behaves like that of a pure fluid provides a convenient means of extending Eq. (6) to mixtures. By incorporating the proper values of γ_0 and T_c, which depend on the liquid composition, Eq. (6) can be used for mixtures. This approach has already been used by several others [8–10]. If a mixture of constant liquid composition obeys the CSP in all respects, then this method would be valid.

This method has been tested on the argon + krypton interfacial tension data. The reference fluid was chosen to be one that obeys Eq. (6) with an exponent of 1.28. This exponent, besides being an average over many fluids, is also close to the average of the values determined separately from the available data for argon (1.263) and krypton (1.295) [3].

Isopleths of interfacial tension data were interpolated from the experimental isothermal data at chosen compositions of $x = (0.2, 0.4, 0.6, 0.8)$, where x is the mole fraction of krypton in the liquid phase. The interfacial tension versus temperature data were then fit by nonlinear least squares to determine values of γ_0 at each composition. The experimental value of T_c at each composition was used in Eq. (6) along with a constant value of $\mu = 1.28$.

The results, shown in Fig. 2, represent the best fit of the argon + krypton interfacial tension data using the CSP along lines of constant composition. Careful inspection of this plot reveals that the pure-component data are fit very well, but the exponent of 1.28 does not adequately describe the curvature in the mixture interfacial tension data. The curves drawn according to the CSP overestimate the interfacial tension at small values and underestimate it at large values. Exponents as high as 1.35 to 1.4 would be needed to reproduce the observed curvature.

3.2. Fugacity Fraction as Composition Variable

The interfacial tension of a mixture depends not only on the bulk liquid composition, but also on the entire composition profile from the bulk liquid, through the interface, to the bulk vapor. Even though the bulk liquid composition was constant in the previous section, the composition profile changed with temperature because the vapor composition was not constant. Thus, instead of holding the liquid composition constant while

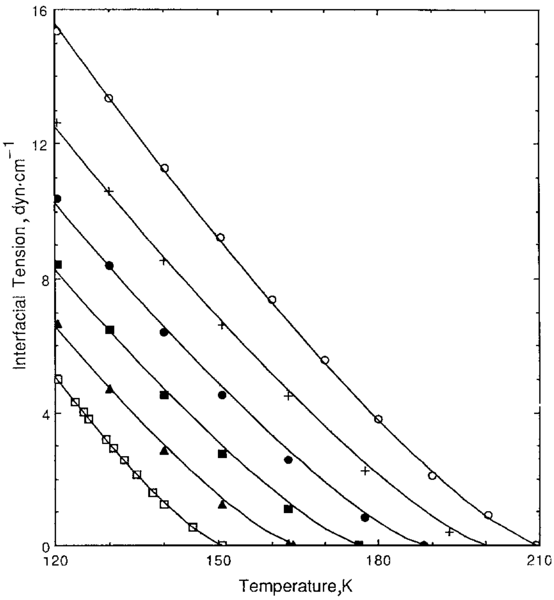

Fig. 2. Interfacial tension versus temperature at constant liquid mole fraction. (□) $x = 0.0$; (▲) $x = 0.2$; (■) $x = 0.4$; (●) $x = 0.6$; (+) $x = 0.8$; (○) $x = 1.0$. The points are interpolated from experimental data along isotherms. The curves are calculated from Eq. (6) with $\mu = 1.28$ and γ_0 adjusted for best fit.

applying the CSP, it would be more logical to hold constant a "field variable," which has the same value everywhere in the interface. One such variable is the fugacity fraction, ζ, defined as

$$\zeta = \frac{f_k}{f_k + f_a} \tag{7}$$

where f_k is the fugacity of krypton and f_a is the fugacity of argon, both defined in the usual way, so as to be asymptotic to the partial pressure in the ideal-gas limit. It is immediately obvious that in the pure-fluid limits, lines of constant ζ correspond exactly to lines of constant composition ($\zeta = x$ in these limits). This choice of composition variable was inspired by the work of Griffiths and Wheeler [11], Leung and Griffiths [12] and Moldover and Gallagher [13].

The mixture interfacial tension is now interpolated from the experimental isothermal data to $\zeta = (0.107, 0.244, 0.421, 0.670)$. These values of ζ were chosen because they are the values at the intersections of the isopleths $x = (0.2, 0.4, 0.6, 0.8)$ with the critical locus. The fugacity values for this calculation were obtained using the Peng–Robinson equa-

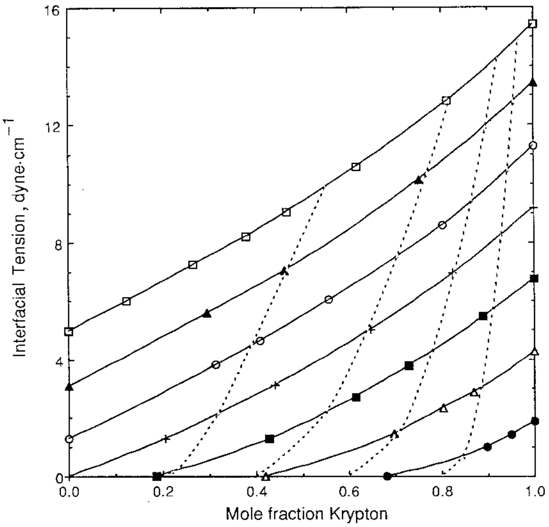

Fig. 3. Interfacial tension versus mole fraction. (□) $T=$ 120.49 K; (▲) $T=$ 129.98 K; (○) $T=$ 140.16 K; (+) $T=$ 150.66 K; (■) $T=$ 163.15 K; (△) $T=$ 177.38 K; (●) $T=$ 193.16 K. The solid curves through the data are interpolated isotherms. The dashed curves cutting across the isotherms are lines of constant fugacity fraction.

tion of state with the interaction parameter k_{12} chosen in the range (0.029–0.049) so as to give the correct critical temperature at the chosen value of x. The lines of constant ζ are superimposed on a plot of the experimental isotherms in Fig. 3. It is the intersections of these curves which are fit to Eq. (6), with the exponent once again held constant at $\mu = 1.28$. The only adjustable parameter in the fit is γ_0. The results are plotted in Fig. 4.

The constant-fugacity fraction fit in Fig. 4 appears to be much better than the constant-composition fit in Fig. 2. Here the exponent of 1.28 gives a good fit of the mixture data as well as the pure-component data. A clearer picture of the quality of the fit is shown in Figs. 5 and 6, which are deviation plots, drawn to the same vertical scale. Here, the large systematic negative deviations of the experimental results from the corresponding-states fit for mixtures along isopleths can be seen clearly, while the plot using the fugacity fraction shows only one deviation greater than 10%. For the fit along the four mixture isopleths, the average fractional error is

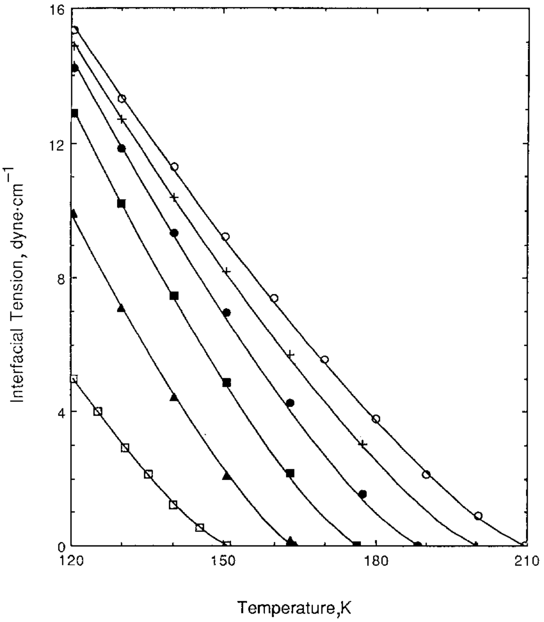

Fig. 4. Interfacial tension versus temperature at a constant fugacity fraction. (□) $\zeta = 0.000$; (▲) $\zeta = 0.107$; (■) $\zeta = 0.244$; (●) $\zeta = 0.421$; (+) $\zeta = 0.670$; (○) $\zeta = 1.000$. The curves are calculated from Eq. (6) with $\mu = 1.28$ and γ_0 adjusted for best fit. The resulting γ_0 values are given in Table I.

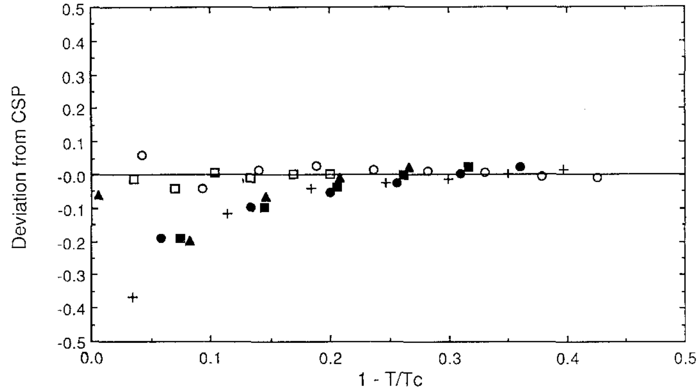

Fig. 5. Deviation plot for fit to CSP using liquid isopleths. The ordinate is (measured γ − calculated γ)/measured γ. The symbols are the same as in Fig. 2.

7.3%, while along the corresponding four lines of constant fugacity fraction, the average fractional error is 3.9%.

3.3. Comparison with the Prediction of Moldover and Rainwater

Moldover and Rainwater have recently produced a prediction of $\gamma(\zeta, T)$ on the basis of two-scale factor universality and the Leung–Griffiths equation of state [14]. This is an extension of a relationship which was found by Moldover to hold for many pure fluids in the critical region [15]. In our notation, the prediction is

$$\gamma_0 = 3.74[k_B T_c(\zeta)]^{1/3}\,[P_c(\zeta)\,C_3(\zeta)\,\alpha(1-\alpha)(2-\alpha)]^{2/3} \tag{8}$$

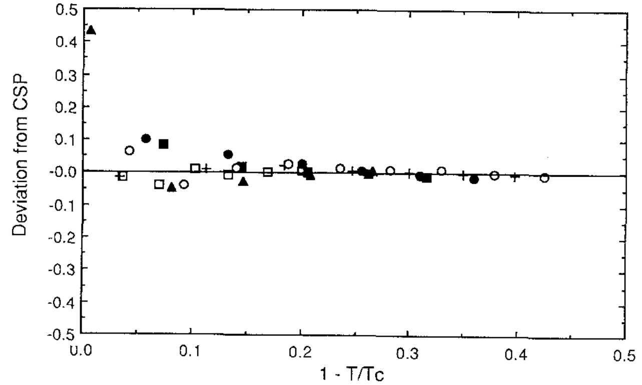

Fig. 6. Deviation plot for fit to CSP using constant fugacity fraction. The ordinate is (measured γ − calculated γ)/measured γ. The symbols are the same as in Fig. 4.

Table I. Interfacial Tension Amplitude, γ_0, in dyne · cm^{-1}

x_c	ζ	T$_c$ (K)	γ_0		
			Expt.	Eq. (8)	Ref. 14
0	0	150.68	39.0	39.0	39.0
0.2	0.107	164.08	53.5	43.7	43.7
0.4	0.244	176.21	56.7	46.9	45.6
0.6	0.421	188.28	53.3	48.6	46.0
0.8	0.670	199.98	48.8	48.1	45.8
1.0	1	209.43	46.3	46.3	46.3

where k_B is Boltzmann's constant, α is the specific heat exponent (here taken to be 0.10), and C_3 is the amplitude of the singular term in the vapor pressure curve which has the exponent $2-\alpha$. C_3 was determined by requiring that γ_0 for each pure component be correctly predicted by this formula.

The predicted values of γ_0 from Eq. (8) are compared with γ_0 values derived from fits to our data in Table I. There is a significant difference in the values, especially at small fugacity fractions. This appears to be related to the hypothesis in Ref. 14 that loci of constant fugacity fraction have a pressure–temperature relationship which parallels that of the pure fluids according to their Eq. (17). The lines of constant fugacity fraction we have calculated have steeper curves of $PT_c(\zeta)/[TP_c(\zeta)]$ vs reduced temperature than the vapor pressure curves for the pure components. We have also used the Moldover–Rainwater definition of ζ to fit all our data, with the result that the average fractional error is 5.6%. That is an improvement over the simple corresponding-states approach but does not match our results, probably because their definition was intended only for the immediate vicinity of the critical line. We did not gather enough data close to the critical line to make a proper test of their prediction in the asymptotic region alone.

4. CONCLUSION AND DISCUSSION

The corresponding-states fit of argon + krypton interfacial tension along lines of constant fugacity fraction is shown to be superior to a fit along lines of constant liquid composition. That this has not been noted previously is probably because of the scarcity of mixture interfacial tension data over a large portion of the liquid–vapor coexistence region, especially for mixtures of simple fluids. Most previous experimental studies have covered the entire composition range but not at enough different temperatures to reveal the temperature–composition dependence of interfacial tension, which has been highlighted here.

The Peng–Robinson equation was chosen for calculation of the fugacity fractions in this study because of the relative ease with which fugacities can be calculated from it. Because it is a cubic equation of state, it must be quantitatively inaccurate very near the critical line, but it still provides the qualitative behavior of the fugacity fraction away from the immediate vicinity of the critical line which a more accurate equation of state would give. We feel that this does not reduce the validity of our conclusion that the constant-fugacity fraction CSP is the correct way to represent interfacial tension of mixtures, but it probably does account for the one case of a large deviation between the experimental and the calculated interfacial tension in the constant-fugacity fraction case at a reduced temperature of 0.006.

Further experiments are planned on mixtures which have large differences between the fugacity fraction and the mole fraction to test this conclusion further.

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