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Capillary Constant of a Xenon–Helium Solution

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ABSTRACT: The differential capillary method has been used to measure the capillary constant of a xenon–helium solution. Experiments have been conducted in the temperature range from (165 to 267) K at pressures up to 4 MPa. An equation approximating the baric dependence of the capillary constant has been suggested.

INTRODUCTION

The capillary constant a^2 is an important property of a liquid–vapor interface, which is the most accessible for measurement. A knowledge of the capillary constant at a known difference of orthobaric densities of liquid ρ' and vapor ρ'' makes it possible to calculate surface tension σ: $\sigma = (1/2)a^2 g(\rho' - \rho'')$, where g is the free fall acceleration. The value of a^2 determines the scale of many capillary phenomena, such as the shape of a pendent drop and shape of the liquid surface at the boundary with a solid.[1,2] When capillary waves are distributed, their frequency is a function of the capillary constant.[3] The capillary constant is included in the criterial equations describing the processes of boiling and condensation, in the determination of the criteria of Bond, Nusselt, and Peclet, and in the expression for the dimensionless diameter of the bubble separation in nucleate boiling.[4,5] In the film boiling it determines the average thickness of the vapor layer and is included as a criterion for stability when the boiling regimes are changing.[4] The capillary constant is the reduction parameter for the calculation of the dimensionless area of surface condensation.[4]

This paper presents the results of measurements of the capillary constant of a xenon–helium solution. The lack of data on the orthobaric densities of this solution does not allow safe determination of its surface tension at present. A xenon–helium solution is gas-saturated in the whole region of its existence. Previously, the capillary constants of gas-saturated solutions were studied.[6−12]

The article includes an introduction and two sections, which describe the technique and the results of investigation.

EXPERIMENT

The capillary constant of a xenon–helium solution has been measured by the differential capillary method.[1,2,9] Russia-made gases without further purification were used in the experiments. The fraction purity of xenon and helium are shown in Table 1. The measuring cell contained three glass capillaries. The internal radii of the capillaries have been determined by calibration with the help of mercury droplets and are as follows: r_1 = 0.6393 mm, r_2 = 0.2297 mm, and r_3 = 0.09607 mm. The error of determination of radii does not exceed 0.05 %. The cell with the capillaries was located in a copper block. The temperature in the block was maintained with a stability of ± 0.005 K. The temperature was measured by a platinum resistance thermometer. Measurements on the thermometer scale were carried out with an uncertainty of ± 0.002 K. The absolute values of temperature on the ITS-90 (International Temperature Scale of 1990) scale have an uncertainty of ± 0.02 K. At temperatures below 200 K, cooling was realized by liquid nitrogen. At T > 200 K the cryostat was filled with an alcohol, and cooling was realized by pumping a cooled alcohol from a low-temperature thermostat through a copper coil.

Table 1. Purities of the Components Used in the Experiment

chemical name	initial mole fraction purity	purification method
xenon	0.99999	none
helium	0.99995	none

Solutions were prepared in the measuring cell. Equilibrium was achieved by an intense agitation of the solution. The pressure in the cell was measured by a set of spring-type pressure gauges with an uncertainty of no more than 0.007 MPa. The difference in the heights of rise of the liquid menisci in the capillaries Δh was determined by a cathetometer with an uncertainty of ± 0.02 mm. The capillary constant was calculated by the formula

$$a^2 = \Delta h/(1/b_i - 1/b_j) \qquad (1)$$

where b_i and b_j are the radii of curvature of the meniscus vertices in the capillaries i and j. The values of b_i were calculated by the Lane equation.[13] The combined standard uncertainty u_c of the capillary constant is $u_c(a^2)$ = 0.003 mm^2 in all measured state parameters. More detailed descriptions of the experimental setup and the experimental procedure are given in the literature.[9,10]

RESULTS OF MEASUREMENTS AND DISCUSSION

The results of measuring a^2 of a xenon–helium solution are presented in Table 2 and Figure 1. The capillary constant was investigated in the temperature range of (165.00 to 267.00) K and at pressures from the saturation line up to 4 MPa. This region of the state parameters is the most important for engineering

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Table 2. Experimental Values of Capillary Constant a^2 at Temperature T and Pressure p of Xenon−Helium Solution[a]

T	p	a^2
K	MPa	mm^2
165.00[b]	0.101	1.265
165.00	0.869	1.268
165.00	1.642	1.272
165.00	2.409	1.275
165.00	3.180	1.279
165.00	3.912	1.282
190.00[b]	0.346	1.034
190.00	0.875	1.037
190.00	1.645	1.040
190.00	2.371	1.044
190.00	3.176	1.048
190.00	3.928	1.051
210.00[b]	0.747	0.846
210.00	1.269	0.848
210.00	1.846	0.855
210.00	2.519	0.853
210.00	3.169	0.858
210.00	3.944	0.866
228.00[b]	1.330	0.666
228.00	1.853	0.674
228.00	2.554	0.677
228.00	3.110	0.683
228.00	3.834	0.687
246.00[b]	2.188	0.485
246.00	2.400	0.488
246.00	2.791	0.491
246.00	3.181	0.496
246.00	3.564	0.499
246.00	3.928	0.504
253.00[b,c]	2.603	0.416
253.00[c]	2.734	0.417
253.00[c]	3.182	0.422
253.00[c]	3.564	0.426
253.00[b,d]	2.602	0.417
253.00[d]	2.824	0.419
253.00[d]	3.178	0.423
253.00[d]	3.566	0.426
253.00[d]	3.940	0.431
253.00[b,e]	2.612	0.416
253.00[e]	3.002	0.419
253.00[e]	3.360	0.425
253.00[e]	3.786	0.430
260.00[b]	3.082	0.344
260.00	3.169	0.345
260.00	3.577	0.352
260.00	3.896	0.356
267.00[b]	3.624	0.268
267.00	3.795	0.272
267.00	3.935	0.274

[a] Standard uncertainties u are $u(T)$ = 0.02 K, $u(p)$ = 0.007 MPa. The combined standard uncertainty u_c is $u_c(a^2)$ = 0.003 mm^2. [b] Data for pure xenon at the saturated line. [c] First series of measurements. [d] Second series of measurements. [e] Third series of measurements.

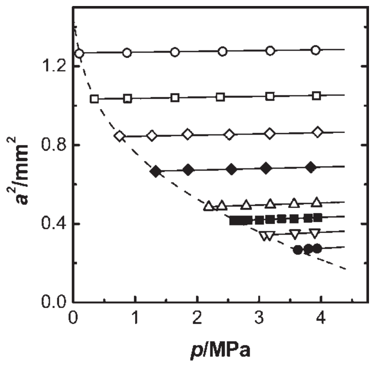

Figure 1. Baric dependence of the capillary constant of a xenon−helium solution. ○, T = 165 K; □, T = 190 K; ◇, T = 210 K; ◆, T = 228 K; △, T = 246 K; ■, T = 253 K; ▽, T = 260 K; ●, T = 267 K. Symbols, experimental data; solid lines, calculation by eqs 2 to 5; dashed line, capillary constant of pure xenon in ref 16.

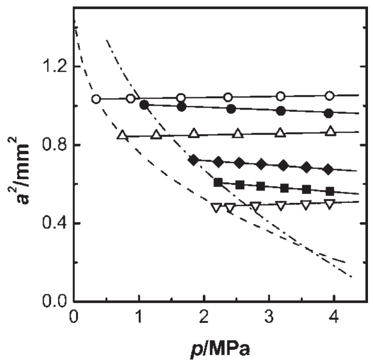

Figure 2. Capillary constant of xenon−helium and argon−helium[11] solutions. ○, Xe−He T = 190 K; △, Xe−He T = 210 K; ▽, Xe−He T = 246 K; ●, Ar−He T = 118 K; ◆, Ar−He T = 128 K; ■, Ar−He T = 132 K. The dashed line, pure xenon, ref 16; dash−dot line, pure argon, ref 9; solid lines, approximation of experimental data.

applications. Three series of measurements were conducted at a temperature of 253.00 K. Each series was carried out with a new portion of the solution in the measuring cell. The results of measurements are in good agreement with each other within the experimental uncertainty. All of the investigated parameters are related to the liquid−vapor phase equilibrium. At the given p and T, pure xenon is a liquid, and pure helium is a gas.

In the whole temperature and pressure range investigated, the baric dependence of the capillary constant is close to linear. The value and the sign of the derivative $(\partial a^2/\partial p)_T$ are mainly determined by the nature of the solvent. When helium is dissolved in xenon, the capillary constant of the solution increases with pressure. This distinguishes xenon−helium solutions from solutions of helium in cryogenic liquids (Ar, O_2, N_2), where a^2 decreases with increasing pressure.[10−12] In Figure 2 data for a xenon−helium system are compared with the results of measuring the capillary constant of an argon−helium solution.[11] A behavior of a^2 similar to that in a xenon−helium solution was observed by us earlier in an ethane−helium system.[10]

The Xe−He and C_2H_6−He solutions are characterized by a stronger intermolecular interaction than helium solutions in Ar, O_2, and N_2. This leads to a difference in the temperature dependence of critical curves close to the solvent critical point[14]

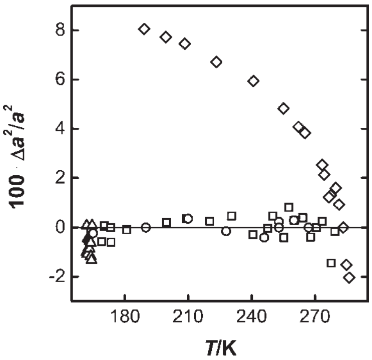

Figure 3. Deviations $\Delta a^2/a^2 = \{a^2(\text{exp}) - a^2(\text{calc})\}/a^2(\text{calc})$ of experimental data for capillary constant of xenon a^2(exp) from the value a^2(calc) calculated on eq 3. ○, this work; □, ref 16; △, ref 19; ◇, ref 18.

and in the baric dependence of the capillary constant. Thus, according to the data by Streett,[14] the derivative $(dp/dT)_c$ on the critical line of xenon−helium solution[15] is positive, whereas in an argon−helium system it is negative.[14]

The results of measurements of the capillary constant have been approximated by an equation of the form

$$a^2 = a_0^2 + A(p - p_0) \tag{2}$$

where $a_0{}^2$ and p_0 are the capillary constant and the pressure of saturated vapors of pure xenon and A is the temperature function.

According to literature,[16] for the capillary constant of pure xenon we have

$$a_0{}^2 = \alpha\varepsilon^n \tag{3}$$

where $\varepsilon = 1 - \tau$, $\tau = T/T_c$, $T_c = 289.76$ K is the temperature at the critical point, $\alpha = 2.737$ mm^2, and $n = 0.913$.

The pressure of saturated vapors of pure xenon is described by the equation[17]

$$\ln(p_0/p_c) = \tau^{-1}(c_1\varepsilon + c_2\varepsilon^{1.5} + c_3\varepsilon^3 + c_4\varepsilon^6) \tag{4}$$

where $p_c = 5.841$ MPa is the pressure at the critical point, $c_1 = -5.945195$, $c_2 = 1.165706$, $c_3 = -0.873158$, and $c_4 = -1.480945$.

The function $A = A(T)$ is presented as follows:

$$A(T) = b_0 \cdot \varepsilon^\kappa \tag{5}$$

where $b_0 = 1.969 \cdot 10^{-3}$ mm^2/MPa, $\kappa = -0.884$.

The maximum error of approximation of experimental data by eq 2 does not exceed 0.64 %.

We do not know of any experimental data on the capillary constant of a xenon−helium system. For pure xenon the values of a^2 obtained in the present work within (0.6 to 1.2) % agree with the results of earlier measurements of our laboratory.[16]

The capillary constant of pure xenon was also measured earlier in papers by Smith et al.[18] and Leadbetter and Thomas.[19] Figure 3 illustrates deviations of experimental data from the value of a^2 calculated by eq 3. For the present paper and publications[16,19] deviations do not exceed 1.2 %, whereas for the paper by Smith et al.[18] at a temperature of 190 K deviations reach 8 %. Such a considerable discrepancy with the data of publications[18] is evidently caused by the systematic error committed by the authors[18] in measuring the capillary constant.

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