

SURFACE TENSION OF He<sup>3</sup>-He<sup>4</sup> SOLUTIONS

B. N. ESEL'SON, V. G. IVANTSOV, and A. D. SHVETS

Submitted to JETP editor September 12, 1962

J. Exptl. Theoret. Phys. (U.S.S.R.) **44**, 483-486 (February, 1963)

The surface tension  $\alpha$  of liquid mixtures of helium isotopes, containing 9.5, 15.0, 19.0, 50.0 and 75.7% He<sup>3</sup>, was measured in the 1.3-4.2° K temperature range. The value of  $\alpha$  decreased smoothly with increase of the He<sup>3</sup> content, and the values were lower than those expected on the assumption of additivity. The results are compared with the conclusions of Prigogine's theory. [14]

THE temperature dependence of the surface tension of pure helium isotopes has been studied in adequate detail. [1-6] Measurements of the surface tension of He<sup>3</sup>-He<sup>4</sup> solutions (up to 3% He<sup>3</sup>) have shown [7] that the He<sup>3</sup> impurity lowers the surface tension of He<sup>4</sup>.

In the present work the surface tension measurements were extended to higher concentrations of He<sup>3</sup> (up to 75%). We used a measuring device (Fig. 1b) and apparatus for observations (Fig. 1a) similar to those used earlier. [7] In the present case the volume of the device was about 0.2 cm<sup>3</sup>, the diameter of the wide tube was 2.89 mm and the capillaries were of diameters from 0.12 to 0.22 mm. To stir the mixture in order to reach equilibrium more quickly, we used an iron rod which could be moved vertically inside the wide tube and which followed the motion of a permanent magnet next to the device. Reciprocating motion was transmitted to the magnet by a wire joining it to an SD-60 motor with a cam on its axle.

In the region of the existence of He II we used a controller [8] which kept the temperature constant to within  $5 \times 10^{-6}$  deg K. The difference of the heights of the liquid levels in the "knee" of the device was measured with a cathetometer KM-5 to within 0.01 mm.

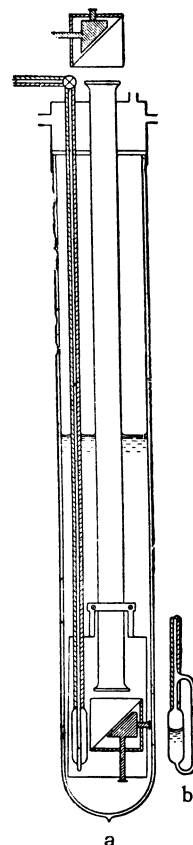
Before and after the measurements on helium-isotope solutions we carried out control experiments on pure He<sup>4</sup>. The results obtained in these experiments agreed well with the published data. [1,2]

The surface tension was calculated from

$$2\alpha (1/b_1 - 1/b_2) = (\rho_l - \rho_v) gh,$$

where  $\alpha$  is the surface tension;  $b_1$  and  $b_2$  are the radii of curvature of the lowest points of the menisci in two tubes of radii  $r_1$  and  $r_2$ ;  $\rho_l$  and  $\rho_v$  are, respectively, the densities of the liquid and the vapor;  $g$  is the acceleration due to gravity;  $h$  is the height between the lowest points of the menisci. The cor-

FIG. 1. Measuring device and optical observation system.



rection for the difference between the radii of curvature of the menisci ( $b_1$  and  $b_2$ ) and the radii of the capillary ( $r_1$ ) and the tube ( $r_2$ ) was calculated by the method of successive approximations using Sugden's tables, [9] and amounted to  $\approx 5\%$ . The density of the liquid was determined from the experimental data [10] and the density of the vapor from the known vapor densities of the pure components, [11,12] on the assumption that they are additive. The concentration of He<sup>3</sup> in the vapor was calculated from the data in [13]. The accuracy of the measurements at all temperatures and concentrations was not less than 4% and for concentrations up to 20% it was higher (about 1%).

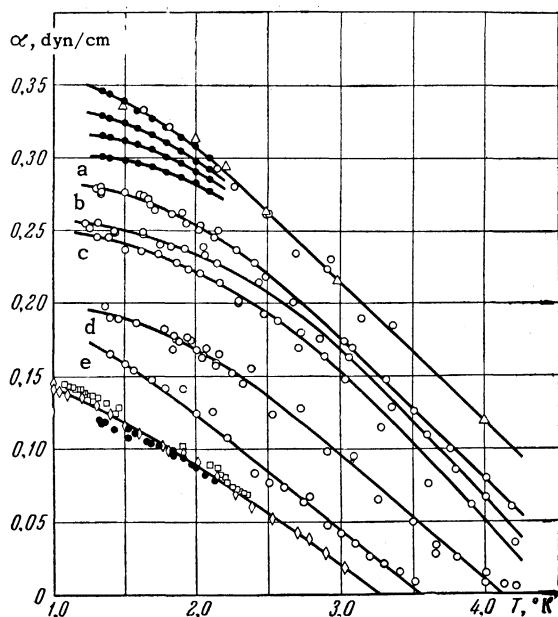


FIG. 2. Temperature dependence of the surface tension of He<sup>4</sup>, He<sup>3</sup>, and their solutions:  $\Delta$ —<sup>[1]</sup>;  $\bullet$ —<sup>[3,7]</sup>;  $\diamond$ —<sup>[4,5]</sup>;  $\square$ —<sup>[6]</sup>;  $\circ$ —results of present work. Curve a represents a solution containing 9.5% He<sup>3</sup>, b—15.0%, c—19.0%, d—50.0%, e—75.7%.

The temperature dependence of the surface tension of the pure helium isotopes and their solutions is shown in Fig. 2. The uppermost curve represents pure He<sup>4</sup>, the lowest one pure He<sup>3</sup>. The three curves between the uppermost one and curve a represent the temperature dependence of the surface tension of solutions containing 0.8, 1.9, and 3.0% He<sup>3</sup> respectively. <sup>[7]</sup> Figure 2 indicates that the surface tension decreases with increase of the concentration of the light isotope and with increase of temperature.

From the curves of the temperature dependence of the surface tension for various concentrations we plotted isotherms, two of which are shown in Fig. 3. These curves clearly show the departure from additivity (represented by the dashed line) in the direction of lower values of  $\alpha$ .

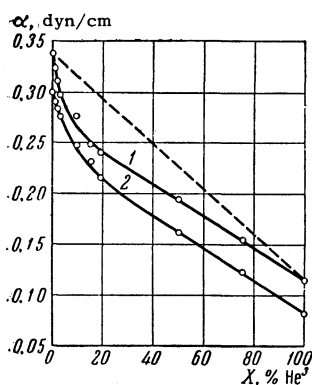


FIG. 3. Dependence of the surface tension on the concentration of the light isotope: 1)  $T = 1.5^\circ\text{K}$ ; 2)  $T = 2.1^\circ\text{K}$ .

The results obtained were compared with the conclusions of Prigogine's theory, <sup>[14]</sup> which relates the surface tension of the solution to the surface tensions of the pure components. It is assumed that: 1) the components obey the quantum rule of corresponding states, and 2) the solution can be described by the average potential model, i.e., that the molecular energies and separations are additive in the space part of the wave function.

Confining ourselves to the second terms of the expansion we find that the excess surface tension

$$\alpha_e = \alpha - \alpha_3 X - \alpha_4 (1 - X) \quad (1)$$

where  $\alpha$ ,  $\alpha_3$  and  $\alpha_4$  are the surface tensions of the solution and of He<sup>3</sup> and He<sup>4</sup>, respectively, and  $X$  is the molar concentration of He<sup>3</sup> in the solution, is given by the following expression:

$$\alpha_e = -\frac{X(1-X)}{2} \frac{\partial^2 \alpha}{\partial (\Lambda^2)^2} (\Lambda_3^2 - \Lambda_4^2)^2 - \frac{X(1-X)\omega}{2kT} (\alpha_4 - \alpha_3)^2, \quad (2)$$

where  $\Lambda = h/d \sqrt{m\epsilon}$  is a nondimensional parameter;  $\Lambda_4 = 2.64$  (for He<sup>4</sup>);  $\Lambda_3 = 3.05$  (for He<sup>3</sup>);  $\omega$  is the surface per single particle.

Figure 4 shows the dependence of the excess surface tension on the concentration of He<sup>3</sup>. It is clear that the theory gives a qualitatively correct description of the phenomenon and that it agrees quantitatively with the experimental results at low He<sup>3</sup> concentrations.

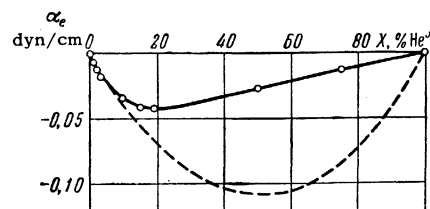


FIG. 4. Dependence of the excess surface tension on the concentration of He<sup>3</sup>: the continuous curve represents the experimental results according to the definition of Eq.(1); the dashed curve is theoretical, calculated from Eq.(2).

It is our intention to extend the measurements of the surface tension toward lower temperatures.

We thank R. I. Medyakova for her help and active participation in the experiments.

<sup>1</sup> van Urk, Keesom, and Kamerlingh-Onnes, Comm. Leid. 179a (1925)  $\equiv$  Proc. K. Akad. Amsterdam **28**, 958 (1925).

<sup>2</sup> J. F. Allen and A. D. Misener, Proc. Cambridge Phil. Soc. **34**, 299 (1938).

<sup>3</sup> B. N. Esel'son and N. G. Bereznyak, DAN SSSR **98**, 564 (1954).

<sup>4</sup>K. N. Zinov'eva, JETP **28**, 125 (1955), Soviet Phys. JETP **1**, 173 (1955).

<sup>5</sup>K. N. Zinov'eva, JETP **29**, 899 (1955), Soviet Phys. JETP **2**, 774 (1956).

<sup>6</sup>D. R. Lovejoy, Can. J. Phys. **33**, 49 (1955).

<sup>7</sup>B. N. Esel'son and N. G. Bereznyak, DAN SSSR **99**, 365 (1954).

<sup>8</sup>V. D. Krasnikov, PTÉ (in press).

<sup>9</sup>S. Sugden, J. Chem. Soc. **119**, 1483 (1921).

<sup>10</sup>T. P. Ptukha, JETP **34**, 33 (1958), Soviet Phys. JETP **7**, 22 (1958).

<sup>11</sup>Mathias, Crommelin, Kamerlingh-Onnes, and Swallow, Comm. Leid. 172b (1925)  $\equiv$  Proc. K. Akad. Amsterdam **28**, 526 (1925).

<sup>12</sup>E. C. Kerr, Phys. Rev. **96**, 551 (1954).

<sup>13</sup>B. N. Esel'son and N. G. Bereznyak, JETP **30**, 628 (1956), Soviet Phys. JETP **3**, 568 (1956).

<sup>14</sup>A. Englert-Chwoles and I. Prigogine, Nuovo cimento Suppl. **9**, No. 1, 347 (1958).

Translated by A. Tybulewicz