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Surface Tension of Helium–Oxygen and Helium–Ethane Solutions

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The capillary constant has been measured, and the surface tension of gas-saturated solutions of He–O_2 and He–C_2H_6 has been calculated in the temperature range from the solidification temperature to approximately $0.9T_C$, where T_C is the critical temperature of the solvent. Measurements have been carried out along isotherms at pressures from the saturation pressure of the pure solvent to 5 MPa. Equations approximating the baric dependence of the capillary constant and the concentration dependence of the surface tension are proposed. Adsorption is determined. The data obtained are discussed within the framework of the method of a finite-thickness layer. It is shown that for the investigated solutions the approximation of a monomolecular surface layer is not justified even at temperatures lower than the normal boiling point.

KEY WORDS: adsorption; capillary constant; ethane; gas-saturated solution; helium; oxygen; surface tension.

1. INTRODUCTION

Of interest are investigations of the properties of solutions with molecules that have sharply different intermolecular interaction parameters. Such solutions include solutions of helium in simple classical liquids. The linear molecular dimensions here differ by approximately a factor of 1.4–1.5, the depth of the potential differs by an order of magnitude, and differences in the molecular masses are just as large. These systems are characterized by a very small solubility of the helium in the liquid phase, while the vapor phase at sufficiently low temperatures is practically fully represented by this very component. Such concentrations variations in bulk phases affect the

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surface tension, the effective thickness of the surface layer, and the distribution of the concentration and the density of the surface layer. A study of the entire spectrum of properties of the solution interphase boundary requires the use of sophisticated physical methods of investigation. However, significant results may already be obtained by measuring the concentration and temperature dependences of the surface tension of these solutions and their analysis in terms of molecular theories of capillarity. Such an approach is especially important at temperatures that are far below the crticial temperature, where the surface layer has a thickness of molecular size, and optical methods can be used to investigate its properties.

This paper presents the results of experimental investigations of the capillary constant and surface tension of two gas-saturated solutions: helium–oxygen and helium–ethane. The system He–C_2H_6 is characterized by a stronger molecular interaction than the system He–O_2. This results in differences in the character of the temperature dependence of the critical curves in the vicinity of the critical point of a solvent. In the classification of Van Konynenbyrg and Scott [1], we see that the He–C_2H_6 solution, with a positive slope of the critical-temperature curve, is of the III-d type, and the He–O_2 solution, for which the line of critical curves with increasing pressure shifts into the region of low temperatures, is of the III-c type. Solutions of helium in H_2, CCl_4, and C_6H_6 also belong to type III-d; solutions of helium in cryogenic liquids (He–Ar, He–N_2) belong to type III-c.

The effect of small amounts of helium on the properties of the interphase boundary of liquids at higher temperatures has been discussed in the literature (see, for instance, Refs. 2 and 3). For solutions of cryogenic liquids (He–H_2, He–Ar, He–O_2) experimental investigations of the surface tension were carried out in 1965–1968 by Blagoy [4] at temperatures close to the triple point of the solvent. A strong effect of small amounts of helium on the surface tension of a liquid caused mainly by the adsorption of the surface-active component was discovered.

The paper is organized as follows. Section 2 describes the experimental equipment and technique. Section 3 gives the results of the measurements of the capillary constant and the surface tension of the two gas-saturated solutions. In Section 4 the data are analyzed in terms of the thermodynamics of surface phenomena. The results are summarized in the conclusion.

2. EXPERIMENTS

To determine the surface tension of the liquid–vapor interface of gas-saturated solutions, use was made of a differential capillary-rise method

[5, 6]. A schematic diagram of a measuring cell with a thermostating unit is shown in Fig. 1. An assembly of three capillaries (1) with different inner radii was installed in an ampoule (2) of borosilicate glass. The values of the capillary radii were $r_1 = 0.6393$ mm, $r_2 = 0.2297$ mm, and $r_3 = 0.09607$ mm. By means of a Kovar-glass transition the ampoule was connected with a system of filling and vacuum processing. The tube (3) is a thin-walled capillary of stainless steel with a heater (4) of constantan wire wound around it. The ampoule was placed in a copper thermostat (5) with observation windows. The thermostat was located in a vacuum chamber, which during operation in the temperature range from 90 to 200 K, was cooled with liquid nitrogen. At temperatures from 200 to 300 K cooling was realized with a silicone liquid, in wich a copper coil was placed and nitrogen vapor was run through. The desired temperature in the thermostat (5) was maintained with two heaters wound on the thermostat outer surface. A copper resistance thermometer incorporated in the bridge circuit

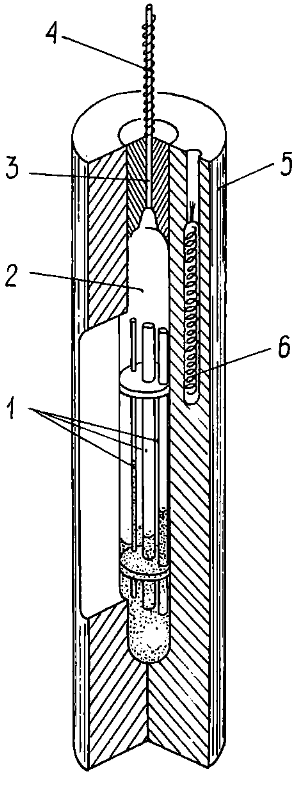

Fig. 1. Measurement cell.

was used to control the temperature. The temperature was measured with a platinum resistance thermometer installed in a hole drilled in the thermostat. The accuracy of thermostating was better than ±0.005 K; the total error of determining the temperature in the experiment was ±0.01 K. The pressure in the ampoule was measured with a model spring-element pressure gauge with a resolution of 0.007 MPa.

Before the measurement the ampoule with the capillaries was evacuated and cooled, and the liquid under investigation was condensed into it. The difference in the heights of the liquid rise $h_{ij} = h_i - h_j$ in the capillaries was measured (the reading was taken at the poles of the menisci of the liquid in the capillaries). The heights of the menisci rise were measured with a cathetometer with an accuracy of ±0.02 mm. The capillary constant was calculated using the following formula:

$$a_{ij}^2 = h_{ij}/(b_i^{-1} - b_j^{-1}) \qquad (1)$$

where b_i and b_j are the radii of the menisci curvature in the ith and jth capillaries, which were determined with the aid of the Lane equation [7]. Complete wetting of the capillary walls was assumed. The use of a cell with three capillaries made it possible to obtain two independent values of the capillary constant, which were averaged.

The procedure began by measuring a^2 of a pure liquid. Then the cell was filled with helium. Mixing was carried out to accelerate the establishment of equilibrium in a two-phase system. A portion of the substance under investigation was frozen into a special vessel cooled with liquid nitrogen. After complete evacuation of the ampoule the vessel was heated to ambient temperature, and the mixture under investigation was driven into a gaseous state and condensed again into the measuring cell. Additional mixing was carried out by establishing a temperature gradient along the ampoule height with the aid of heaters on the thermostating unit and the supply pipe. Equilibrium was considered achieved when the difference of the levels in the capillaries remained constant during a period of 10–20 min. The establishment of equilibrium in a solution was checked by the coincidence of values of the capillary constant with increasing and decreasing pressure.

The concentration of helium was determined from the values of temperature and pressure by using phase-equilibrium diagrams [8, 9] for the solutions under investigation.

The surface tension was calculated as

$$\sigma = 0.5ga^2(\rho' - \rho'') \qquad (2)$$

where $g = 9.8162 \, m \cdot s^{-2}$ is the gravitational acceleration constant, ρ' and ρ'' are the densities of the liquid and vapor phases of a solution, respectively.

Experimental measurements of the density of phase equilibrium lines of helium–oxygen and helium–ethane solutions are not available. The density of the vapor phase ρ'' was determined from a virial equation of state with three virial coefficients. Due to the low solubility of helium ($x'_1 \leqslant 1$ mol%), the molal volume of the liquid phase was assumed to be equal to its value for a pure solvent. Here and below helium is considered the first component of the solution, and a liquid solvent the second. The reduced molecular weight $M = M_1 x_1 + M_2 \cdot x_2$ was used to calculate the density of the liquid phase. Data for the density of pure oxygen and ethane were taken from Refs. 10 and 11. For a He–O_2 system the calculated values of ρ' agree within 0.5% with the density determined from the dielectric constant of the solution [12].

The impurities of the substances used to prepare the solutions do not exceed the following: He, 0.01%; O_2, 0.07%; and C_2H_6, 0.01%. The total relative uncertainty of the capillary constant is determined by the uncertainty of the calibration of the capillaries, the measurement of the capillary constant, the error of the reference data associated with the measured temperature and pressure, and amounts to 0.5% at low temperatures, increasing to 1.5–2% at the upper range of the temperature interval of the measurements. The uncertainty of the surface tension is estimated at 1–2.5%. In the region of low temperatures the greatest uncertainty in the values of σ is introduced by the error of the pressure measurement. Upon approach to the critical point the contribution to the uncertainty of the difference of densities $\rho' - \rho''$ increases significantly.

3. RESULTS

The capillary constant of the gas-saturated solutions was measured along isotherms at pressures up to 5 MPa. Data on a^2 in the helium–oxygen system have been obtained in the temperature range from 90 to 146 K along 12 isotherms, and in the helium–ethane system along 8 isotherms, in the range from 110 to 273 K. The results of the capillary-constant measurements and the deduced surface tensions are presented in Table I.

In the entire temperature range investigated the capillary constant varies linearly with pressure and concentration at constant temperature (Figs. 2 and 3). However, while in the He–O_2 system increasing pressure (concentrations of a dissolved gas) always resulted in a decreasing capillary constant, in the He–C_2H_6 system it took place only at temperatures

Table I. Capillary Constant and Surface Tension of Solutions

p (MPa)	x'_1 (mol%)	a_2^2 (mm^2)	σ ($\mathrm{mN \cdot m^{-1}}$)
	Helium–oxygen		
$T = 91.37$ K	$p_s = 0.114$ MPa	$a_0^2 = 2.342\ \mathrm{mm}^2$	$\sigma_0 = 13.03\ \mathrm{mN \cdot m^{-1}}$
0.543	0.04	2.336	12.97
1.034	0.09	2.331	12.90
1.571	0.14	2.324	12.83
2.097	0.19	2.313	12.74
2.571	0.23	2.304	12.68
3.124	0.29	2.297	12.60
3.625	0.33	2.291	12.54
$T = 99.84$ K	$p_s = 0.251$ MPa	$a_0^2 = 2.058\ \mathrm{mm}^2$	$\sigma_0 = 10.94\ \mathrm{mN \cdot m^{-1}}$
0.469	0.03	2.055	10.91
0.885	0.10	2.050	10.88
1.410	0.18	2.041	10.81
1.964	0.27	2.033	10.74
2.674	0.37	2.028	10.67
3.172	0.43	2.020	10.59
3.623	0.51	2.012	10.55
$T = 108.80$ K	$p_s = 0.500$ MPa	$a_0^2 = 1.748\ \mathrm{mm}^2$	$\sigma_0 = 8.79\ \mathrm{mN \cdot m^{-1}}$
0.969	0.10	1.741	8.74
2.083	0.34	1.723	8.65
2.652	0.46	1.715	8.58
3.037	0.55	1.709	8.55
3.393	0.62	1.703	8.52
4.015	0.75	1.696	8.48
$T = 119.81$ K	$p_s = 1.011$ MPa	$a_0^2 = 1.354\ \mathrm{mm}^2$	$\sigma_0 = 6.23\ \mathrm{mN \cdot m^{-1}}$
1.020	0.04	1.352	6.22
1.202	0.07	1.349	6.20
2.032	0.37	1.338	6.13
2.538	0.55	1.328	6.07
3.153	0.77	1.315	6.00
3.671	0.96	1.308	5.95

Table I. *(Continued)*

p (MPa)	x'_1 (mol%)	a_2^2 (mm^2)	σ (mN $\cdot$ m^{-1})
	Helium–oxygen		
$T = 134.64$ K	$p_s = 2.188$ MPa	$a_0^2 = 0.825$ mm^2	$\sigma_0 = 3.13$ mN $\cdot$ m^{-1}
2.305	0.08	0.822	3.11
2.724	0.35	0.810	3.05
3.305	0.73	0.793	2.96
3.532	0.88	0.784	2.92
3.787	1.04	0.775	2.88
4.019	1.18	0.770	2.85
$T = 139.60$ K	$p_s = 2.739$ MPa	$a_0^2 = 0.640$ mm^2	$\sigma_0 = 2.20$ mN $\cdot$ m^{-1}
2.795	0.04	0.640	2.19
2.999	0.21	0.627	2.15
3.175	0.35	0.622	2.12
3.348	0.49	0.610	2.08
3.740	0.81	0.592	2.00
$T = 142.46$ K	$p_s = 3.009$ MPa	$a_0^2 = 0.530$ mm^2	$\sigma_0 = 1.70$ mN $\cdot$ m^{-1}
3.293	0.17	0.516	1.64
3.454	0.32	0.509	1.59
3.646	0.49	0.490	1.53
3.822	0.65	0.480	1.49
4.015	0.82	0.468	1.46
$T = 144.58$ K	$p_s = 3.388$ MPa	$a_0^2 = 0.445$ mm^2	$\sigma_0 = 1.33$ mN $\cdot$ m^{-1}
3.548	0.16	0.427	1.27
3.681	0.29	0.423	1.25
3.791	0.40	0.399	1.18
4.019	0.62	0.385	1.13
$T = 146.59$ K	$p_s = 3.680$ MPa	$a_0^2 = 0.357$ mm^2	$\sigma_0 = 0.985$ mN $\cdot$ m^{-1}
3.857	0.20	0.330	0.926
3.932	0.28	0.319	0.893
4.043	0.41	0.295	0.830

Table I. *(Continued)*

p (MPa)	x'_1 (mol%)	a_2^2 (mm^2)	σ (mN $\cdot$ m^{-1})
	Helium–ethane		
$T = 113.15$ K	$p_s = 1.27 \times 10^{-4}$ MPa	$a_0^2 = 9.424$ mm^2	$\sigma_0 = 28.99$ mN $\cdot$ m^{-1}
1.008	0.008	9.473	28.97
2.003	0.017	9.510	28.91
2.981	0.025	9.536	28.89
3.996	0.034	9.576	28.85
5.003	0.042	9.626	28.82
$T = 133.5$ K	$p_s = 1.86 \times 10^{-3}$ MPa	$a_0^2 = 8.520$ mm^2	$\sigma_0 = 25.30$ mN $\cdot$ m^{-1}
1.004	0.021	8.549	25.25
2.001	0.042	8.585	25.23
3.006	0.063	8.613	25.18
4.009	0.093	8.650	25.16
5.001	0.124	8.679	25.12
$T = 153.15$ K	$p_s = 1.26 \times 10^{-2}$ MPa	$a_0^2 = 7.609$ mm^2	$\sigma_0 = 21.72$ mN $\cdot$ m^{-1}
1.002	0.045	7.630	21.69
2.007	0.090	7.656	21.67
2.998	0.136	7.681	21.64
4.099	0.182	7.702	21.61
5.007	0.220	7.716	21.57
$T = 193.15$ K	$p_s = 0.158$ MPa	$a_0^2 = 5.775$ mm^2	$\sigma_0 = 15.05$ mN $\cdot$ m^{-1}
1.008	0.104	5.799	15.04
2.011	0.216	5.820	15.03
3.006	0.309	5.840	15.03
4.007	0.403	5.862	15.02
4.982	0.475	5.878	15.02
$T = 233.15$ K	$p_s = 0.778$ MPa	$a^2 = 3.845$ mm^2	$\sigma_0 = 8.75$ mN $\cdot$ m^{-1}
1.026	0.062	3.851	8.75
3.008	0.489	3.886	8.77
5.009	0.802	3.910	8.79
$T = 253.15$ K	$p_s = 1.422$ MPa	$a_0^2 = 2.845$ mm^2	$\sigma_0 = 5.85$ mN $\cdot$ m^{-1}
1.690	0.120	2.850	5.86
4.290	0.809	2.880	5.92
5.050	0.947	2.887	5.93
$T = 263.15$ K	$p_s = 1.859$ MPa	$a_0^2 = 2.342$ mm^2	$\sigma_0 = 4.46$ mN $\cdot$ m^{-1}
2.039	0.060	2.344	4.46
3.104	0.446	2.347	4.50
4.171	0.820	2.349	4.54
$T = 273.15$ K	$p_s = 2.387$ MPa	$a_0^2 = 1.827$ mm^2	$\sigma_0 = 3.19$ mN $\cdot$ m^{-1}
3.181	0.345	1.822	3.23
4.043	0.693	1.814	3.26
5.063	0.983	1.809	3.30

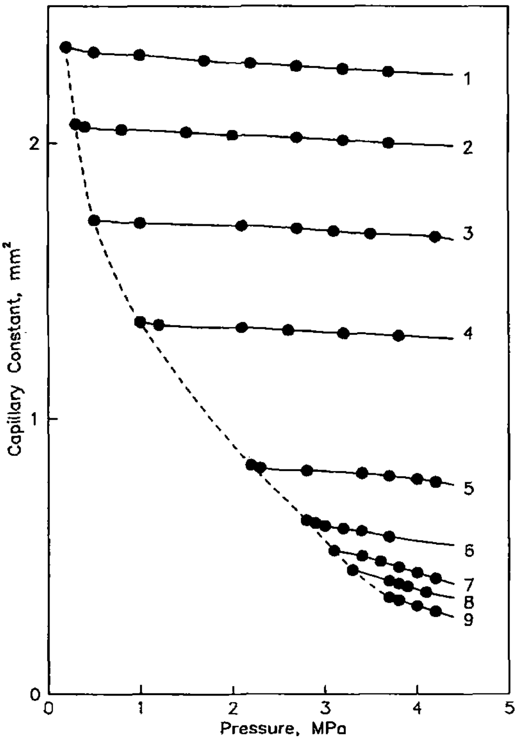

Fig. 2. Capillary constant of helium–oxygen solution as a function of pressure along isotherms: (1) $T = 91.37$ K; (2) 99.84 K; (3) 108.80 K; (4) 119.81 K; (5) 134.64 K; (6) 139.0 K; (7) 142.46 K; (8) 144.58 K; (9) 146.59 K. The dashed line shows the capillary constant of pure oxygen.

exceeding 268 K. At these temperatures the pressure increase was accompanied by an increasing capillary constant. Despite the low solubility of helium in oxygen and ethane, one observes significant changes in the value of the capillary constant reaching 10% of the value of a^2 of a pure solvent in the can of oxygen at high temperatures. In the He–C_2H_6 system a 1% increase in the helium concentration in the liquid phase at the lowest temperatures (113.15 K) resulted in an increase of a^2 by a factor of 3/2. In the He–O_2 system such an increase in the helium concentration ($T = 91.37$ K) decreased the capillary constant by 7%.

Expanding the capillary constant in the vicinity of the saturation line of the pure solvent in terms of pressure to first order, we have

$$a^2 = a_0^2 + (da^2/dp)|_{p=p_s}(p - p_s) \tag{3}$$

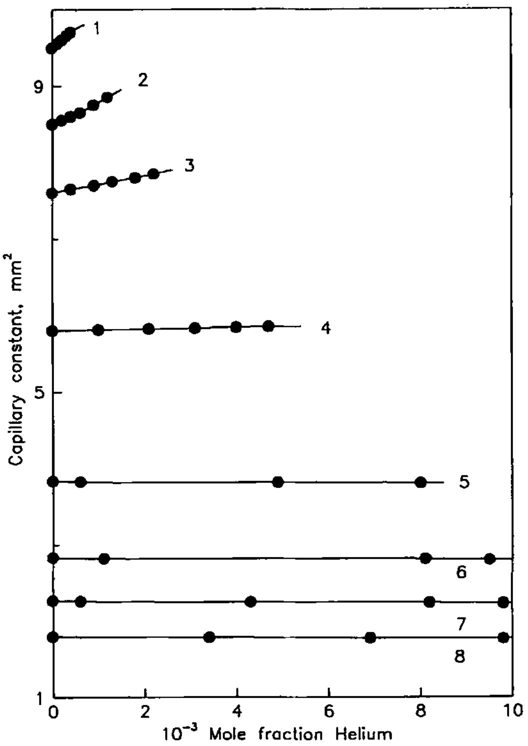

Fig. 3. Capillary constant of helium–ethane solution as a function of concentration along isotherms: (1) $T = 113.15$ K; (2) 133.15 K; (3) 153.15 K; (4) 193.15 K; (5) 233.15 K; (6) 253.15 K; (7) 263.15 K; (8) 273.15 K.

where a_0^2 is the capillary constant of the pure solvent, and p_s is its saturation pressure. The temperature dependence of a_0^2 for oxygen and ethane was investigated previously [13, 14] and can be approximated by an equation of the form

$$a_0^2 = a_*^2 t^n \tag{4}$$

where $t = (T_C - T)/T_C$, with T_C being the critical temperature of the solvent. For oxygen $T_C = 154.58$ K, $a_*^2 = 5.243$ mm^2, and $n = 0.907$; for ethane $T_C = 305.33$ K, $a_*^2 = 14.59$ mm^2, and $n = 0.929$. The derivative $(da^2/dp)|_{p=p_s}$ is represented by the form

$$da^2/dp = b_0 + b_1 t^{-\varphi} \tag{5}$$

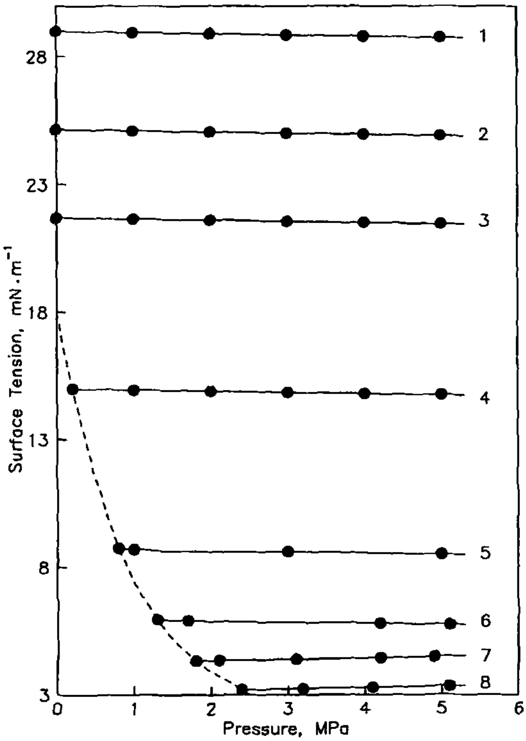

Fig. 4. Surface tension of helium-ethane solutions as a function of pressure along isotherms: (1) $T = 113.15$ K; (2) 133.15 K; (3) 153.15 K; (4) 193.15 K; (5) 233.15 K; (6) 2532.15 K; (7) 263.15 K; (8) 273.15 K.

with $b_0 = 1.305 \cdot 10^{-2}\,\mathrm{mm}^2 \cdot \mathrm{MPa}^{-1}$, $b_1 = 1.622 \cdot 10^{-4}\,\mathrm{mm}^2 \cdot \mathrm{MPa}^{-1}$, and $\varphi = 2.3$ (He–O_2) and $b_0 = 2.402 \cdot 10^{-2}\,\mathrm{mm}^2 \cdot \mathrm{MPa}^{-1}$, $b_1 = -7.820 \cdot 10^{-4}$ $\mathrm{mm}^2\,\mathrm{MPa}^{-1}$, and $\varphi = 1.63$ (He–C_2H_6). Equations (3)–(5) reproduce the experimental data within 1–1.5%.

Isotherms of the surface tension of the solutions are also close to linear as is evident from Fig. 4. The derivative $(d\sigma/dp)_T$ of the He–O_2 system is negative in the entire temperature range but becomes less negative with increasing temperature from 91 to 127 K. Our data for the surface tension in this temperature range agree within 1% with the results of earlier measurements reported by Blagoy [4]. An increase in the temperature ($T > 127$ K) results in a decrease in the value of the derivative $(d\sigma/dp)_T$. At a constant concentration the value of deviations of the solution surface tension from that of a pure solvent is maximum in the vicinity of the critical point and in the vicinity of the solution crystallization temperature (Fig. 5).

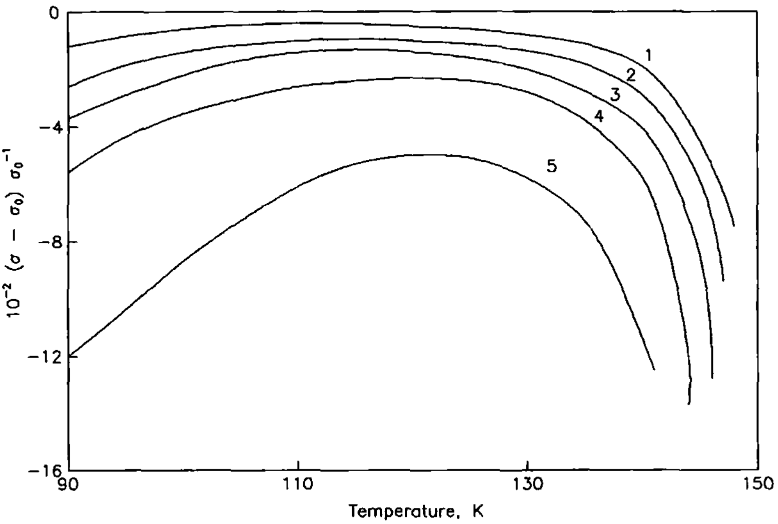

Fig. 5. Deviations of the surface tension of helium–oxygen solution from the surface tension of a pure solvent along the lines of constant values of concentration: (1) $x_1 = 0.1$ mol%; (2) 0.2 mol%; (3) 0.3 mol%; (4) 0.5 mol%; (5) 1 mol%.

Qualitatively different results have been obtained for the helium–ethane system. Despite the increase in the capillary constant with increasing pressure, the surface tension of a solution at low temperatures behaves in much the same way as in the He–O_2 system, i.e., decreases with increasing pressure (concentration). Such a character of the dependences $\sigma(p)$, $\sigma(x'_1)$ is retained to a temperature of 210 K. A transition to higher temperatures is connected with a change of the sign of the derivatives $(d\sigma/dp)_T$ and $(d\sigma/dx'_1)_T$.

Near the line of phase equilibrium of a pure solvent, one can write

$$\sigma = \sigma_0 + (d\sigma/dx'_1))|_{x'=0}\, x'_1 \tag{6}$$

The temperature dependence of the surface tension of oxygen can be represented by [13] as

$$\sigma_0 = \sigma_* t^{\mu}(1 + \sigma_1 t) \tag{7}$$

where $\sigma_* = 41.72\ \mathrm{mN \cdot m^{-1}}$, $\mu = 1.62$, and $\sigma_1 = -0.098$. For ethane [14],

$$\sigma_0 = \sigma_* t^{\mu}(1 + \sigma_1 t + \sigma_2 t^6) \tag{8}$$

where $\sigma_* = 60.57\ \mathrm{mN \cdot m^{-1}}$, $\mu = 1.300$, $\sigma_1 = -0.245$, and $\sigma_2 = 0.309$. The derivative $(d\sigma/dx'_1)|_{x'1=0}$ has been approximated by the expression

$$d\sigma/dx'_1 = c_0 t^{-0.5} - c_1 \exp(c_2 t) \tag{9}$$

Here $c_0 = -8.1964 \times 1\bar{0}^{-2}\ \mathrm{mN \cdot m^{-1} \cdot mol\%^{-1}}$, $c_1 = -3.7348 \times 10^{-3}\ \mathrm{mN\ m^{-1} \cdot mol\%^{-1}}$, and $c_2 = 14.534$ (He–O_2) and $c_0 = 3.7333 \times 10^{-2}\ \mathrm{mN \cdot mol\%^{-1}}$, $c_1 = -1.0260 \times 10^{-3}\ \mathrm{mN \cdot mol\%^{-1}}$, and $c_2 = 12.925$ (He–C_2H_6). The error of approximation by Eqs. (6)–(9) of experimental data is 1–1.5%.

4. THERMODYNAMIC ANALYSIS OF THE MEASUREMENTS

A pressure increase in a gas-saturated solution is accompanied with an increasing density of the gaseous phase and increasing helium content in the interphase layer. The molar quantity of helium adsorbed on a unit of the surface area is determined by the Gibbs adsorption equation. According to this equation, for the isotherm of gas adsorption on a liquid surface, one can write [16]

$$d\sigma = -\Gamma_{1(2)}\, d\mu_1 = -RT\Gamma_{1(2)}\, d\ln p_1 \tag{10}$$

where $\Gamma_{1(2)}$ is the relative adsorption of helium, and μ_1 and p_1 are its chemical potential and partial pressure, respectively. At temperatures that are far from the critical point $p_1 \simeq p$, and consequently, the linear character of $\sigma(p)$ indicates a linear relation between the relative adsorption and the pressure. For the investigated gas-saturated solutions the Henry law is valid in the whole concentration range. Then from Eq. (10) we have

$$\Gamma_{1(2)} = -\frac{p}{RT}\left(\frac{d\sigma}{dp}\right)_T = -\frac{x'_1}{RT}\left(\frac{d\sigma}{dx'_1}\right)_T \tag{11}$$

The results of calculating the adsorption from Eq. (11) are given in Figs. 6 and 7. Despite the low solubility of helium in the liquid phase, the adsorption in gas-saturated solutions is quite considerable and increases abruptly with decreasing temperature reaching, at concentrations of 1 mol%, a value of $2\ 10^{-6}\ \mathrm{mol \cdot m^{-2}}$, which is comparable with the maximum adsorption value i systems with complete solubility (solutions like Ar–Kr [4, 15]) that is observed at concentrations of the more voltile component of 50–70 mol%.

Now we consider thermodynamic relations that describe the pressure dependence of the surface tension in the framework of the method of a

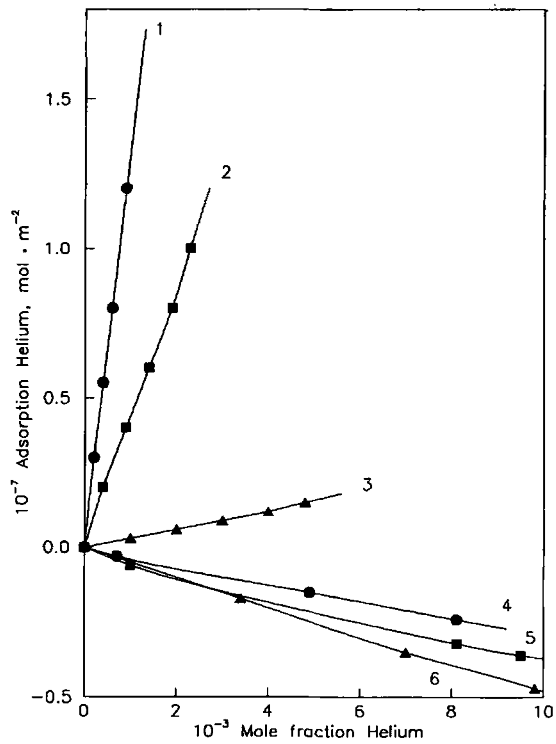

Fig. 6. Concentration dependence of the relative adsorption of the first component in helium–ethane solution along isotherms: (1) $T = 133.15$ K; (2) 153.15 K; (3) 193.15 K; (4) 233.115 K; (5) 253.15 K; (6) 273.15 K.

finite-thickness layer. With changing pressure the redistribution of a substance between the phases and the surface layer proceeds in accordance with [16]

$$s\left(\frac{d\sigma}{dp}\right)_T = v^\sigma - v' - \frac{x_1^\sigma - x_1'}{x_1'' - x_1'}(v'' - v') \tag{12}$$

where s is the molar surface, v is the molar volume, and the superscript σ pertains to the surface layer.

For gas-saturated solutions far from the critical point $x_1'' > x_1'$, $v' > v'$, and the sign of the derivative $(d\sigma/dp)_T$ in Eq. (12) will be determined by the value of

$$A = \left|\frac{x_1'' - x_1'}{x_1^\sigma - x_1'}\right| \Big/ \left|\frac{v'' - v'}{v^\sigma - v'}\right| \tag{13}$$

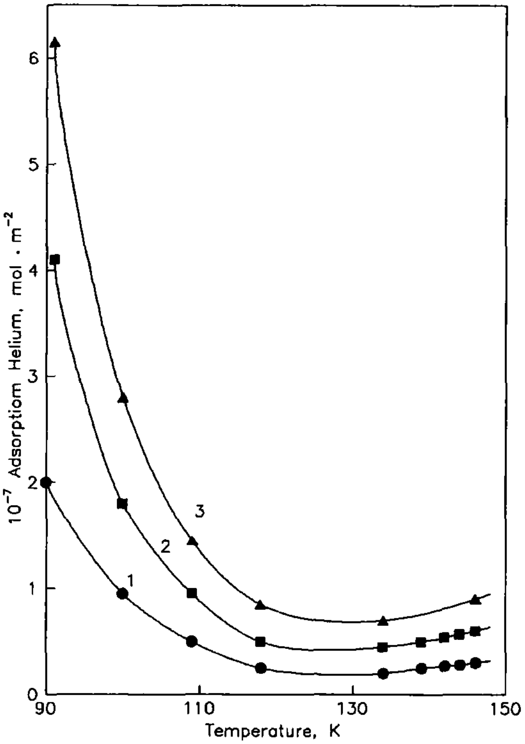

Fig. 7. Temperature dependence of the relative adsorption of the first component in helium–oxygen solution along the lines of constant values of concentration: (1) $x_1 = 0.1$ mol%; (2) 0.2 mol%; (3) 0.3 mol%.

Due to the small value of the radius of action of intermolecular forces and $v'' > v'$, the molar volume $v'' \gg v^\sigma$, so that the value in the denominator of Eq. (13) is very large. If in this case the helium concentration in the surface layer x_1^σ exceeds its content in both the existing phases or even if $x_1^\sigma \approx x_1''$, $A \ll 1$, and from Eq. (12) we have

$$s\left(\frac{d\sigma}{dp}\right)_T \approx -\frac{x_1^\sigma - x_1'}{x_1'' - x_1'}(v'' - v') \qquad (14)$$

i.e., the surface tension will encrease with increasing pressure, which is observed in solutions He–O_2 and He–C_2H_6 at low temperatures.

With increasing temperature the difference $v'' - v'$ decreases, as well as the concentration of helium in the vapor phase x_1''. In this case the composition of the surface layer does not differ much from the composition of the liquid phase, and the value of a as given by Eq. (13) will exceed unity considerably, i.e., $A \gg 1$. As soon as this occurs, Eq. (12) will be transformed into

$$s\left(\frac{d\sigma}{dp}\right)_T \approx v^\sigma - v' \tag{15}$$

When the molar volume of the surface layer exceeds that of the liquid phase, the surface tension will increase with increasing pressure, though this dependence may be a weak one. Apparently, this situation occurs in the system He–C_2H_6 at temperatures above 210 K.

In addition to the surface tension and adsorption, an important characteristic of the interphase boundary is its thickness. Thermodynamics cannot yield the true effective thickness of the surface layer but makes it possible to evaluate a lower boundary of possible thickness values. One can do it taking into account not only the conditions of equilibrium, but also the conditions of stability of the surface layer with respect to its thickness, i.e., the ability of the surface layer to recover its equilibrium thickness when it undergoes casual changes. As applied to a binary system, the conditions of stability of the surface layer may be written in two equivalent forms [16]:

$$E = s\left(\frac{d\sigma}{ds}\right)_{T,p,x_1} \geqslant 0, \qquad \left(\frac{dx_1^\sigma}{dx_1'}\right)_{T,p} \geqslant 0 \tag{16}$$

where E is the conditional modulus of elasticity of the surface layer. In the limit $x_1' \to 0$, we have, for an ideal solution,

$$E_{x=0} = \frac{s_{02}(d\sigma/dx_1)^2_{x_1=0}}{\begin{pmatrix} 2[(d\sigma/dx_1^\sigma)(ds/dx_1^\sigma)]_{x_1=0}\,[1-(s_{02}/RT)(d\sigma/dx_1')]_{x_1=0} \\ -(a_{02}^2/RT)(d\sigma/dx_1')^2_{x_1=0} + s_{02}(d^2\sigma/dx_1'^2)_{x_1=0} \end{pmatrix}} \tag{17}$$

The subscript $x_1 = 0$ signifies the limiting value in the transition $x_1 \to 0$. For the investigated systems the second derivative of the surface tension with respect to composition is equal to zero, and from Eqs. (16) and (17) it follows that

$$\frac{ds}{dx_1^\sigma}\frac{d\sigma}{dx_1'} \approx (s_{01} - s_{02})\frac{d\sigma}{dx_1'} > 0 \tag{18}$$

with

$$a = a_{01}x_1^\sigma + a_{02}(1 - x_1^\sigma) \tag{19}$$

Inequality (18) means that at low temperatures, when $-d\sigma/dx'_1 < 0$, the surface active component must be the substance with the smallest molecules. In helium–ethane solution at $T > 210$ K, where $d\sigma/dx'_1 > 0$, on the contrary, the surface-active component is the one with larger molecules, i.e., ethane.

According to Eq. (17) the conditional modulus of elasticity depends on the value of s and, consequently, on the thickness of the surface layer. For a pure liquid with a hard surface layer ($E = \infty$), we obtain from Eq. (17)

$$s_{02} = \frac{2RT(\gamma - 1)(d\sigma/dx'_1)_{x_1=0}}{(2\gamma - 1)(d\sigma/dx'_1)_{x_1=0}} \tag{20}$$

where $\gamma = s_{01}/s_{02}$. On the other hand, s_{02} may be evaluated approximately by the formula

$$s_{02} = \frac{v_{02}^{2/3} N_A^{1/3}}{n} \tag{21}$$

Here N_A is Avogadro's number, and n is the number of monolayers in the surface layer of a pure component. By the data of the Van der Waals model [17] and ellipsometry [18] near the temperature of normal oxygen boiling, $n \simeq 2$ and $s_{02} = 40.2 \times 10^3\ \mathrm{m}^2 \cdot \mathrm{mol}^{-1}$ ($T = 99.84$ K). From Ref. 20 and experimental data on the derivative $d\sigma/dx'_1$ for the molar surface of the first component, we have $s_{01} = 24.34 \times 10^3\ \mathrm{m}^2 \cdot \mathrm{mol}^{-1}$. If this value is referred to a monolayer, the helium density in the surface layer calculated from Eq. (21) will be 5.5 times greater than the density of liquid helium. On the other hand, if it is assumed that the helium density in the surface layer is comparable with the density of liquid helium at a temperature of normal boiling, the thickness of the surface layer must make up 3.5 monolayers.

At given s and relative adsorption $\Gamma_{1(2)}$, the composition of the surface layer may be calculated by the formula [19]

$$x_1^\sigma \approx \frac{x'_1 + s_{02}\Gamma_{1(2)}(1 - x'_1)}{1 - (s_{01} - s_{02})\,\Gamma_{1(2)}(1 - x'_1)} \tag{22}$$

Relation (22) assumes that the molar surface changes additively according to Eq. (19). According to Eq. (22) the dependence between the values of x_1^σ and x'_1 is close to linear. In a helium–oxygen system with a concentration of helium in the volume of liquid phase $x'_1 = 0.5$ mol%, its content in the surface layer x_1^σ is approximately 2.4 mol%.

5. CONCLUSIONS

Helium is characterized by a low solubility in a liquid phase. A thermodynamic analysis shows [16] that a necessary condition for low solubility and low adsorbability is the increase in the surface tension with increasing pressure or the decrease in the surface tension with decreasing pressure. An increase in the surface tension with pressure was observed in systems like He–CCl_4 and He–C_6H_6 [3] at temperatures from 0.5 to $0.6T_c$. However, such pressure and concentration dependences of the surface tension do not necessarily apply to helium solutions. There are a large number of systems in which increasing pressure is accompanied by a decreasing surface tension. They include, in particular, helium solutions in cryogenic liquids.

The experimental data for the capillary constant and the surface tension of solutions He–O_2 and He–C_2H_6 indicate a considerable effect on the character of the pressure and concentration dependences of the surface tension of the density factor. If the capillary constant of a He–O_2 system at all temperatures decreases with increasing pressure, the capillary constant of a He–C_2H_6 system has, at least at low temperatures, a qualitatively different pressure dependence. However, for both systems investigated the surface tension decreases with increasing pressure, $\sigma(p)$ and $a^2(p)$ being linear within the accuracy of the measurements.

The He–C_2H_6 system takes an intermediate place in the cryogenic → high-temperature solutions series. If the helium–benzene system is studied as a high-temperature system, the relative depth of the potential well $\varepsilon_{C_6H_6}/\varepsilon_{He}$ of such a system is approximately two times larger than that of the He–C_2H_6 system and four times larger than that of the system He–O_2. Perhaps it is this very fact that leads to a change in the character of pressure and concentration dependences of the He–C_2H_6 system at temperatures above 210 K.

Despite the low solubility of helium in the liquid phase, the investigated systems are characterized by a large value of adsorption. A thermodynamic analysis shows that the concentration of helium in the surface layer is four or five times greater than its content in a liquid volume. The approximation of a monomolecular surface layer for such solutions is not justified even at temperatures that are close to the temperature of normal boiling. It is interesting to investigate the distribution of the density of an adsorbed component in an interphase layer and, also, to consider the dependence of the adsorption and other surface properties on the parameters of intermolecular interaction of a solvent. This research is in progress.

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