SURFACE TENSION COEFFICIENT OF THE n-PENTANE + n-HEPTANE SYSTEM NEAR THE "LIQUID–GAS" CRITICAL POINT

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The surface tension coefficient of the "n-pentane + n-heptane" binary system near the liquid–gas critical point is experimentally measured for five concentrations of n-heptane. Measurements are made by the capillary rise method at temperatures in the range of 293 K to T_c for each concentration. Analysis is based on predictions of different theoretical models.

Introduction. Many interphase and surface phenomena of practical and theoretical interest are associated with the behavior of the surface tension coefficient near a critical point. In particular, in recent years [1-5] critical properties of liquids and liquid mixtures have been a matter of concern to resolve problems related with exclusion of residual mineral oil from strata. Among all the critical properties encountered in solving this problem, of special interest is surface tension, which specifies flow properties (type, mode, and mechanism of displacement) of a liquid in a porous medium. To model the processes of oil replacement from strata under conditions close to critical, it is necessary to have all-inclusive information on the condition of the liquid and the liquid mixture near the critical point, for instance, on surface and interphase tension coefficients. When the surface tension near the critical point tends to zero, a qualitative picture of liquid dynamics in a porous medium drastically changes.

Thus an intimate connection exists between physical processes occurring on replacement of oil from strata and critical phenomena [6].

Near the critical point, the phenomenon of phase transition of wetting is also related with the surface tension coefficient σ [7-10], which plays an important role in distribution of liquid phases inside a porous medium. Surface and interphase tension coefficients also determine the stability limit of the surface layer of wetting which inevitably develops near the critical point [11].

A more sophisticated determination of the surface tension of liquids and liquid mixtures near the "liquid–gas" critical points is required to solve the purely fundamental problems of the physics of surface phase transitions and surface layers. The present work is devoted to obtaining fundamental data on the surface tension coefficient for this system near the critical point for different concentrations of a mixture.

Experiment. In order to determine the surface tension coefficient, we used the method of capillary rise of the liquid level in capillary tubes of different diameters.

Experiments were conducted on an experimental set-up, whose design was described in detail in [12, 13]. Using capillaries with a small diameter allowed us to approach the critical point. At temperatures far from T_c we used capillaries with a large diameter. Near T_c capillaries with small diameters ensured a high accuracy of measurements. Therefore in the experiment we simultaneously took five capillaries with the following diameters (mm): $d_1 = 0.0956 \pm 0.0002$, $d_2 = 0.1982 \pm 0.0002$, $d_3 = 0.4094 \pm 0.0002$, $d_4 = 0.6650 \pm 0.0002$, $d_5 = 0.9916 \pm 0.0002$.

Inner diameters of the capillaries were measured by a "Carl Zeiss" universal microscope graduated in 0.2 μm. Measurements were made as follows. Capillaries with soldered ends were placed into a cuvette with a transparent bottom. The cuvette was filled with benzene. Since glass and benzene have close refractivities, the capillary walls are absolutely not seen, while the interior part filled with air is distinctly observed. Such a method has allowed not only measurement of capillary diameters but also checking of diameter uniformity along a capillary and determination of a section with strictly

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TABLE 1. Surface Tension of the System n-Pentane + n-Heptane for Different Concentrations of the Mixture (T, K; σ, 10^3 N/m)

x = 0 mole % (pure n-heptane)		x = 25.5 mole % (C_5H_{12})		x = 55.8 mole % (C_5H_{12})		x = 74.7 mole % (C_5H_{12})		x = 100 mole % (pure n-pentane)	
T	σ	T	σ	T	σ	T	σ	T	σ
303,15	19,02	513,28	0,433	496,36	0,305	487,32	0,160	302,72	14,76
313,15	18,05	513,94	0,403	497,02	0,277	487,93	0,133	318,15	13,32
345,15	14,90	514,33	0,386	497,26	0,267	488,21	0,122	335,29	11,45
381,58	11,70	515,49	0,335	498,08	0,235	488,81	0,098	347,86	10,11
428,66	7,68	516,11	0,309	498,92	0,202	489,08	0,087	432,40	2,252
451,45	5,81	517,35	0,258	499,33	0,185	489,18	0,084	446,79	1,223
486,26	3,06	518,56	0,211	500,35	0,150	489,63	0,067	460,03	0,414
520,88	0,840	519,96	0,160	500,99	0,128	490,00	0,054	463,48	0,242
526,15	0,554	520,17	0,153	501,48	0,112	490,17	0,049	463,91	0,174
531,28	0,306	521,91	0,096	502,07	0,093	490,36	0,043	466,30	0,123
533,89	0,194	523,16	0,060	503,18	0,061	490,79	0,030	467,26	0,072
535,73	0,124	523,69	0,046	503,81	0,044				
537,59	0,061	524,02	0,038	504,20	0,035				

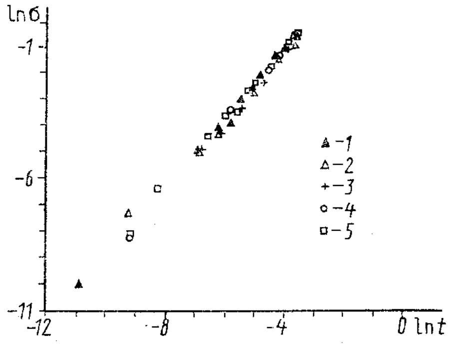

Fig. 1. Dependence of ln σ on ln t for the n-pentane + n-heptane system at different concentrations in the neighborhood of the critical point: 1) 0; 2) 25.5%; 3) 55.8; 4) 74.7; 5) 100%.

similar sizes. The error in measurement of the inner diameter of capillaries has not exceeded 0.1%. The description of the experimental set-up and the measurement procedure is described in detail in [14, 15].

In order to prepare a tested sample of the mixture we used 98.66% pure n-pentane and n-heptane (98.413%). Preliminarily these samples were cleaned from isomers by freezing. After freezing and evacuation in several steps we obtained the samples of 99.9% pure n-pentane and 99.5% pure n-heptane. We then prepared the mixture samples of the desired concentrations. For our investigation we chose five different samples with concentrations of 0, 25.5, 55.8, 74.7, and 100 mole% of n-pentane in the mixtures n-pentane + n-heptane. The data on the density difference of co-existing phases, necessary in surface tension measurements, are taken from [16, 17] for pure components and from [18] for mixtures.

Surface tension was calculated by the working equation

$$\sigma = \frac{g(\rho_\ell - \rho_v)}{2\cos\theta}\bar{a}^2.$$

Here $\bar{a}^2$ is the mean capillary constant, which is determined from the following relation

$$a_{ij}^2 = \frac{\Delta H_{ij}}{\frac{1}{b_i} - \frac{1}{b_j}}.$$

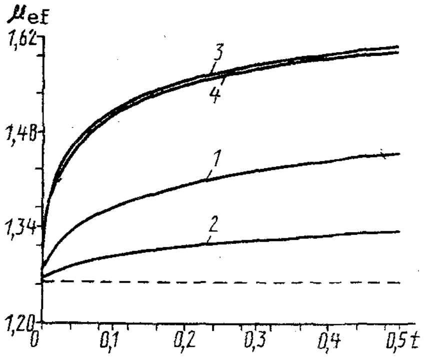

Fig. 2

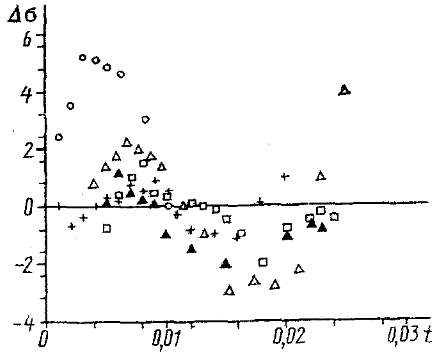

Fig. 3

Fig. 2. Effective critical index of surface tension as a function of temperature for the system of n-pentane + n-heptane for different concentrations: 1) 0; 2) 100%; 3) 25.5; 4) 55.8%.

Fig. 3. Deviations of $\Delta\sigma = \sigma_{\mathrm{exp}} - \sigma_{\mathrm{calc}}$ as a function of temperature for the system n-pentane + n-heptane at σ_{calc} calculated by Eq. (2). Designations are the same as in Fig. 1. $\Delta\sigma$, 10^6 N/m.

Since the tested substances wet glass well, at $T \to T_c$ the wetting angle has been assumed equal to zero ($\theta = 0$). The capillary constant $\bar{a}^2$ was calculated from the measured height differences of the liquid level in different capillaries at the same temperature. The liquid height in the capillary was measured by a cathetometer graduated in 0.005 mm. Meniscus curvature radii were calculated by the method of successive approximations. As a first approximation, the menisci radii were equal to the radii of capillaries. Subsequent approximations were made by using the Sagden tables.

We have also taken the correction for diameter variation of capillaries with temperature into account. The linear expansion coefficient of glass, from which the capillaries are manufactured, is 8.5×10^{-6} 1/deg. The total error of the surface tension measurement near the critical point is 3%, at large distances from the critical point — 0.25 to 0.3%.

Results. Measurements have been carried out for five different concentrations of n-pentane in the binary mixture of n-pentane + n-heptane: 0, 25.5, 55.8, 74.7, and 100 mole%. The measurements have covered a temperature range from room temperature to critical T_c values. The measurement results are compiled in Table 1 and in Fig. 1. Because of the absence of experimental data on $\Delta\rho$ for co-existing phases of the tested mixtures Table 1 lists only some results of σ measurements near the critical point. In the literature experimental data on surface tension for the mixture tested are absent. Therefore we have compared the results for pure components with experimental data [19-21]. The discrepancy does not exceed 3% near the critical point and 1% at a distance from the asymptotic region.

Discussion. The asymptotic behavior of the surface tension coefficient near the critical point as well as many thermodynamic quantities is described, according to the present-day theory of critical phenomena, by the power law [22, 23]

$$\sigma = \sigma_0 t^{\mu} . \tag{1}$$

Preliminary rough processing of the experimental data shows that Eq. (1) is applicable for the description of σ in a very narrow neighborhood of the critical point $5\cdot10^{-4} < t < 5\cdot10^{-3}$. The nonasymptotic behavior of σ at a distance from T_c is described by the equation in terms of the Wagner corrections for the asymptotic law in the form [24-27]

$$\sigma = \sigma_0 t^{\mu} + \sigma_1 t^{\mu+\Delta} + \sigma_2 t^{\mu+2\Delta} + \dots . \tag{2}$$

The expression (2) is obtained within the framework of the theory of renorm-groups, which gives $\Delta = 0.5$ for the universal class of $D = 3$ and $n = 1$. Similar results are produced by numerical solution of the Ising lattice model [28-31] with the same correction index Δ. The Wagner coefficients are usually determined experimentally for each concrete system and cannot be predicted by the theory of renorm-groups.

TABLE 2. Results of Analysis of Surface Tension of the n-Pentane + n-Heptane System Based on Eqs. (1) and (2) for Different Mixture Concentrations

Parameter	x, mole % C_5H_{12}			
	0	25,5	55,8	100
	for equation (1)			
μ	1,26±0,01	1,25±0,01	1,26±0,01	1,26±0,01
σ_0, 10^3 N/m	50,93±0,34	36,31±0,47	39,51±0,19	55,14±0,10
T_c, K	540,243±0,001	526,289±0,002	506,204±0,003	469,724±0,002
$\lvert t\rvert \cdot 10^3$	5,8—10,2	4,9—9,6	6,1—8,9	6,6—11,9
χ_ν^2	1,03	0,90	1,00	0,83
	for equation (2)			
μ	1,26±0,01	1,24±0,01	1,23±0,02	1,26±0,01
σ_0, 10^3 N/m	48,13±0,88	28,63±0,65	27,38±0,25	52,22±0,16
σ_1, 10^3 N/m	42,02±6,14	91,99±4,69	82,19±2,10	13,03±1,09
T_c, K	540,229±0,002	526,216±0,002	506,196±0,001	469,829±0,001
$\lvert t\rvert \cdot 10^3$	5,8—26	4,9—25	6,1—20	6,6—31
χ_ν^2	1,189	1,012	1,104	1,186

TABLE 3. Critical Amplitudes and Critical Parameters of the n-Pentane + n-Heptane System

x, mole %	T_c, K	P_c, MPa	σ_0, 10^3 N/m	C_3^{calc} (9)	C_3^{exp} [14]
0	540,243	2,700	50,932	34,937	36,044
25,5	526,289	3,060	36,313	18,475	—
55,8	506,204	3,313	39,512	19,749	—
74,7	492,209	3,389	53,809	31,115	—
100	469,724	3,357	55,146	33,563	33,589

The qualitative behavior of σ at a distance from T_c is characterized by the effective critical index, which is determined by the relation

$$\mu_{ef}=\frac{\partial \ln \sigma}{\partial \ln t}. \tag{3}$$

Then using (3), we may write, with the Wagner correction from (2) taken into account,

$$\mu_{ef}=\mu_0+\frac{\Delta\sigma_1^* t^\Delta}{1+\sigma_1^* t^\Delta}, \tag{4}$$

where $\sigma_1^* = \sigma_1/\sigma_0$.

Figure 2 presents μ_{ef} as a function of t. As is seen, at distance from T_c the value of μ_{ef} approaches the classical value $\mu = 1.5$. The classical region, where μ_{ef} is close to 1.5, covers different temperature ranges for different concentrations. From Fig. 3 one can see that the region of the scale behavior of σ for the pure components is essentially broader than for the mixtures.

The obtained experimental values of σ have been approximated by the Wagner expansion (2) with the first correction term taken into account. Results of the approximation are represented in Table 2. Because the functional dependence of σ on t is, on the whole (provided T_c and μ are controllable), nonlinear, we use the Bevingston least-square method [32] to minimize the Wagner expansion parameters. Optimal values of the model parameters are determined on the basis of χ_ν^2 minimization, where

$$\chi_\nu^2=\frac{1}{N-N_T}\sum_{i=1}^{N}[Y_i-Y_i(x)]^2 W_i \tag{5}$$

(N_T is the number of controllable model parameters).

On analyzing the experimental points, each of them has been assigned a weight to take account of errors in the measurement of T and σ

$$W_i = \frac{1}{\sigma_i^2} = \frac{1}{\sigma_{s,t}^2 + \left(\frac{\partial\Phi}{\partial t}\right)\sigma_t^2}, \tag{6}$$

where $\sigma_{s,t}$, σ_t are the errors in measurements of the surface tension coefficient and temperature.

Optimal values of the controllable parameters are determined from the conditions

$$\frac{\partial\chi_v^2}{\partial a_i} = 0,$$

For this, the program "Curfit" has been employed. The program allows determination of all minimized parameters and their standard deviations. The best approximation is at $\chi_\nu^2 = 1$. Measuring σ and T with χ_ν^2 minimization we have assumed $\sigma_t = 0.01$ and $\sigma_{st} = 0.005 \times 10^{-3}$ N/m. Deviations of experimental σ from those calculated by (2) are presented in Fig. 3.

The thermodynamic potential model developed by Leung–Griffiths for binary solutions near the line of critical points [23, 33] predicts the asymptotic behavior of specific heat at constant volume on the saturation line in the form

$$C_V(\xi,\ t) = \frac{P_{\text{к}}(\xi)\,C_3(\xi)}{T_{\text{к}}(\xi)\,\rho_{\text{к}}(\xi)}(2-\alpha)(1-\alpha)\,t^{-\alpha}, \tag{7}$$

where ξ changes from 0 to 1 just as a concentration. Expression (7) and the principle of the two-scale factor of versatility [34-36] predict the asymptotic behavior of the surface tension coefficient of the binary mixture:

$$\sigma(\xi,\ t) = 3{,}74\,[k_B T_c(\xi)]^{1/3}\,[P_c(\xi)\,C_3(\xi)\,\alpha\,(1-\alpha)(2-\alpha)]^{2/3}\,t^{\frac{4-2\alpha}{3}}. \tag{8}$$

The critical amplitude of (8) is determined in terms of the critical parameters of the mixture and $C_3(\xi)$, which enters Eq. (7) for heat capacity. Equation (8) is verified for many pure substances [37] and binary mixtures [38, 39]. Calculated results for our n-pentane + n-heptane system are listed in Table 3, which also includes C_3 values recovered from the C_4 values measured for pure components [14] and from the results of our measurements of the surface tension coefficient. Because of the absence of data for mixtures, Table 3 does not give C_3 values for different concentrations. As is seen from Table 3, results of our measurements are quite consistent with data of independent calorimetric measurements.

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NOTATION

T, temperature; T_c, P_c, ρ_c, critical temperature, pressure, and density; μ, β, Δ, universal critical indices; g, free fall acceleration; R, capillary radius; σ_0, B_0, critical amplitudes; σ, surface tension coefficient; ρ_l, ρ_v, densities of co-existing phases; θ, wetting angle; b, curvature radius of the meniscus; H, liquid height in the capillary; d, capillary diameter; n, number of components of the order parameter; $t = 1 - T/T_c$; $\Delta\rho = \rho/\rho_c - 1$; α, critical heat capacity; ξ, dimensionless parameter of the Leung–Griffiths model equation of state.

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