International Journal of Thermophysics, Vol. 20, No. 6, 1999

Prediction of the Surface Tension of Refrigerants and Their Binary Mixtures[1]

V. P. Zhelezny[2, 3] and E. G. Bysko[2]

The use of scaling principles for the prediction of surface tension was studied. The temperature dependences of the capillary constant, density difference on the saturation line, and surface tension were investigated. New relations containing only a few constants were proposed, which made it possible to calculate the capillary constant and surface tension. On the basis of theoretical and experimental studies, equations have been determined for the calculation of the surface tension of poorly studied refrigerants over wide regions of the state parameters. Relations are also proposed that may be used for calculating the surface tension of binary mixtures at specified compositions of the liquid phase. An equation of the surface tension for reduced isotherms was proposed. Results of investigations of the surface tension of binary mixtures, R116/23, R22/14, R134a/152a, and R22/142b, are presented.

KEY WORDS: experiment; mixture; prediction; refrigerants; surface tension.

1. INTRODUCTION

Selection of new ozone-safe refrigerants is one of the ways to improve existing refrigerators and to design new ones. Effective use of new working substances can be possible only if reliable data on their thermophysical properties are available. However, experimental determination of the surface tension of new scarcely studied ozone-safe refrigerants and their mixtures is very expensive and requires considerable time. An efficient approach is to combine the use of empirical methods with theory. This leads to the prediction of thermophysical properties of substances based on the theory of thermodynamic similarity.

---

[1] Paper presented at the Thirteenth Symposium on Thermophysical Properties, June 22-27, 1997, Boulder, Colorado, U.S.A.

[2] State Academy of Refrigeration, Dvoryanskaya 1/3, Odessa 65026, Ukraine.

[3] To whom correspondence should be addressed.

In this paper we propose new methods of prediction of the surface tension of refrigerants by combining literature information with the results of large-scale experimental investigations at the Odessa State Academy of Refrigeration (OSAR) [1–5].

2. SURFACE TENSION OF PURE REFRIGERANTS

The accumulated volume of experimental surface tension data for the refrigerants, the success in generalization of the results of studies in Refs. 6 and 7, and the successful use of scaling principles for describing the thermodynamic properties in a wide region near the critical point [8, 9] permit a new principle for a thermodynamically consistent method of prediction.

The simplest formulation of this new approach can be done in the case of predicting the thermophysical properties on the saturation line of non-associated liquids. In this case the thermodynamic functions are dependent on only one parameter, namely, temperature, and the character of intermolecular interactions will not influence the degree of association.

Use of scaling methods is the phenomenological basis of these prediction procedures. Use of simple power laws, the existence of similarity relations among critical indices, and the universal character of the amplitudes' relation leads to a wide variety of thermodynamically consistent prediction methods. A first step in this direction has been made by Zhelezny et al. [8] where data on the capillary constant a^2, the density difference on the boiling and condensation lines $\Delta\rho = \rho' - \rho''$, and the surface tension σ were generalized.

In this approach, temperature dependences of these properties can be written as

$$a^2 = a_0^2 t^{n\psi(t)}, \qquad \Delta\rho = \rho_0 t^{\beta f(t)}, \qquad \sigma = \sigma_0 t^{\mu F(t)} \tag{1}$$

where a_0^2, ρ_0, and σ_0 are amplitudes, which characterize the individual properties of substances; T_C is the critical temperature; $t = 1 - T/T_C$; n, β, and μ are exponents in the given approach that have the sense of the similarity criteria; and $\psi(t)$, $f(t)$, and $F(t)$ are universal crossover functions.

The use of individual values for n, β, and μ for every substance does not contradict the theory of critical phenomena. First, the range of validity of Eq. (1) is far from the critical region asymptotic behavior, which, according to Sengers [10], lies near values of reduced temperatures less then 5×10^{-4}. Second, even the most accurate experiments on light scattering generally do not give the asymptotic values of the critical indices but, instead, give "effective" values in some restricted region of the reduced temperature [11].

It seems that the universality of substance behavior near a phase transition is not absolute, and it is consistent with the thermodynamic similarity theory. Not all substances are thermodynamically similar, because there are more than two individual constants which characterize the nature of the substance.

Novikov [6] has an interesting observation on this subject. During phase transitions the third individual constant appeared to some extent (in the form of a space dimension in the phase mathematical model, and it was not necessary for this to be equal to three). Some authors [12–14] have other opinions, that a noninteger dimension was characteristic for chaotic dynamical systems, such as gases and liquids. In this treatment deviations of estimated values of the critical indices from theoretical values (at a space dimension which equals 3) may be considered, as one may say, as a measure of the system randomness. So, there are classes of nonuniversality instead of an absolute one, and they may be regarded as analogue of groups of thermodynamically similar substances in the liquid and gaseous states with individual values of indices.

Studies of the temperature dependence of n, β, and μ have shown that the similarity relations between effective values $n\psi(t)$, $\beta f(t)$, and $\mu F(t)$ [1, 3, 8, 9] remained. This fact was well supported by light scattering experiments [11].

This result is of principal significance for the theory of thermodynamic similarity, because the connection between indices and amplitudes [10, 11, 15] leads to thermodynamic consistency of thermophysical properties calculated by the proposed method without using additional experimental information.

At present, there are no theoretical grounds for the universality of the crossover functions. However, the existence of generalized relations for isothermal compressibility and isobaric capacity [9], which are the fluctuations of density and entropy, demonstrate the universality of their behavior, and according to Sementchenko [16], they determine the character of variation of first genus thermodynamic parameters. So the universality of crossover functions $\psi(t), f(t)$, and $F(t)$ was explained in this manner. Such a character of varying the level of "randomness" of a thermodynamic system may also be taken as a hypothesis to explain the universal character of crossover functions for various nonassociating substances.

Analytical forms of the functions $\psi(t), f(t)$, and $F(t)$ may be of various kinds, but they all attempt to identify when the temperature extrapolates to the critical value. So at $t = 0$, Eq. (1) must be transformed to usual scaling equations describing thermodynamic properties in the narrow vicinity of the critical point.

Several forms of functional dependences of $\psi(t)$ and $f(t)$, taking into account approximations of $\psi(t)$ and $f(t)$ reported here, have been used in analysis of temperature dependences of capillary constant, difference of orthobaric densities, and surface tension:

$$\psi(t)=\sum_{i=0}^{6} A_i t^i, \qquad f(t)=\sum_{i=0}^{4} B_i t^i \tag{2}$$

Equations (1) and (2) describe well the data on density and capillary constant of nonassociated substances [8]. Coefficients of Eq. (2) have the following values:

$A_0=0.9461046216$; $A_1=-0.736851447$; $A_2=7.09746254$;
$A_3=-5.61131146$; $A_4=93.33439971$; $A_5=-121.111959$;
$A_6=61.5441037$; $B_0=1.000000$; $B_1=-0.636293937$;
$B_2=2.05856476$; $B_3=-2.64876431$; $B_4=1.21556154$

Equation (1) have good extrapolation properties. Each of them contains two constants, so they may be successfully used for prediction. Constants a_0^2, ρ_0, and σ_0 reflect individual properties of substances, and indices n, β, and μ have the sense of additional criteria of thermodynamic similarity.

Equations (1) and (2) proposed here were checked for various classes of nonassociated liquids. Deviation of the results of calculation [Eq. (1)] from reliable experimental data was comparable with the experimental uncertainty (approximately 0.2% in the case of $\Delta\rho$, and not over 1.5% for σ) [3, 8].

The surface tension is connected with the capillary constant by

$$\sigma\cos\theta=(\Delta\rho/2)\,ga^2 \tag{3}$$

where g is the acceleration of gravity and θ is the wetting angle.

Taking into account Eqs. (1) and (2), one can write

$$\sigma\cos\theta=(\rho_0 a_0^2/2)\,gt^{n\psi(t)+\beta f(t)} \tag{4}$$

As stated previously [17] for hydrocarbon systems, the wetting angle θ can be set equal to zero.

It will be seen from Eq. (4) that

$$\mu F(t)=n\psi(t)+\beta f(t) \tag{5}$$

The universal function $F(t)$ can be obtained by substituting theoretical values of the indices $\beta=0.3245$, $\mu=1.2586$, and $n=0.9341$ [1, 14, 15] into Eq. (5).

Zhelezny [1] and Lyasota [4] also proposed new approximating relations for $\psi(t)$, $f(t)$, and $F(t)$

$$\psi(t) = 1 - 0.04762(t^{1.5}/\ln t) \tag{6}$$

$$f(t) = 1 - 1.227817(t^2/\ln t) + 1.328263(t^3/\ln t) \tag{7}$$

$$F(t) = 1 - 0.03534(t^{1.5}/\ln t) - 0.316563(t^2/\ln t) + 0.34246(t^3/\ln t) \tag{8}$$

These authors recommend their use over the temperature interval $2 \times 10^{-2} \leqslant t \leqslant 0.75$.

As is well known, individual features of a substance manifest themselves more strongly at low temperatures. Widening of the temperature interval of description of surface tension with using Eqs. (6) to (8) lowered the quality of prediction in the vicinity of the critical point. For this reason the values of critical indices μ and β ratios were different (see Table I). The mean value of the quantity of (μ/β) is equal to 3.881, according to calculations with Eqs. (1) and (2), and the theoretical estimation gives practically the same value: $(\mu/\beta) = 3.879$, and then the calculation by Eqs. (1) and (6) to (8) gives $(\mu/\beta) = 3.737$.

Of course, for the purposes of the surface tension prediction, there is the sense to put $n = 0.9341$ and $\mu = 1.2586$, which correspond to theoretical estimates and, hence, to reduce the number of the constants. Then according to the one-parameter law of corresponding states, a dependence of reduced surface tension on the defining criterion of similarity must exist.

Table I. Values of the Constants of Eqs. (1) and (6) to (8)

Substance	a_0^2 (mm^2)	n	ρ_0 (kg · m^{-3})	β	σ_0 (mN · m^{-1})	μ
R12	5.7037	0.9440	2167.0	0.3464	60.611	1.291
R14	4.2380	0.9210	2354.9	0.3455	48.940	1.332
R22	6.7004	0.9288	2048.8	0.3436	67.320	1.272
R23	5.9703	0.9307	2091.9	0.3377	61.240	1.268
R32	8.8201	0.9305	1746.2	0.3385	75.520	1.269
R116	3.9023	0.9230	2377.7	0.3352	45.500	1.258
R125	4.9555	0.9163	2245.9	0.3367	54.572	1.253
R134a	6.2185	0.9202	2060.5	0.3415	62.840	1.261
R142b	7.2594	0.9374	1745.7	0.3427	62.140	1.280
R143a	6.9426	0.9526	1768.2	0.3487	60.200	1.301
R152a	9.0385	0.9362	1478.3	0.3407	65.520	1.277
R218	4.0702	0.9394	2417.9	0.3345	48.260	1.274
R318	4.5563	0.9300	2324.1	0.3392	51.930	1.269
RC318	4.5868	0.9490	2432.8	0.3330	54.718	1.282
R329	4.4610	0.9297	2404.1	0.3389	52.590	1.269

Lyasota [4] has shown that such a generalized relation has an approximately linear character and can be approximated by the following equation:

$$\sigma^* = \sigma_0 R^{-1/3} P_C^{-2/3} T_C^{-1/3} = (0.1289 + 0.1656\omega)\, 10^{-7} \tag{9}$$

where ω is Pitzer's similarity criterion.

In this approach the value of the surface tension calculation error will be determined both by the deviation of individual substances from the generalized relation and the deviation of individual values of μ from their theoretical estimation. Results of the calculations we obtained have shown [4] that the error of prediction without using experimental data would be essentially dependent on temperature, and this fact also had physical justification. It is perfectly evident, that for molecules with complicated form and a high value of the dipole moment, primary orientation near the phase boundary surface may exist. This phenomenon was more appreciable at temperatures near the triple point, where essential growth of orientation forces had to be taken into account along with decreasing kinetic energy of molecules.

The following equation can be obtained from the equations written for the difference of orthobaric densities and surface tension [Eq. (1)]:

$$\sigma = \sigma_0 \rho_0^{-[\mu F(t)/\beta f(t)]}\, \Delta\rho^{\mu F(t)/\beta f(t)} \tag{10}$$

Prediction of σ with the help of Eq. (10) has a significant advantage over the above-mentioned method, because the ratio of individual indices μ/β differs insignificantly from the theoretical value of 3.879 compared with the difference in the values of μ (see Table I).

By this method, Eqs. (1) and (6) to (10) can be used for the calculation of surface tension for nonassociated liquids of various classes, including new ozone-safe refrigerants, without using any empirical information.

For calculation of refrigerant surface tensions in the temperature region $2 \times 10^{-2} \leqslant t \leqslant 0.75$, we also propose the following relation:

$$\sigma = \sigma_0 (\Delta\rho/\rho_0)^{3.739 F_1(t)} \tag{11}$$

where

$$F_1(t) = 0.99217 + 0.162479t - 1.1323944t^2 + 0.7944604t^3 \tag{12}$$

The structure of Eq. (11) is similar to the McLeod–Bachinski formula [18]. However, the exponent differs considerably from the value of four. Additionally, the function $F_1(t)$ varies with temperature within 17% approximately. These facts place less emphasis on phenomenological methods, which use a parachore for calculating surface tension.

In summary, we recommend the proposed formula both for the prediction of σ and for calculation of the surface tension on the basis of restricted experimental information. The formulae proposed here may be used over practically the entire temperature region of the liquid phase, giving results within the accuracy of the experimental measurements.

On the basis of many years of experimental studies of surface tension which have been made at the Odessa State Academy of Refrigeration (OSAR), the constants of Eqs. (1) and (6) to (8) were determined for a number of refrigerants widely used in industry. The values of these constants are given in Table I. Values of constants a_0^2, n, σ_0, and μ given in Table I were obtained by statistical treatment of experimental data [1–5].

Values of the capillary constant which have been measured experimentally [1–5] were calculated with the following formula:

$$a_{ik}^2 = \Delta H_{ik}/(b_i^{-1} - b_k^{-1}) \tag{13}$$

where b_i and b_k are curvature radii of liquid surfaces in the capillaries, and ΔH_{ik} is the difference in the levels of the liquid in the capillaries. The results of the calculation were processed statistically. Random value distributions, the mathematical expectation for every group of measurements having equal accuracy, were evaluated. Sampling of the values of a_{ik}^2 was studied for revealing gross errors. Because an accuracy of individual values of a_{ik}^2 is a variable, then the statistical weight of every member of the sampling P_{ik} has been taken into account. The weighted-mean value of the capillary constant was calculated by the following formula:

$$\bar{a}^2 = \sum_{\substack{i=1 \\ i \neq k}}^{n} a_{ik}^2 P_{ik} \Bigg/ \sum_{\substack{i=1 \\ i \neq k}}^{n} P_{ik} \tag{14}$$

This kind of experimental data treatment ensured the constant value of the relative error in determining the capillary constant over a wide temperature interval.

Values of constants given in Table I are recommended for use in the calculations of a^2, $\Delta\rho$, and σ in the temperature interval $10^{-2} \leqslant t \leqslant 0.60$.

A method of predicting the surface tension and capillary constant of refrigerants was reported in Ref. 19. This method was based on an invalid assumption on the constancy of indices n, β, and μ over the entire temperature interval of liquid phase existence. However, the universal complex of amplitudes C_a proposed by authors of the article [19] is of interest for prediction of the capillary constant and surface tension.

$$C_a = a_0^2 g m/(K k_B T_C Z_C^{3/2} Y_C^n) \tag{15}$$

where m is the molecular mass and k_B is Boltzmann's constant;

$$K=(k_B T_C P_C^{-1})^{1/3}, \qquad Z_C=P_C m(\rho_C k_B T_C)^{-1},$$

$$Y_C=(\gamma_C T_C P_C^{-1})-1, \qquad \gamma_C=\frac{\partial}{\partial T}(P(T, \rho_C))_{T\to T_C}$$

If all the values in Eq. (15) are expressed in SI units, then it is obvious that for the studied refrigerants C_a is practically constant and equal to $(3.387 \pm 0.074) \times 10^{-12}$. This result gives the possibility to calculate the amplitude a_0^2 for slightly studied substances to within an accuracy of 2%.

3. SURFACE TENSION OF BINARY MIXTURES OF REFRIGERANTS

With the use of an apparatus described in detail in previous papers [3, 5], an experimental study of the surface tension coefficient of binary mixtures of refrigerants R116/23, R22/14, R134a/152a, and R22/142b was made. Capillary constants were measured by the modified method of capillary rise [1–5].

During this study the saturated vapor pressure of refrigerant mixtures was also measured. The composition of the mixture was determined by weighing to within an accuracy of 0.9×10^{-3} mol/mol. Variations in the compositions of the vapor and liquid phases were checked by the measured (P, T)-parameters using phase equilibrium data for these mixtures obtained at the OSAR.

Results of the experimental data treatment showed that the concentration of vapor and liquid phases of zeotropic mixtures varied significantly with temperature. One must take this into account during the data treatment.

The method of calculation of σ for binary mixtures of nonassociated liquids was based on the formalism which has been discussed in a previous section. Analysis showed that Eq. (1) described the experimental data for the capillary constant and surface tension, for a fixed concentration of the liquid mixture, with an accuracy comparable with that of the experimental measurements. The similar behavior of the temperature dependence of a^2 and σ for pure substances and binary mixtures resulted in the following equations along isotherms for these properties:

$$a_j^2=a_i^2(a_{0j}^2/a_{0i}^2)\, t^{(n_j-n_i)\,\psi(t)} \qquad (16)$$

$$\sigma_j=\sigma_i(\sigma_{0j}/\sigma_{0i})\, t^{(\mu_j-\mu_i)\,F(t)} \qquad (17)$$

Table II. Values of Coefficients in Eqs. (18) and (19)

Coefficients	R134a/152a	R22/142b	R116/23	R22/14
A_0	6.5404	6.666	3.9124	6.7152
A_1	−1.1402	−0.0961	0.5480	−29.7775
A_2	0.0342	0.729	1.5197	90.2230
A_3	—	—	—	−149.8023
A_4	—	—	—	131.3477
A_5	—	—	—	−44.4393
B_0	65.414	—	45.4245	67.4849
B_1	−35.910	—	6.5249	−285.0608
B_2	33.166	—	9.4901	805.0045
B_3	—	—	—	−1181.0152
B_4	—	—	—	899.5116
B_5	—	—	—	−256.6684
C_0	0.9343	0.9280	0.9232	0.9310
C_1	−0.1383	−0.0364	0.05227	−0.0263
C_2	0.1256	0.0464	−0.04529	0.0719
D_0	1.2741	—	1.2668	1.2837
D_1	−0.1984	—	0.0371	0.2707
D_2	0.1832	—	−0.0398	−0.3205
D_3	—	—	—	0.0989

Analysis has shown that it is the constants a_{0j}^2 and σ_0 that corresponded to individual properties of the mixture to compare with n_j and μ_j. So, without particular loss of accuracy the values of n_j and μ_j can be calculated with the additivity rule. Then Eqs. (16) and (17) become as follows:

$$a_j^2 = a_i^2(a_{0j}^2/a_{0i}^2)\, t^{[n_i(x-1)+n_k(1-x)]\,\psi(t)} \tag{18}$$

$$\sigma_j = \sigma_i(\sigma_{0j}/\sigma_{0i})\, t^{[\mu_i(x-1)+\mu_k(1-x)]\,F(t)} \tag{19}$$

where a_j^2 and σ_j are the capillary constant and surface tension of a binary mixture of ith and kth components, and a_i^2 and σ_i are the capillary constant and surface tension of the ith component; and x is the liquid-phase mole concentration. Deviations of experimental data from results calculated with Eqs. (18) and (19) were within 1.5%.

The main merits of the proposed equations for isotherms of the capillary constant and surface tension are their high accuracy, the need for few data, and their use for calculating the surface tension of binary mixtures of nonassociated liquids over a wide region of the state parameters.

The values of constants a_0^2, σ_0, n, and μ for the studied mixtures obtained with the treatment of experimental data were approximated by the following equations:

$$a_0^2 = \sum_{i=0}^{n} A_i x^i, \qquad \mathrm{mm}^2; \qquad n = \sum_{i=0}^{n} C_i x^i \tag{20}$$

$$\sigma_0 = \sum_{i=0}^{n} B_i x^i, \qquad \mathrm{mN \cdot m^{-1}}; \qquad \mu = \sum_{i=0}^{n} D_i x^i \tag{21}$$

Values of coefficients in Eqs. (20) and (21) for the studied mixtures are presented in Table II.

ACKNOWLEDGMENTS

The authors express their gratitude to L. D. Lyasota and Ju. A. Semeniyk, collaborators of the Thermophysical Engineering Chair of the OSAR, for their help in experimental studies on the surface tension of refrigerants.

REFERENCES

1. V. P. Zhelezny, *Teplofiz. Svoistva Veschestv I Materi. GSSD* (National Standard Reference Data Service of the USSR) **31**:175 (1990) (in Russian).
2. V. P. Zhelezny, *Teplofiz. Svoistva Veschestv I Materi. GSSD* (National Standard Reference Data Service of the USSR) **16**:70 (1982) (in Russian).
3. V. P. Zhelezny, *Teplofiz. Svoistva Veschestv I Materi. GSSD* (National Standard Reference Data Service of the USSR) **20**:117 (1985) (in Russian).
4. L. D. Lyasota, *Surface Tension of Refrigerants and Their Mixtures*, Ph.D. thesis (Odessa State Academy of Refrigeration, 1989) (in Russian).
5. V. P. Zhelezny and L. D. Lyasota, Experimental apparatus for investigation of surface tension at low temperatures, UkrNINTI (Ukrainian Institute of Scientific and Engineering Information) No. 11616-Yk 87 (1987) (in Russian).
6. I. I. Novikov, *Teplofiz. Svoistva Veschestv I Materi. GSSD* (National Standard Reference Data Service of the USSR) **26**:4 (1989) (in Russian).
7. L. P. Filippov, *Methods of Calculations and Prediction of Substances' Properties* (MGU Press, Moskow, 1988).
8. V. P. Zhelezny, V. R. Kamenetsky, and V. K. Romanov, *Russ. J. Phys. Chem.* **56**:60 (1982).
9. V. P. Zhelezny, Yu. A. Kachurka, L. D. Lyasota, and Yu. A. Semenyuk, *Proc., VIII All-Union Conf. Thermophys. Prop., Novosibirsk, USSR* (1988), pp. 31–32.
10. J. M. H. Levelt Sengers and J. V. Sengers, *Perspectives in Statistical Physics*, H. J. Raveche, ed. (North-Holland, Amsterdam, 1980), Chap. 14.
11. V. L. Ginsburg, U. I. Goldberg, and V. A. Golovko, *Light Scattering Near Phase Transitions* (Nauka, Moscow, 1990).
12. G. Nickolis and I. Prigogin, *Cognition of the Complexity* (Mir, Moscow, 1991).
13. P. Berge, I. Pomo, and K. Vidal, *Order in Chaos* (Mir, Moscow, 1991).
14. V. A. Rabinovich and Ju. E. Sheludyak, *Thermophys. High Temp.* **33**:546 (1995) (in Russian).

15. M. A. Anisimov, V. A. Rabinovich, and V. V. Sychev, *Thermodynamics of Critical State of Individual Substances* (Energoatomizdat, Moscow, 1990).
16. V. K. Semenchenko, *Selected Chapters of Theoretical Physics* (Prosveschenie, Moscow, 1966).
17. V. P. Zhelezny, in *Studies of Heat- and Mass Transfer Processes. Transactions of Scientific Papers* (Naukova dumka, Kiev, 1979), pp. 137–140.
18. D. B. Macleod, *Trans. Faraday Soc.* **19**:38 (1923).
19. B. LeNeindre and Y. Garrabos, in *Proceedings of the International Congress "CFCS, The Day After,"* Joint Meeting of IIR Commission B1, B2, E1 and E2, Padova (1994), pp. 549–556.