Some methodological aspects of experimental investigation and prediction of surface tension of refrigerants and their binary mixtures[1]

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

---

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

[2] State Academy of Refrigeration, Odessa 270100, Ukraine

[3] To whom correspondence should be addressed.

ABSTRACT

Ability of using of the main scaling principles for the prognosis of the surface tension coefficient was studied. Temperature dependence of the capillary constant, density difference on the saturation line, surface tension were investigated. New relations containing few constants were proposed which made it possible to calculate the capillary constant, surface tension both on the basis of the initial information and without it.

On the basis of the theoretical and experimental studies we obtained the constants of the equations for the calculation of the surface tension of poor-studied refrigerants in the wide regions of liquid phase parameters of state.

Here it was pointed out that the relations proposed may be used for calculating the surface tension of binary mixtures with the fixed concentration of liquid phase. The equation of the surface tension reduced isotherm was proposed. Results of investigation of surface tension of binary mixtures R116/R23, R22/R14, R134a/R152a, R22/R142b were given.

Key words: experiment, mixture, prediction, refrigerants, surface tension

1. INTODUCTION

Well-grounded choice of new ecologically safe refrigerants is one of the ways to improve the existed refrigerators and design the new ones. Effective using of new working substances can be possible if only the reliable data on their thermophysical properties were existed. However, experimental determination of surface tension of poor-studied ozone-safe refrigerants and their mixtures is very expensive and needs too many time.

So it may be seen that the efficient way is to combine the pragmatism of the empirical study with the organising beginnings of theoretical investigations. This way leads to the using of the methods of prognosis of thermophysical properties of substances based on the thermodynamic similarity theory.

In our paper we propose new methods of generalization and prognosing of surface tension of refrigerants which have been obtained in Odessa State Academy of Refrigeration (OSAR) by the analysis and treatment of the corresponding literature information and the results of our big-scale experimental investigations [1-5].

2. SURFACE TENSION OF PURE REFRIGERANTS

Accumulated volume of experimental data surface tension of refrigerants, and the success in generalization of the results of studies in [6-7], and successful using of the scaling principles for describing the thermodynamic properties in wide region near the critical point [8-9] - all this permit, on our opinion, to pass on to new in principle, thermodynamically consistent methods of prognosing.

The most simple formulation of the main grounds of this new approach can be done in the case of prognosing of thermophysical properties on the saturation line of non-associated liquids. In this case thermodynamical functions are depended on the only

one parameter, namely temperature, and the character of intermolecular interaction will not influence the degree of association.

Using of the main scaling methods is the phenomenological grounds of these prognosing procedures. Using of simple power dependences, existence of similarity relations among critical indices, universal character of the amplitudes' relation lead to wide variety of thermodynamically consistent prognosing methods. First step in this direction has been made by the paper [8] where data on capillary constant a^2, density difference on the boiling and condensation lines $\Delta\rho=\rho'-\rho''$, and surface tension σ were generalized.

In this approach temperature dependences of these properties can be written as the following equations:

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

where a_o, ρ_o, σ_o - amplitudes, which characterize the individual properties of substances, $t=1-T/T_K$ - reduced temperature; T_K - critical temperature; n, β, μ - exponents in the given approach; they have the sense of the similarity criteria; $\psi(t)$, $f(t)$, $F(t)$ - universal cross-over functions.

Using of individual values n, β and μ for every substance does not contradict the theory of critical phenomena thanks to several reasons. Firstly, the range of validity of Eqns (1) is far from asymptotic one, which, according to Sengers [10], lies near values of reduced temperatures below $5 \ 10^{-4}$. Secondly, even the more accurate experiments on light scattering did not give the asymptotic $(T-T_K)$, or "right" values of the critical

indices. They gave, as it is the most likely, their “effective” values in some restricted region of the reduced temperature [11].

It seems that the universality of substance behaviour near 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 substance.

I.I.Novikov [6] has an interesting opinion on this subject. During phase transitions the third individual constant was appeared at some extent (in the form of space dimension in the phase mathematical model, and it was not obligatory be equaled to three). Some authors [12-14] have an opinion, that non-enteger dimension was characteristic for chaotic dynamical systems, such as gases and liquids. In this treatment some deviation of estimated values of the critical indices from the theoretical ones (at space dimension which equals to 3) may be considered, as one may say, as a measure of the system randomness. So, there are classes of unuversality instead of absolute one, and they may be regarded as analogs of groups of therodynamically similar substances in the liquid and gaseous states with individual values of indices.

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

This result is of principle significance for the theory of thermodynamic similarity, because the connection between indices and amplitudes [10, 11, 15] leads to

thermodynamic consistence of thermophysical properties calculated by the proposed method without using additional experimental information.

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

Analytical form of the functions $\psi(t)$, $f(t)$, $F(t)$ may be of various kind, but they all strive to identity when the temperature strives to the critical one. So at t=0 Eqns (1) must be transformed in usual scaling equations describing thermodynamic properties in narrow vicinity of the critical point.

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

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

Data on $\Delta\rho$ and a^2 in the temperature region $10^{-2} \le t \le 0.6$ were described well. Coefficients of Eqns (2) have the following values:

A_0=0.9461046216; A_1=-0.736851447; A_2=7.09746254; A_3=-35.6113146;

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.

Equations (1) have good extrapolating properties. Every of them contain two constants, so they may be successfully used for solving the tasks of prognosing. Constants a_o, ρ_o, σ_o reflect individual properties of substances, and indices n, β, μ have the sense of additional criteria of thermodynamic similarity.

Relations (1) and (2) proposed here were checked for various classes of non-associated liquids. Deviation of the results of calculation (Eqns (1)) from reliable experimental data was commensurable with the experimental uncertainty (approximately equals to 0.2% in the case of $\Delta\rho$, and is not over 1.5% for σ) [3, 8].

Coefficient of surface tension was connected with capillary constant by the following relation:

$$\sigma Cos\theta = \Delta\rho / 2\, ga^2, \qquad (3)$$

where g - acceleration of gravity; Θ - boundary angle of moistening.

Talking into account (1) and (2) one can write:

$$\sigma Cos\theta = \left(\rho_0 a_0 / 2\right)\ gt^{n\psi(t)+\beta f(t)}. \qquad (4)$$

As it has been stated previously [17] for hydrocarbon systems, the boundary angle of moistening Θ can be equalled to zero.

It will be seen from Eq. (4) that

$$\mu F(t) = n\psi(t) + \beta f(t). \qquad (5)$$

Universal function *F(t)* can be obtained by substituting theoretical values of the indices β=0.3245, μ=1.2586, *n*=0.9341 [1, 14, 15] in the Eq. (5).

A little later in the papers [1, 4] new approximating relations for ψ*(t), f(t), F(t)* have been proposed. Authors recommended to use them in more wide temperature interval 2 $10^{-2} \le t \le 0.75$.

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

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

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

As it is well known, individual features of a substance manifests itself more strongly at low temperatures. Widening of the temperature interval of description of surface tension with using the formulas (6)-(8) lowered the quality of prognosing in the vicinity of the critical point. By this reason the values of critical indices' μ and β ratios were different (see Table 1). Mean value of the quantity of*(μ/β)* is equal to 3.881, according to calculations with Eqns. (1), (2), and the theoretical estimation gives practically the same value: *(μ/β)*=0.879, then the calculation by the formulae (1), (6)-(8) gives *(μ/β)*=3.737.

Of course, for the purposes of the surface tension prognosis, there is the sense to put *n*=0.9341, μ=1.2586 which corresponds to theoretical estimation, and hence to lower the number of the constants. Then, according to one-parameter law of corresponding states, a dependence of reduced surface tension on the defining criterion of

similarity must exist. In the paper [4] it was shown that such generalized relation had approximately linear character, and can be approximated by the following equation:

$$\sigma^* = \sigma_0 R^{-1/3} P_K^{-2/3} T_K^{-1/3} = (0.1289 + 0.1656\omega)\ 10^{-7}. \qquad (9)$$

where ω - 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 one of individual values of μ from their theoretical estimation. Results of the calculations we obtained shown that the error of prognosing without using experimental data would be essentially depended on temperature, and this fact had too justified physical groundings. It is perfectly evident, that for molecules with complicated form and high value of 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 the place 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 (1):

$$\sigma = \sigma_0 \rho_0 t^{-\frac{\mu F(t)}{\beta f(t)}} \Delta\rho^{\frac{\mu F(t)}{\beta f(t)}}. \qquad (10)$$

Prognosing of σ with the help of Eq.(10) has significant advantage over the above-mentioned method, because the ratio of individual indices μ/β insignificantly differs from the theoretical value of 3.879 compared with the difference in the values of μ (seeTable 1).

By this way, relations (1), (6)-(10) can be used for the calculation of surface tension for non-associated liquids of various classes, including new ozone-safe refrigerants, without using any empirical information.

For calculation of refrigerants' surface tension in the temperature region 2 $10^{-2} \le t \le 0.75$ we proposed the following relation too:

$$\sigma = \sigma_0 (\Delta\rho / \rho_0) t^{3.739 F_1(t)}, \qquad \text{where}$$

$$F_1(t) = 0.99217 + 0.162479t - 1.1323944t^2 + 0.7944604t^3. \qquad (12)$$

Structure of the Eq.(11) is similar to the McLeod-Bachinski formula. However, the exponent considerably differs from the value of four. Additionally, the function $F_1(t)$ varies its value with temperature within 17% approximately. These facts make an emphasis on invalidity of phenomenological methods which use parachore for calculating surface tension.

Summing all that, one may recommend proposed formula both for solving tasks of prognosing σ and calculation of surface tension on the basis of restricted experimental information, formulae proposed here may be used practically in the whole temperature region of the liquid phase, giving the results with the accuracy of the experimental study.

On the basis of many-year experimental studies of surface tension which have been made in Odessa State Academy of Refrigeration (OSAR), the constants of the Eqns. (1), (6)-(8) were determined for a number of refrigerants widely used in the industry. The values of these constants were in the Table 1.

Method of prognosing of surface tension and capillary constant of refrigerants was reported in [18]. This method was based on invalid assumption on the constancy of

indices n, β, μ in all temperature interval of liquid phase existence. However, universal complex of amplitudes $Ç_{à}$ proposed by authors of the article [21] is of certain interest for the prognosing of capillary constant and surface tension.

$$Ç_a = a_o^2 gm \Big/ \left(k_{Á} T_C Z_C^{3/\ 2} Y_C^n\right), \qquad (13)$$

where g - acceleration of gravity; m - molecular mass; $k_{Á}$ - Boltzmann's constant; $K = \left(k_{Á} T_C P_C^{-1}\right)^{1/3}$; $Z_C = P_C m \left(\rho_C k_{Á} T_C\right)^{-1}$; $Y_C = \left(\gamma_C T_C P_C^{-1}\right) - 1$; $\gamma_C = \frac{\partial}{\partial T}\left(P\left(T, \rho_C\right)\right)_{T \to T_C}$.

If to use all the values in (13) expressed in SI then it is obvious that for the studied refrigerants the complex (13) is practically constant and equal to (3.387±0.074) 10^{-12}. This obstacle gives the possibility to calculate the amplitude a_o^2 for slightly studied substances with the accuracy within 2%.

Values of constants a_o, n, σ_o given in Table 1 were obtained by statistical treatment of experimental data [1-5].

Values of capillary constant which have been measurement experimentally

$$a_{ik}^2 = \Delta H_{ik} \Big/ \left(b_i^{-1} - b_k^{-1}\right), \qquad (14)$$

were processed statistically. Random value distribetion, mathematical expectation for every group of measurements having the equal accuracy were evaluated. Sampling of the values of a_{ik}^2 was studied for revealing a rough mistake. Because an accuracy of individual values of a_{ik}^2 is a variable value, then statistical weight of the every member of the sampling P_{ik} has been taken into account. Weighted-mean value of capilary constant was calculated by the following formula:

$$\bar{a}^2 = \sum_{\substack{i=1 \\ i \neq k}}^{n} a_{ik}^2 P_{ik} \Bigg/ \sum_{\substack{i=1 \\ i \neq k}}^{n} P_{ik} \,. \qquad (15)$$

This hind of experimental data treatment ensured the constant value of the relative error in determinig the capillary constant in wide temperature interval.

Values of constants given in Table 1 were recommended to use in the calculations of a^2, $\Delta\rho$ and σ in the temperature interval $10^{-2} \leq t \leq 0.60$.

3. SURFACE TENSION OF BINARY MIXTURES OF REFRIGERANTS

With the help of the units which have been described in detail in the papers [3, 5], an experimental study of the surface tension coefficient of binary mixtures of refrigerants R116/R23, R22/R14, R134a/R152a, R22/R142b was made. Capillary constant was measured by the modified method of capillary rising [1-5].

During this study a pressure of saturated vapour of refrigerants' mixtures was measured too. Concentration of the mixture was determined by the weight method with the accuracy within 0.05%. Variations in composition of vapour and liquid phases were checked by the measured *(P,T)*-parameters with the using of data on phase equilibrium in these mixtures obtained in OSAR.

Results of the experimental data treatment show that the concentration of vapour and liquid phases of zeotropic mixtures was sufficiently varied with temperature increasing. This obstacle one must take into account in order to eliminate methodological defects during the experimental data treatment.

Method of calculation of σ for binary mixtures of non-associated liquids was based on the formalism which have been talked about in the foregoing chapter. Analysis

showed that Eq.(1) described the experimental data on capillary constant and surface tension, related to the fixed concentration of liquid mixture, with the accuracy comparable with that of experimental study. Similar character of temperature dependence of a^2 and σ for pure substances and binary mixtures permitted to obtain the equations for isotherms of these properties:

$$a_j^2 = a_i^2\left(a_{oj}^2 / a_{oi}^2\right)t^{\left[n_i(x-1)+n_K(1-x)\right]\psi(t)}, \qquad (16)$$

$$\sigma_j = \sigma_i\left(\sigma_{oj}/\sigma_{oi}\right)t^{\left[\mu_i(x-1)'+\mu_K(1-x)\right]F(t)}, \qquad (17)$$

where a_j^2 and σ_j - capillary constant and surface tension of binary mixture of *i*-th and *k*-th component, and a_i^2 and σ_i - capillary constant and surface tension of *i*-th component; *x* - liquid phase concentration (*x*, mol.%).

Deviations of experimental data from results calculated with Eqns. (16), and (17) were within 1.5%.

Main merits of the proposed equations of isotherms of capillary constant and surface tension were high accuracy, little volume of initial information and possibility of their using for the prognosing of the surface tension coefficient of binary mixtures of non-associated liquids in wide region of the state parameters.

For the region of concentratin $10^{-3} \le x \le 1$ the values of constants a_o^2, σ_o, n μ for the studied mixtures obtained by the treatment of experimental data were approximated by the following equations:

$$a_0^2 = \sum_{i=0}^{n} A_i x^i \text{, mm;} \qquad n = \sum_{i=0}^{n} C_i x^i \text{;} \qquad (18)$$

$$\sigma_0 = \sum_{i=0}^{n} B_i x^i \text{, mN/m;} \qquad \mu = \sum_{i=0}^{n} D_i x^i . \tag{19}$$

Values of coefficients in Eqns. (15), (16) for studied mixtures were presented in Table 2.

4. CONCLUSION

In our paper the results of the treatment of experimental data obtained at the Thermophysical Properties Laboratory of OSAR were presented. Equations proposed here, permit both to approximate experimental data and solve tasks of prognosing with the using of minimal volume of experimental data. In this article the results of investigations of refrigerants' surface tension were summed; the aim of the before-mentioned studies is the working-out of thermodynamically self-consistent method, based on the scaling principles, for the prognosing of thermodynamic properties of substances on their saturation lines.

Authors express their gratitude to Drs. L.D.Lyasota, Ju. A. Semeniyk and collaborators of the Thermophysical Properties Laboratory, OSAR for their help in experimental studies of surface tension of refrigerants.

REFERENCES

1. Zhelezny, V.P. *Teplofizicheskie svoistve veschestv i materialov, GSSSD (National Standard Reference Data Service of the USSR)*. (1990), 31: 175-188.
2. Zhelezny, V.P. *Teplofizicheskie svoistve veschestv i materialov, GSSSD (National Standard Reference Data Service of the USSR)*. (1982), 16: 70-79.
3. Zhelezny, V.P. *Teplofizicheskie svoistve veschestv i materialov, GSSSD (National Standard Reference Data Service of the USSR)*. (1985), 20: 117-127.
4. Lyasota, L.D. Surface tension of refrigerants and their mixtures. *Ph.D. Thesis, State Acadeny of Refrigeration, Odessa* (1989).
5. Zhelezny, V. P. and Lyasota, L.D. Experimental apparatus for investigation of surface tention at low temperatures. *UkrNIINTI (Ukranian Inst. of Scientific and Engineering Information)*, (1987), No. 11616-Yk 87.
6. Novikov, I.I. *Teplofizicheskie svoistve veschestv i materialov, GSSSD (National Standard Reference Data Service of the USSR)*. (1989), 26: 4-21.
7. Filippov, L.P. Methods of calculations and prognosing of substances' properties. MGU Press: Moscow, (1988), 252 pp.
8. Zhelezny, V.P., Kamenetsky, V.R. and Romanov, V.K. *Russian J. of Physical Chemistry* (1982), 56(1): 60-61.
9. *Zhelezny, V.P., Kachurka, Y.A., Lyasota, L.D. and Semenyuk, Y. A. *Proc. VIII All-Union Conf. on Thermophys. Prop., Novosibirsk, USSR* (1988), 31-32. **Aharony, A., Ahles, G. *Phys. Rev. Lett.* (1980), 44, 782.
10. Sengers J.M.N.L., Sengers J.V. Perspectives in statistical physics. Ed.H.J.Raveche. Amsterdam: North-Holland, (1980),. Ch.14.

11. Ginsburg, V.L., Goldberg, U.I., and Golovko, V.A. Light scaterring near phase transitions. Nauka: Moscow, (1990), 414pp. No. 5-02-00678-5.
12. Nickolis, G. and Prigogin, I. Cognition of the complexity. Mir: Moscow, (1991), 342 pp.
13. Berge, P., Pomo, I. and Vidal, K. Order in chaos. Mir: Moscow, (1991), 361 pp.
14. Rabinovich, V.A. and Sheludyak, Ju.E. *Thermophysics of high temperatures (in Russian)*. (1995), 33(14): 546-552.
15. Anisimov, M.A., Rabinovich, V.A. and Sychev, V.V. Thermodynamics of critical state of individual substansies. Energoatomizdat: Moscow, (1990), 190pp. No. 5-283-00124-5.
16. Semenchenko, V. K. Selected chapters of theoretical physics. Prosveschenie: Moscow, (1966), 396 pp.
17. Zhelezny, V.P. Study of boundary angle of wetting at temperatures near critical one. *Studies of heat - and mass transfer processes. Transactions of scientific papers.* Kiev: Naukova dumka, (1979), 137-140.
18. LeNeindre, B. and Garrabos,Y. Prediction of the surface tension of fluorocarbon refrigerants. *Proc. of the Int. Cong. "CFC$_S$, The After" Joint Meeting of IIR Commission B1, B2, E1 and E2. - Padova.,* (1994), 549-556.

Table 1. Values of the constants of Eqns. (1), (6)-(8)

Substance	$\grave{a}_o$,mm	n	$\hat{A}_{\hat{i}}$	β	$\sigma_{\hat{i}}$, mH/m	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	-	-	-	-	75.520	1.269
R116	3.9023	0.9230	2377.7	0.3352	45.500	1.258
R125	-	-	-	-	54.572	1.253
R134a	6.2185	0.9202	-	-	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

Table 2. Values of coefficients in Eqns.(15) and (16)

Coefficients	R134a/R152a	R22/R142b	R116/R23	R22/R14
A_o	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_o	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_o	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_o	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