Prediction of surface tension of binary mixtures with the parachor method

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Abstract. The parachor method for the estimation of the surface tension of binary mixtures is modified by considering temperature-dependent values of the parachor parameters. The temperature dependence is calculated by a least-squares fit of pure-solvent surface tension data to the binary parachor equation utilizing the Peng-Robinson equation of state for the calculation of equilibrium densities. A very good agreement between experimental binary surface tension data and the predictions of the modified parachor method are found for the case of the mixtures of carbon dioxide and butane, benzene, and cyclohexane, respectively. The surface tension is also predicted for three refrigerant mixtures, i.e. propane, isobutane, and chlorodifluoromethane, with carbon dioxide.

1 Introduction

The parachor method [1] relates the surface tension of liquids to the densities of the liquid and the vapor phase. In the simplest case of a pure substance, the surface tension σ [N/m] is evaluated as $\sigma^{1/4} = P(\varrho_l - \varrho_v)$ [2, 3], where ϱ_l [mol/m^3] is the density of the liquid phase and ϱ_v [mol/m^3] is the density of the vapor phase. The relation involves a substance-specific constant P called the parachor. Its value was estimated for a wide range of substances from experimental surface tension data [4, 5]. Also, a correlation between the parachor and the critical volume was identified [6].

More advanced methods of the surface tension prediction are based on the gradient theory coupled with various equations of state, e.g. the Peng-Robinson EOS [7], PC-SAFT EOS [8], or PCP-SAFT EOS [9]. However, the parachor method presents a simple alternative, with a straightforward implementation and a sufficient precision for engineering applications.

In the case of multicomponent mixtures of N components the parachor relation takes the form

$$\sigma = \left(\sum_{i=1}^{N} P_i \left(\varrho_l x_i - \varrho_v y_i \right) \right)^n, \quad (1)$$

where x_i is the mole fraction of the liquid component i, and y_i is the mole fraction of the vapor component i. Several binary systems were already investigated with the parachor method [10, 11], and a good agreement with available experimental surface tension data [12, 13] was observed.

The exponent n in Eq. (1) was often discussed in the literature, and, instead of the original value of 4, values of 3.57, 3.66, or 3.88 were found more appropriate in some cases. Higher exponents seem more suitable for higher densities (intermediate temperatures), while lower exponents

work better for lower densities (close to the critical point); see [5, 14] for a more detailed discussion.

Also, the constant nature of the parachor was put to question. Zhelezny *et al.*[6] investigated the temperature dependence of the parachor, and they found a considerable increase, by tens of percent, in the parachor value in the limit of the critical point.

In this work, the parachor method will be applied to the prediction of the surface tension of binary mixtures of carbon dioxide. The goal is to investigate the possible temperature-dependence of the parachor parameters, i.e. the parachors P_i and the exponent n in Eq. (1), or, in other words, to assess the improvement in predictive capability of the parachor method by allowing the parachor parameters to vary with temperature. In section 2, an overview of the method is given. In section 3.1, the surface tension predicted with constant parachor parameters is compared to the available experimental data for the binary mixtures of carbon dioxide and n-butane, benzene, and cyclohexane, respectively. In section 3.2, the derivation of the temperature-dependent parachor parameters is given, and the predictions of the parachor method with temperature-dependent parameters are presented. In section 3.3, the surface tension of the refrigerant mixtures of carbon dioxide and propane, isobutane, and chlorodifluoromethane (R22), respectively, is predicted. The surface tension of these refrigerant mixtures is valuable for nucleation studies [15], since no experimental data are available so far. Finally, in section 3.4, the scaling behavior of the temperature-dependent parachor is studied, focusing on the correlation between the parachor and the critical volume of a given substance [6].

2 Parachor method

In order to estimate the surface tension of a binary mixture according to Eq. (1), the densities of the vapor phase ϱ_v and

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of the liquid phase ϱ_l are required at the vapor-liquid equilibrium (VLE). For the binary mixtures considered in this work, except R22, the available experimental VLE data from the literature are accurately represented by the predictive Peng-Robinson equation of state (PPR78 EOS) of Vitu *et al.* [16]. PPR78 features a temperature-dependent interaction parameter k_{ij}. In order to evaluate the PPR78 equation, the values of k_{ij} given in Vitu's work were fitted to a polynomial function of temperature. For the case of R22, the original Peng-Robinson EOS was used with the interaction parameter $k_{ij} = 0.009$, as predicted by Vrabec *et al.* [17].

The calculation of the surface tension with the parachor method proceeds as follows. The surface tension is being evaluated as a function of the temperature T [K] and the composition of the liquid phase, given by the carbon dioxide mole fraction x_2. The respective EOS is used to evaluate the corresponding equilibrium composition of the vapor phase, y_2, and the vapor pressure p [Pa], by means of a bubble-point calculation (see e.g. Smith and Van Ness [18], p. 490). Having the equilibrium compositions x_2, y_2 at hand, the equilibrium vapor and liquid densities ϱ_v and ϱ_l are obtained by solving the cubic EOS at p, T, and x_2, or y_2, respectively. This procedure results in the evaluation of y_i, ϱ_v, and ϱ_l for use in Eq. (1) at a given T, and x_2.

Now, to evaluate Eq. (1), the parachor parameters P_1, P_2, n remain to be specified. Either the value reported in the literature can be used, or the parameters can be fitted to available experimental data with Eq. (1). Both approaches will be discussed further, focusing of the possibility of the temperature dependence of the parachor parameters.

3 Results and discussion

Two different cases will be discussed in order to study the possibility of a temperature dependence of the parachor parameters.

First, constant values of P_1, P_2, and n will be assumed. This is a standard approach, applied for example by Gasem *et al.* [10], who fitted the three parameters to experimental VLE data (i.e. surface tension, liquid and vapor densities) of binary mixtures. The estimated surface tension based on the parachors of Gasem *et al.* is discussed in section 3.1.

Second, temperature-dependent values of P_1 and n will be considered. The parachor of carbon dioxide is taken constant $P_2 = 79.2$ [10] in this case, because all the mixtures investigated in this work are studied above the critical point of the pure carbon dioxide, and therefore the dependence on its reduced temperature is irrelevant. The predictions of the surface tension by the parachor method in case the model parameters P_1 and n are allowed to vary with temperature are discussed in section 3.2.

3.1 Constant parachors

In the work of Gasem *et al.* [10] the parachors of several substances were calculated from the experimental data for the VLE densities and the surface tension of binary mixtures. A least-squares optimizing procedure was applied to

Table 1. Parachors by Gasem *et al.* [10] corresponding to the exponent $n = 3.57$ of Eq. (1).

Compound	Parachor
carbon dioxide	79.2
n-butane	199.7
benzene	200.4
cyclohexane	234.9

fit the parameters P_1, P_2, and n to the available experimental data for mixtures of carbon dioxide and n-butane, benzene, cyclohexane. The value of the exponent fitted by Gasem *et al.* is $n = 3.57$, and their parachor values are given in table 1.

The surface tension of the three above mentioned binary mixtures calculated according to Eq. (1) with the parachor parameters from table 1 are shown in figure 1. In all three cases the experimental binary surface tension data (circles) are reproduced satisfactorily. However, large discrepancies can be observed in the surface tensions of pure solvents (squares), especially in the cases of benzene and cyclohexane. Moreover, no definite rule can be spotted in the nature of this discrepancy; the surface tension is both overestimated (butane at low temperatures), but also underestimated (other cases). For benzene, the measured surface tension is 35% higher than the surface tension predicted by the parachor method. This presents a strong argument for parachors and/or exponent being dependent on the thermodynamic state of the system rather than being universal constants.

3.2 Temperature dependent parachor and exponent

The possibility of the temperature dependence of the parachor parameters will be investigated in the following two cases:

case 1 The value of P_1 is allowed to vary with temperature, while the exponent is assumed constant, $n = 4$.
**case 2** Both parameters P_1 and n are considered temperature-dependent.

As already noted, the parachor of the carbon dioxide is taken constant, $P_2 = 79.2$. Actually, the precise value of P_2 does not have a significant influence on the results. Only in case a considerably different value of P_2 would be used, e.g. multiplied by a factor of 2, the convexity of the resulting functional dependence $\sigma(x_2)$ would be slightly changed.

In both the above specified cases, the parachor parameters are calculated from the available experimental surface tension data of the pure solvents only. No binary experimental surface tension data are involved in the calculation. The two parameters P_1 and n of Eq. (1) are fitted to the surface tension data with a least-squares optimization procedure implemented in Python[1].

Figure 2 shows the results of the optimization procedure for the case 1. The parachors of the solvents are fitted

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[1] scipy.optimize.minpack.leastsq
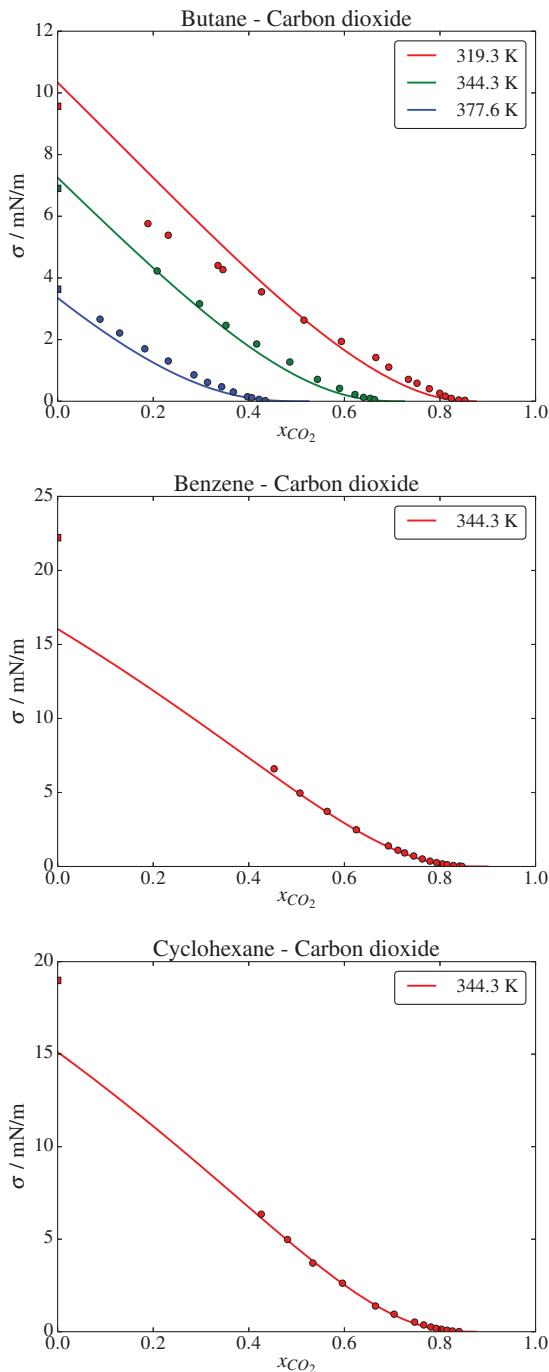
Fig. 1. Surface tension of binary mixtures predicted with the parachor parameters by Gasem *et al.* [10]. The experimental surface tension data [12,13] are plotted as circles, and the pure solvent surface tension [19] is plotted with squares.

assuming a constant exponent $n = 4$, and plotted as a function of the reduced temperature $T_r = T/T_c$, where T_c is the critical temperature of the pure solvent. A common feature of all the parachors is that they are almost constant up to a reduced temperature of roughly 0.8. Above this value, the parachors increase steeply, by more than 30 % when approaching the critical point.
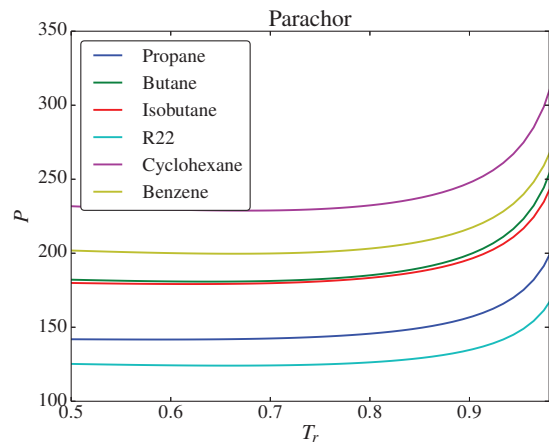
Fig. 2. Solvent parachors fitted with a constant exponent $n = 4$ (case 1).

Figure 3 shows the fitted solvent parachors and the corresponding exponent n for the case 2. The parachors feature a common functional dependence on T_r, similarly to the case 1. However, the parachor is almost a linearly increasing function of the reduced temperature. The exponent n is a linearly decreasing function of temperature; n being around 4.5 at $T_r = 0.5$, and around 2.5 when approaching the critical temperature of the solvent. Interestingly, n is almost identical for all the binary mixtures considered in this analysis.

The predictions of the parachor method comparing the two scenarios of parachor parameters estimation, case 1 and case 2, are shown in figure 4. The predictions of case 1 are plotted as dashed lines, and the predictions of case 2 are drawn as full lines. For all the three mixtures, the predictions of case 2 show a better agreement with the binary experimental surface tension data, although for benzene and cyclohexane the improvement is almost negligible.

3.3 Parachor method predictions for refrigerant mixtures

The binary mixtures of a refrigerant and carbon dioxide were investigated extensively in bubble nucleation studies [15]. There is a wide range of experimental bubble nucleation data available in the literature [20]. However, the theoretical explanation of the measured nucleation rates was not given with sufficient precision yet. One of the reasons for the failure of the theoretical predictions of bubble nucleation rate in the binary case is the lack of knowledge of the surface tension of these mixtures. So far, the theoretical predictions utilized the pure-solvent surface tension [15], which is considerably higher than the surface tension of the mixture at higher concentrations of carbon dioxide. As the nucleating mixtures are typically rich in carbon dioxide, the approximation of the binary surface tension with the pure-solvent surface tension is rather crude.

The surface tension of three refrigerant – carbon dioxide mixtures, i.e. with propane, isobutane, and R22, respectively, is shown in figure 5 as predicted by the parachor
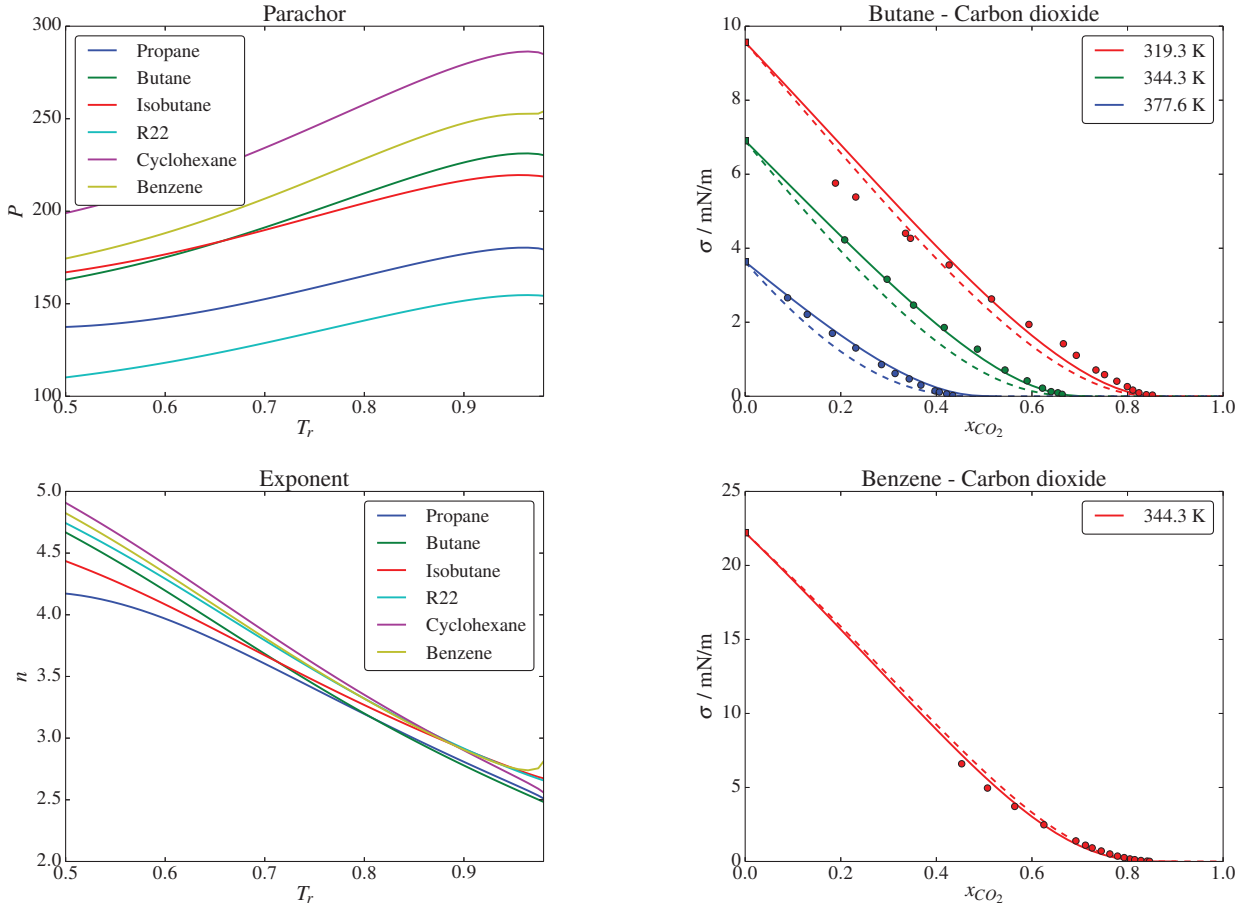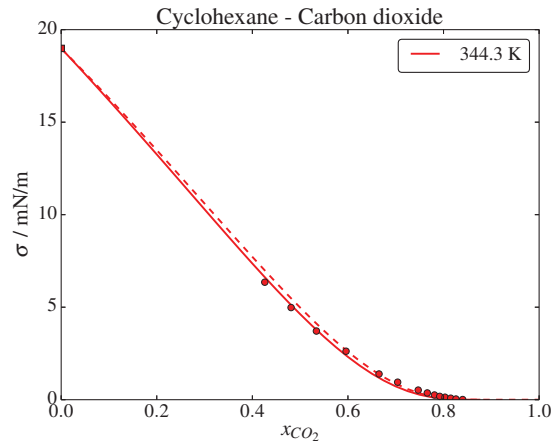
Fig. 3. Solvent parachors and exponent fitted with Eq. (1) to the surface tension data of pure solvents (case 2).

method. The case 2 version of parachor parameters fitting was used; the parachor parameters used in calculating the surface tension in figure 5 are those from figure 3.
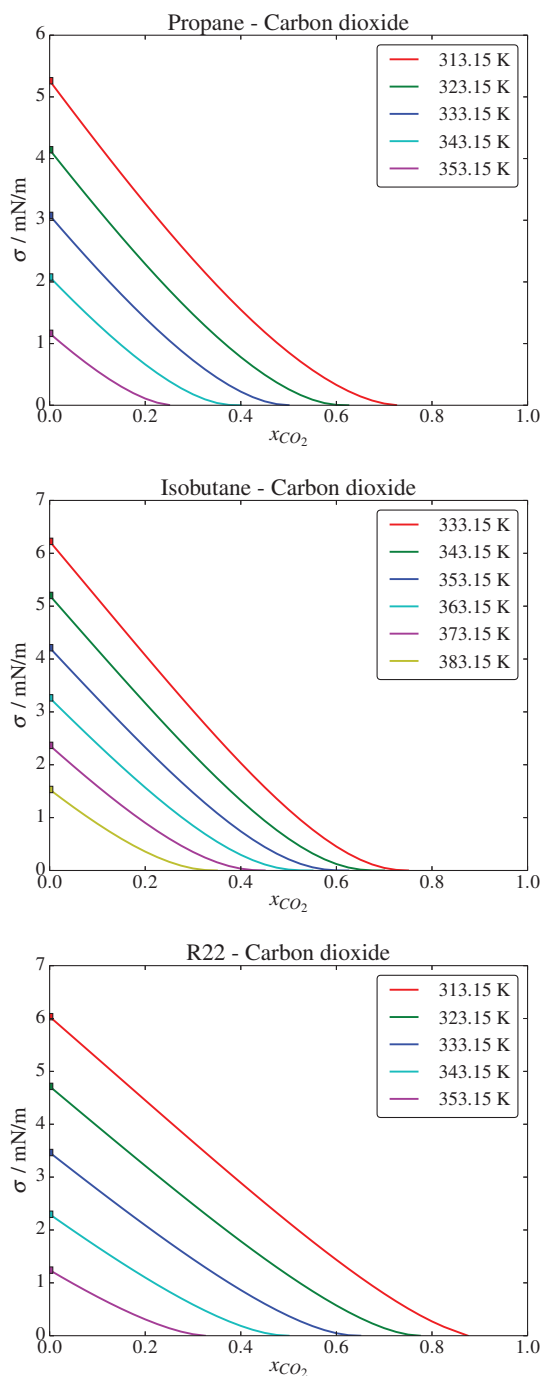
3.4 Parachor scaling

Zhelezny *et al.* [6] found a correlation between the critical parachor P_c and the molecular volume v_c [cm^3/mol]. Their critical parachor is defined as $P_c = M\sigma_0^{\beta/\mu}/\varrho_0$, where M is the molecular weight, σ_0 and ϱ_0 are the constants of the critical scaling of the surface tension $\sigma = \sigma_0(1 - T_r)^\mu$ and of the VLE density difference $\varrho_l - \varrho_g = \varrho_0(1 - T_r)^\beta$, respectively, and $\beta = 1.260$ and $\mu = 0.325$ are the critical exponents.

The relation, $P_c = 0.75v_c$, between the critical parachor and the critical volume was confirmed for a set of 26 substances (refrigerants, alkanes, atmospheric gases) by Zhelezny *et al.* To investigate the scaling behavior of the temperature-dependent parachors calculated in this work, the parachors from the case 2 (figure 3) are plotted in figure 6 and are scaled by the critical volume of the respective substance. The factor 0.75 found in the work of Zhelezny *et al.* was omitted in this scaling, because it is related to their specific choice of the critical parachor P_c, which uses
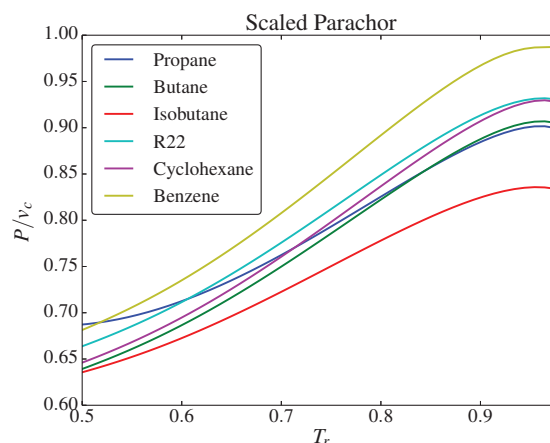

Fig. 4. Comparison of the surface tension of binary mixtures predicted by two methods of parachor parameter estimation, case 1 (dashed lines) and case 2 (full lines). The experimental surface tension data [12, 13] are plotted as circles, and the pure solvent surface tension [19] is plotted with squares.

Fig. 6. Parachor values from case 2 scaled by the critical volume v_c [cm^3/mol].

ane, and R22. But the remaining two substances, i.e. benzene and isobutane, show a 10 % deviation from the behavior of the other substances. Moreover, the scaled parachor of isobutane is lower, and the scaled parachor of benzene is higher than the scaled parachors of the other substances. The scaled parachors roughly coincide at low reduced temperatures only, e.g. at $T_r = 0.5$ the scaled parachors P/v_c equal 0.66 ± 0.02.

4 Conclusion

A modification of the parachor method for the prediction of the surface tension of binary mixtures of carbon dioxide was studied in this work by considering the possibility of temperature-dependent parameters of the parachor relation. For the case of binary mixtures of carbon dioxide, a procedure for the calculation of the temperature-dependent parachor parameters from the experimental pure-solvent surface tension data was presented, and a considerable improvement of the predictive capability of the parachor method was observed. Although the parachor parameters were fitted to the experimental surface tension of pure solvents only, the binary surface tension data from independent literature sources are estimated very accurately. The absence of the need for a binary mixing rule, or a binary interaction parameter, to accurately estimate the binary surface tension data makes this method quite robust.

A quite simple temperature dependence of the parachor parameters resulted from this analysis. The individual solvent parachors increase almost linearly with the reduced temperature. The exponent of the parachor equation decreases with the reduced temperature uniformly for all the binary mixtures investigated in this work.

Fig. 5. Surface tension of refrigerant mixtures with carbon dioxide relevant to bubble nucleation studies [15] predicted by the parachor method with temperature-dependent parachor P_1 and exponent n (case 2).

the exponent $n = \beta/\mu = 3.87$. Since, in this analysis, the exponent n is resulting from the fitting procedure, and its value reaches 2.5 close to the critical point, the factor 0.75 has no relevance here.

No definite statement, however, can be made about the scaled parachors in figure 6. The dependence of the scaled parachor on the reduced temperature is almost identical for the 4 out of 6 substances, i.e. propane, butane, cyclohex-

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