Colloid Polym Sci 275:561–566 (1997)

ORIGINAL CONTRIBUTION

K.S. Birdi

Prediction of critical temperature of *n*-alkanes and *n*-alkenes from surface tension vs. temperature data

Received: 29 October 1996
Accepted: 13 December 1996

Prof. Dr. K.S. Birdi (✉)
School of Pharmacy
Department of Analytical
and Pharmaceutical Chemistry
Universitetsparken-2
2100 Copenhagen, Denmark

Abstract The surface tension versus temperature data of homologous series of *n*-alkanes and *n*-alkenes is analyzed. Critical temperatures are shown to be predicted from these data, with a very high precision, after some corrections are made. The corrections are shown to arise from the effect of the critical pressure on the extrapolated data to surface tension approaching zero.

Key words Surface tension – critical temperature – surface entropy – alkanes – alkenes

Introduction

In order to understand the molecular structure of liquid surfaces, it is important to be able to describe the interfacial forces as a function of temperature and pressure. At the interfaces, molecules exhibit unique properties, undergoing ordering caused by the asymmetric nature of the interfacial region. As temperature increases the kinetic energy increases due to the increase in the molecular movement. This effect on the change in surface tension gives information on the surface entropy. Although a large number of reports are found in the literature at this stage, the complete understanding of the surface energy and entropy is not satisfactorily understood at molecular level.

In order to analyze surface thermodynamic relations of different molecules it is useful to consider the model system as a homologous series of normal alkanes and alkenes, since very reliable and accurate data is available in the literature. Furthermore, linear hydrocarbon chains, i.e., *n*-alkanes and *n*-alkenes, are among the most common building blocks of organic matter. They form part of organic and biological molecules like lipids, surfactants, and liquid crystals, and determine their properties to a large extent. As major constituents of oils, fuels, polymers and lubricants they also have an immense industrial importance.

In the case of all liquids, as temperature increases, the magnitude of surface tension decreases. At the critical temperature T_c and pressure P_c the magnitude of γ is zero [1, 2]. The critical constants of a compound are both of fundamental [3] and practical interest. The purpose of this study is to report on the prediction of T_c from γ versus temperature data for different homologous *n*-alkanes and *n*-alkenes. The accuracy of prediction is found to be very high ($\pm 2\%$).

Corresponding states theory and surface entropy of liquids

The effect of temperature on surface tension is different for different fluids [4]. This quantity is defined as the surface entropy, S_s $[= -\mathrm{d}\gamma/\mathrm{d}T]$. Thus one can obtain much useful information from this as regards thermodynamics and the molecular interactions in liquids. The most useful information as provided by S_s is that both the sensitivity and the range of temperature is larger than that available for any other thermodynamic quantity, such as heat of evaporation, density, heat capacity etc.

Measurements have shown that for most liquids, the magnitude of γ decreases almost linearly with temperature within a narrow range [1, 2, 4]:

$$\gamma_t = \gamma_0[1 - \alpha t] \,, \qquad (1)$$

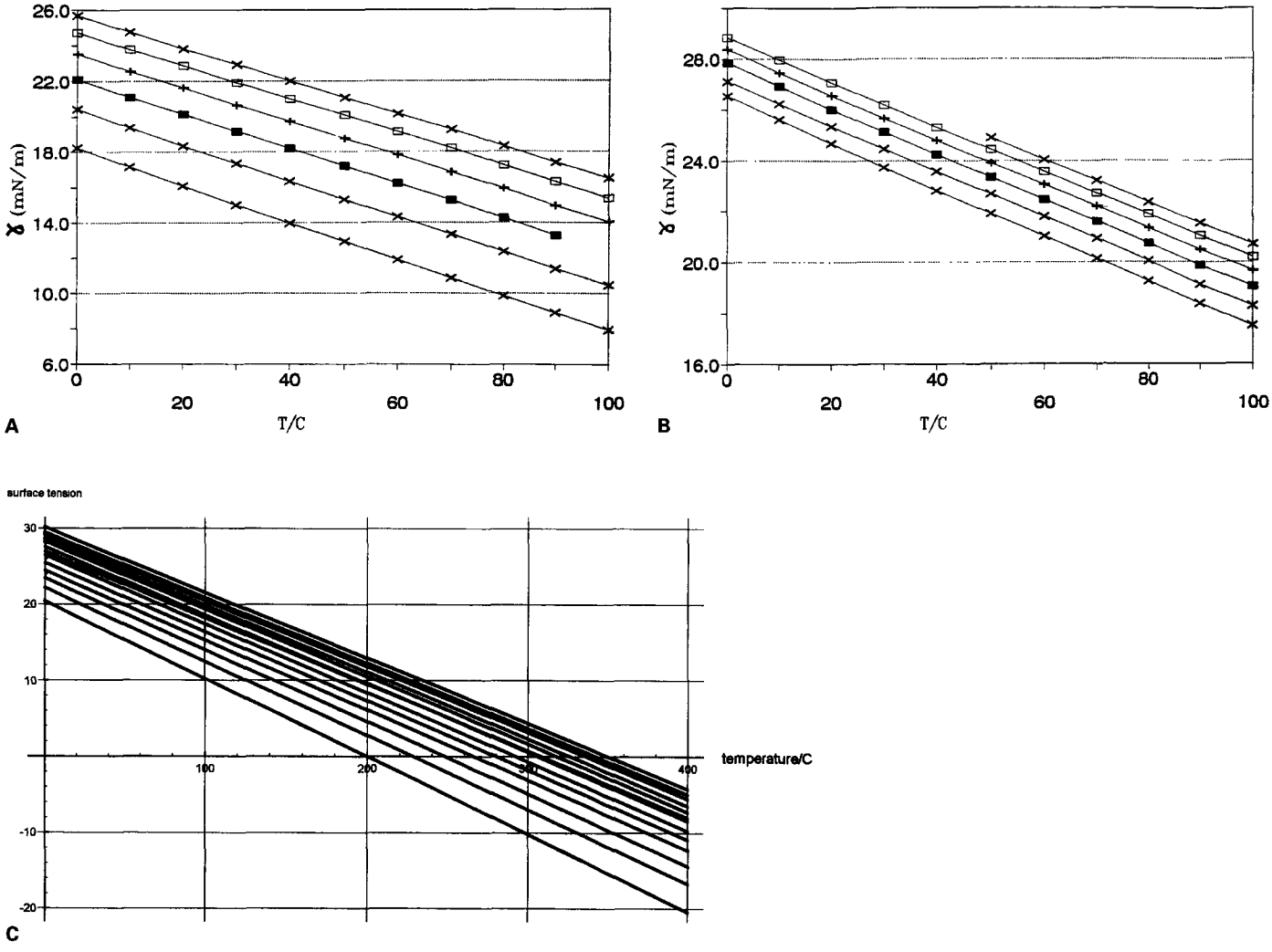

Fig. 1 Variation of γ (mN/m) vs. temperature for n_c for *n*-alkanes [6]: [**A**] for n_c from 5–10; [**B**] 11–16; [**C**] 5–16. The plots are extrapolated for data points ranging from 10–100 °C

where α is a constant, and t is temperature (°C). It was found that the coefficient α is approximately equal to the rate of decrease of density [ρ] with rise of temperature:

$$\rho_t = \rho_0[1 - \alpha t] \tag{2}$$

values of constant α were found to be different for different liquids. Furthermore, the value of α was related [5] to T_c.

At the critical temperature T_c and critical pressure P_c and ρ of liquid and vapor are identical, and the surface tension γ and total surface energy, like the energy of vaporization, must be zero. At temperatures below the boiling point, which is 2/3 T, the total surface energy and the energy of evaporation are nearly constant.

Surface tension versus temperature data of *n*-alkanes and *n*-alkenes: The surface tension γ variation with temperature is given in Fig. 1a–c for different liquid *n*-alkanes with the number of carbon atoms from 5 [C_5] to 18 (C_{18}) [2, 6].

These data clearly show that the variation of γ with temperature is a characteristic physical property of a given liquid, analogous to other bulk properties such as boiling point, heat of vaporization, density, viscosity, compressibility, and refractive index. In other words, the molecules at the surface of alkanes exhibit dependence on chain length which can be related to some of these bulk properties. The surface entropy, S_s ($= -\, d\gamma/dT$) is almost a linear function of n_c [Tables 1 and 2]. These data provide very useful information about the molecular structures at the surface. This observation becomes even more important, when considering that the sensitivity [2] of γ measurements can be as high as ca. $\pm$ 0.001 dyn/cm [= mN/m]. It is also observed that the magnitude of γ (extrapolated

Table 1 Linear equation [$\gamma = A_0 - S_s T$, where T is in C] for data of γ vs. temperature for n-alkanes of Fig. 1 [6]

Alkane [n_c]	A_0	S_s [$-d\gamma/dT$]	Calculated value of γ at $T = -540$ C (see text)
5	18.25	0.1102	77
6	20.44	0.1022	75
7	22.10	0.098	76
8	23.52	0.0951	75
9	24.72	0.0935	75
10	25.67	0.092	75
11	26.46	0.0901	75
12	27.12	0.08843	75
13	27.73	0.0872	75
14	28.30	0.0869	75
15	28.78	0.08565	75
16	29.18	0.0854	75
17	29.6	0.0846	75
18	29.98	0.08423	75
19	30.26	0.0837	75
20	30.54	0.0833	75

Magnitude of A_0 is the extrapolated value of γ at $T = 0$ C. S_s = [mNm/T].

Table 2 Comparison of measured and estimated $T_{c,\gamma\to 0}$ at $\gamma = 0$ for different n-alkanes by extrapolation from the data in Fig. 1. Measured values of T_c and P_c are also given [4]

n_c	$T_{c,\gamma\to 0}$ [°C] estimated	$T_{c,\text{at } P_c}$ measured	Δ	Δ [n_c]	P_c [bar]
5	166	197	31	6	33.2
6	200	234	34	6	30.1
7	216	267	51	7	27.4
8	240	296	56	7	24.9
9	260	320	60	7	23.4
10	279	344	65	6.5	21.2
11	294	364	70	6.3	19.9
12	307	385	78	6	18.5
13	318	403	85	6	17.2
14	326	420	94	6	14.4
15	336	434	98	6	15.2
16	342	449	107	6	14.1
17	350	460	110	6	13
18	356	475	119	6	12
19	361	483	121	6	11.1
20	367	494	127	6	11

$\Delta = T_{c,\text{at } P_c} - T_{c,\gamma\to 0}$.

value) at $T = 0$ °C, increases with alkane chain length, n_c. This means that γ increases with increasing van der Waals interactions between chains, analogous to heat of vaporization, melting point and other molecular properties.

The surface tension versus temperature data for a homologous series of n-alkenes is given in Fig. 2 (Tables 3 and 4). The differences between these two homologous series are significant, i.e. within the accuracy of measurements.

These data thus stress how useful such physical measurement can be related to the molecular property of a homologous series of molecules. These data also show that the magnitude of γ is proportional to the chain length of the alkanes and alkenes. This is to be expected based on the previous relation given by Stefan on the dependence of the magnitude of γ on the heat of evaporation [2].

The data of surface tension versus temperature can be analyzed as follows. It is well known that the *corresponding states theory* can provide much useful information about the thermodynamics and transport properties of fluids. For example, the most useful two-parameter empirical expression which relates the surface tension γ to the critical temperature is given as [5, 7]

$$\gamma = k_0[1 - T/T_c]^{k_1} , \tag{3}$$

where k_0 and k_1 are constants. van der Waals derived this equation and showed that the magnitude of the constant $k_1 = 3/2$, although the experiments indicated that $k_1 = 1.23$ ca. Guggenheim [8] has suggested that $k_1 = 11/9$.

Moreover, the quantity $k_0 = [V_c]^{2/3}/T_c$ was suggested [9] to have a universal value ca. 4.4. However, for many liquids the value of k_1 lies between 6/5 and 5/4. Thus the correct relation is given as [Eq. (3)]

$$\gamma = [V_c]^{2/3}/T_c[1 - T/T_c]^{k_1} . \tag{4}$$

It is thus seen that surface tension is related to T_c and V_c. van der Waals also found [1, 2, 4] that k_0 was proportional to $(T_c^{1/3}(P_c))^{2/3}$.

Although the theory predicts that the exponent (k_1) is valid only asymptotically close to the critical point, the surface tension obtained from the corresponding states theory with additional expansion terms has been shown to be valid for many pure substances over their entire liquid range.

The measured variation in γ with temperature data, near room temperature, was almost linear with temperature for all the alkanes with the number of carbon atoms n_c from 5 to 18. This means that the magnitude of surface entropy is constant over a range of temperature. This is also observed for the alkenes series. Similar observation is made from the analyses of several other homolog series of organic fluids (alcohols, dienes, etc.) [10, 6].

The γ data of alkanes were analyzed using Eq. (3). The constants k_0 (between 52 and 58) and k_1 (magnitude ranging between 1.2–1.5) were found to be dependent on the number of carbon atoms n_c and since T_c is also found to be dependent on n_c, the expression for all the different alkanes which individually were fit to Eq. (3), gave rise to a general equation relating γ as a function of n_c and T [2].

Colloid & Polymer Science, Vol. 275, No. 6 (1997)

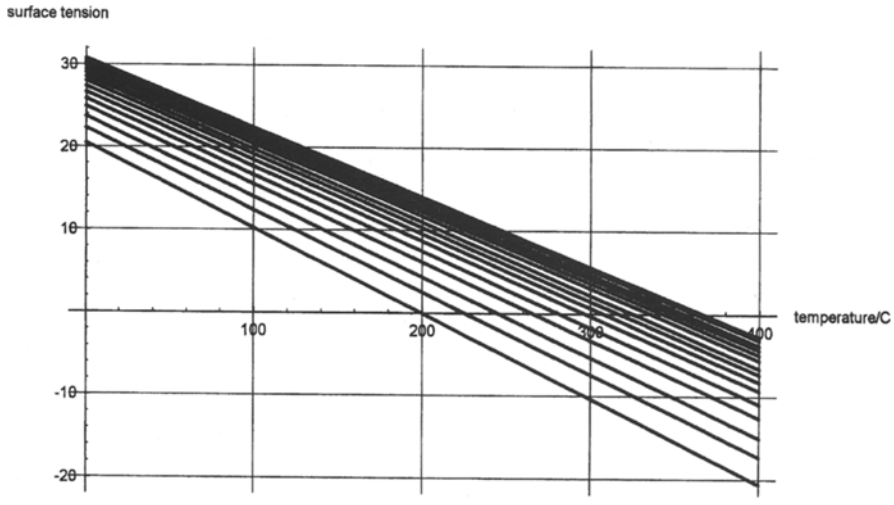

Fig. 2 (a) Variation of γ (mN/m) vs. temperature for n_c for *n*-alkenes: n_c from 6 (lowest curve) to 20 (uppermost line) (data from Table 3). The plots are extrapolated for data points in the range from 10 to 100 °C

Table 3 Linear equation ($\gamma = A_0 - S_s T$, where T is in °C) for data of γ vs. temperature for *n*-alkenes in Fig. 2 [6]

Alkene [n_c]	A_0	$S_s[-d\gamma/dT]$ surface entropy	Calculated value of γ at $T = -540$ °C (see text)
6	20.47	0.10271	76
7	22.28	0.099	76
8	23.68	0.0968	76
9	24.9	0.0938	75
10	25.84	0.092	75
11	26.67	0.090	75
12	27.38	0.0891	75
13	28.01	0.08839	76
14	28.56	0.0879	75
15	29.04	0.0866	75
16	29.47	0.086	76
17	29.85	0.0854	75
18	30.19	0.085	76
19	30.49	0.084	75
20	3.79	0.084	75

Magnitude of A_0 is the extrapolated value of γ at $T = 0$ °C. S_s = [mN/m/T].

Table 4 Comparison of measured [4] and estimated $T_{c,\gamma\to 0}$ at $\gamma = 0$ for different *n*-alkenes by extrapolation from the data in Fig. 2

n_c	$T_{c,\gamma\to 0}$ [°C] estimated	$T_{c,\text{at } P_c}$ measured	Δ	$\Delta[n_c]$
6	199	231	32	5
7	225	260	35	5
8	244	294	50	6
9	265	320	55	6
10	281	341	60	6
12	307	374	67	6

$\Delta = T_{c,\text{at } P_c} - T_{c,\gamma\to 0}$.

Estimation of $T_{c,\gamma\to 0}$ from surface tension versus temperature data of *n*-alkanes and *n*-alkenes

In the case of *n*-alkanes, the linear part (Fig. 1) of data was extrapolated to $\gamma = 0$, in order to estimate $T_{c,\gamma\to 0}$. The analyses of the alkanes data for C_5 to C_{20} is of much interest in this context, both from theoretical and practical point of view. If one merely extrapolates the linear part of the measured data (at 1 atm) then the estimated $T_{c,\gamma\to 0}$ is found to be somewhat lower (ca. 15–30%, dependent on n_c) then the directly measured values, Table 2. The same is valid from the analysis of data for *n*-alkenes, Table 4 (Fig. 2).

The difference between the estimated $T_{c,\gamma\to 0}$ (lower than T_c in all cases) and the measured T_c (range measured from 200–500 °C; at P_c) per carbon atom is found to be $\simeq 6$ °C (both for alkanes and alkenes). The constant factor 6 will be expected to be related to the effect of pressure on γ (i.e., $d\gamma/dP$). This finding is of great significance. The correction needed arises from the effect of P_c on γ (as described herein).

One can thus show from these data that for *n*-alkanes and *n*-alkenes

$$T_c = T_{c,\gamma\to 0} + 6n_c \,. \tag{5}$$

This equation allows one to estimate T_c of *n*-alkanes and *n*-alkenes with very high accuracy from the measurement of S_s. Further, this shows convincingly that increase in pressure gives rise to an increase in surface tension, i.e., $d\gamma/dP = +$. However, the need for this correction is expected, since if we consider the fact that at the critical point the pressure is not 1 atm but P_c, then a correction would be needed. For example, the T_c and P_c for alkanes of n_c equal to 12 and 16 are: 658 K (385 °C) and 18 atm; 722 K (449 °C) and 14 atm, respectively (Table 2).

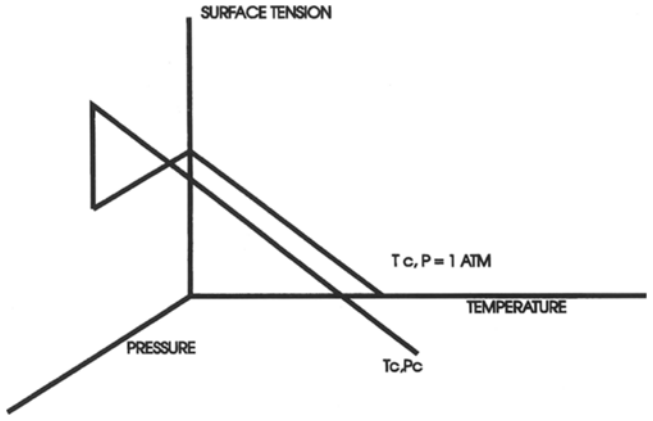

Fig. 3 Variation of surface tension γ vs. T and P (schematic) [10]

In order to modify the data of γ versus T, at 1 atm, to include the effect of pressure P_c then this would give an increase in surface tension, since $d\gamma/dP$ is positive for liquids [2]. In other words, the analyses of surface tension versus temperature data need to be reformulated which includes the effect of P_c on the surface tension data, as shown below (schematic, Fig. 3). The measured γ data is obtained at 1 atm. The extrapolated line is moved from 1 atm to P_c, and moved up by a value which corresponds to $d\gamma/dP$ (positive). It is thus possible to estimate the magnitude of $d\gamma/dP$ from such data.

Thus the correction needed based on the above is as follows:

$$T_c = \gamma_{t,\mathrm{ref}} + S_s t_{\mathrm{ref}}/S_s + 6(n_c)\,, \tag{6}$$

where $\gamma_{t,\mathrm{ref}}$ is the surface tension at a given temperature (and at 1 atm), S_s is the surface entropy. The correction term, second on the right-hand side, arises from the need to obtain γ at T_c at pressure equal to P_c.

It is obvious that when more systematic surface tension data becomes available, a more detailed molecular description of the significance of this observation can be given. For example, there exists no such analyses of alkane

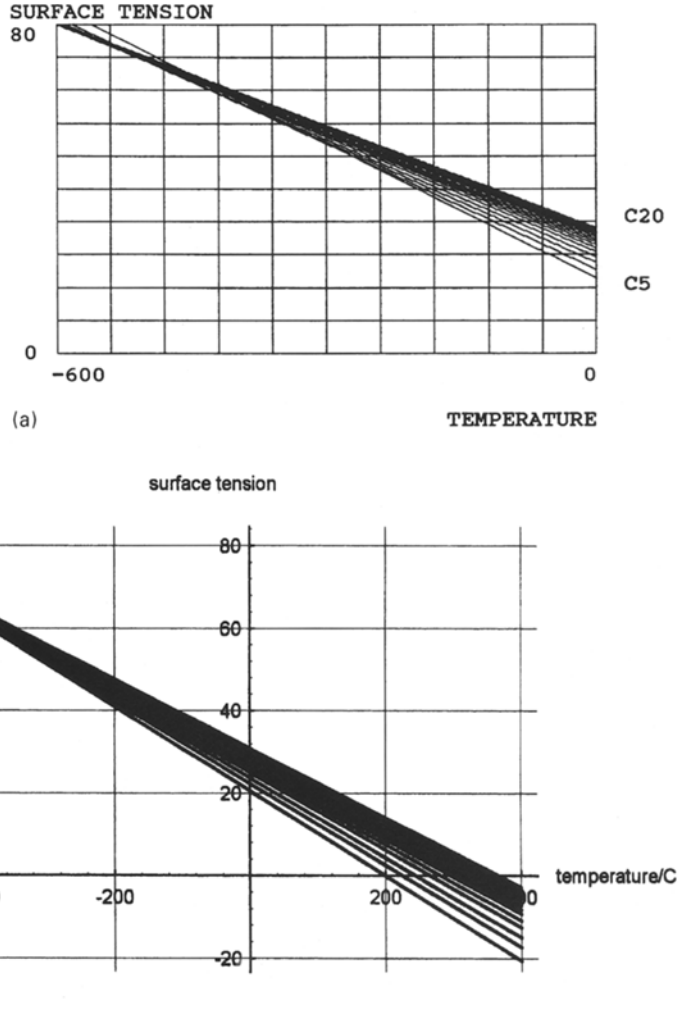

Fig. 4 Extrapolation of γ vs. T data: (a) alkanes; (b) alkenes

mixtures (of two or more components). These latter systems are of much interest in the oil recovery processes. Preliminary analyses of other homologous series has shown that the data do not fit the relation as given in Eq. (5). Preliminary analyses shows that strong deviation is observed even with alcohols and other alkyl derivatives [10].

Furthermore, the γ versus temperature data for the homologous series of *n*-alkanes and *n*-alkenes shows some unique characteristics. The data for alkanes on extrapolation to hypothetical "*super-cooled*" region converge at $T_{sc} = -540\,^{\circ}C$ ca. and $\gamma_{sc} = 75$ mN/m. The calculated values of γ_{sc} are given in Tables 1 and 3, for homologous series of alkanes and alkenes. The magnitude of γ_{sc} is ca. 75 mN/m in all cases (Fig. 4).

This shows that the alkane molecules in their hypothetical super-cooled state at T_{sc} [$-540\,^{\circ}C \sim 2(-273)\,^{\circ}C$], exhibit the same surface tension ($\gamma_{sc} = 75$ mN/m) regardless of chain length. The analysis shows that this characteristic is also observed for alkenes. These data also exhibit a super-cooled temperature T_{sc} [approximately $-540\,^{\circ}C$], where all the alkene molecules have the same γ_{sc} ($= 75$ mN/m ca.).

This characteristic property can be ascribed to the fact that long molecules' axes will tend to lie along a preferred direction at the interface. This is well recognized in such structures as "liquid crystal" phases. Thus at the super-cooled state at T_{sc} [$-540\,^{\circ}C$], the attractive forces and the repulsive forces in different alkanes exhibit a super-cooled state where the dependence on n_c disappears. In other words, all alkanes and alkenes behave as pseudo-methanes. Another possibility could be that the holes in the alkanes are all filled at super-cooled state T_{sc}, as expected from Eyrings [11] theory for liquids. From these observations, one can rewrite Eq. (6), in the case of *n*-alkanes data, which relates T_c to S_s and the above super-cooled point,

$$T_c = \gamma_{sc}/S_s + 6n_c + T_{sc} = 75/S_s + 6n_c - 540\,, \qquad (7)$$

where $\gamma_{sc} = 75$ mN/m and $T_{sc} = -540\,^{\circ}C$. From this relation one can estimate the values of T_c (within few % accuracy) if one knows S_s (or if γ is known for any temperature). Since the change in γ with temperature can be measured with a very high sensitivity (± 0.001 mN/m), then one can estimate T_c with a very high accuracy. On the other hand, similar analyses of more complicated molecules is much too complex [10] as expected.

These observations need further theoretical analyses at this stage. However, it is sufficient to stress that the method to extrapolate the data to hypothetical states is justified in the case of alkanes and alkenes.

Surface tension of any fluid can be related to various interaction forces, e.g. van der Waals (dipole and induction) and hydorgen bonding. The above analyses of the alkanes thus provides information about the van der Waals forces only. In other homologous series, such as alcohols, we can expect that there are both van der Waals and hydrogen bonding contributions. One can thus combine these two kinds of homolog series of molecules and analyze the contribution from each kind of interaction.

Since the shape and orientation of molecules is known to affect the thermodynamic properties of real fluids and fluid mixtures [3], more investigations are needed on this aspect. Surface tension measurements thus are found to provide much useful information about this aspect. Since the sensitivity of surface tension data is very high, this additionally makes the data more useful for such analyses. These analyses thus confirm the assumptions made as regards the molecular structure of the interfacial region as compared to the bulk phase. The surface entropy thus provides a very useful description of the molecular interactions in the interface of a liquid.

References

1. Rowlinson JS, Widom B (1982) Molecular Theory of Capillarity. Clarendon Press, Oxford
2. Birdi KS (1989) Lipid & Biopolymer Monolayers at Liquid Interfaces. Plenum Press, New York
3. Kloubek J (1989) Collection Czech Chem Commun 54:3171; (1990) Colloid Surfaces 48:323
4. Reid RC, Prausnitz, Poling BE (1987) The Properties of Gases and Liquids. McGraw-Hill, New York (1987)
5. Partington JR (1951) An advanced Treatise on Physical Chemistry, Vol. II. Longmans, Green & Co, London
6. Timmerman P (1966) Selected Properties of Hydrocarbons and Related Compounds, API Project 44, Vol. 1. Thermodynamics Research Center, Texas
7. Bakker G, Kapillarität und Oberflächenspannung (1928) Handbuch der Exsperimentalphysik. 3d. vi, Leipzig
8. Guggenheim EA (1945) Trans Faraday Soc 41:150
9. Hildebrand JH, Scott RL (1950) Solubility of Nonelectrolytes. Reinhold, New York
10. Birdi KS (ed) (1997) Handbook of Surface and Colloid Chemistry. CRC-Press, London, in print
11. Eyring H, Jhon MS (1969) Significant Liquid, Structures. Wiley, London